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DEGLI STUDI DI BARI
ALDO MORO

Maria Montrone

Functional Organic Materials for Energy

Thesis submitted for the degree of Philosophiae Doctor

Interuniversity Ph.D. Program in Industry 4.0

Polytechnic of Bari/ Department of Chemistry University of Bari "Aldo Moro"

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Extended Abstract

Functional organic materials are emerging as versatile and sustainable key solutions in the field of energy-efficient construction and smart building management. Their unique and tunable electrical, optical, and thermal properties make them ideal candidates for developing adaptive and intelligent systems aligned with the principles of environmental sustainability and the circular economy. Within this rapidly evolving field, functional organic materials can be engineered to exhibit specific chemico-physical characteristics, enabling the creation of dynamic building components able to respond to environmental stimuli and optimize energy performance.

Among these, donor–acceptor–donor (D–A–D) small molecules stand out due to their well-defined electronic structure, light-weight, easy tuning of HOMO and LUMO energy levels and processability on flexible substrates. In this thesis work, two classes of D–A–D compounds were investigated for their potential in developing next-generation smart building materials: (i) *benzothieno[3,2-b][1]benzothiophene* (BTBT)-and *benzothieno[3,2-b][1]benzothiophene tetraoxide* (BTBTO_{x4})-based semiconductors and (ii) *croconaine*-based organic dye.

BTBT and BTBTO_{x4} are planar π -conjugated cores based on fused ring systems, that exhibit remarkable charge transport properties, making them excellent building blocks for both p-type and n-type organic semiconductors. Six new small molecules, PT_{Z2}-BTBT, PT_{Z2}-BTBTO_{x4}, MPA₂-BTBT, MPA₂-BTBTO_{x4}, POC_{Z2}-BTBT, and POC_{Z2}-BTBTO_{x4}, were designed and synthesized via a microwave-assisted Buchwald–Hartwig cross-coupling reaction, with D–A–D architectures, combining BTBT/BTBTO_{x4} as electron-accepting cores and phenothiazine, bis(4-methoxyphenyl)amine and 3,6-bis(4-(octyloxy)phenyl)-9H-carbazole as donor groups. Electrical characterization revealed a hole-transport capability for BTBT-derivatives and ambipolar transport behavior for BTBTO_{x4}-derivatives.

In addition to their charge-transport capabilities, BTBTO_{x4}-based compounds demonstrated thermally activated delayed fluorescence (TADF) properties, making them promising materials for high-efficiency organic light-emitting diodes (OLEDs). Theoretical and photophysical studies confirmed their TADF behavior, with oxygen-induced quenching experiments and time-resolved photoluminescence supporting delayed fluorescence emission. Among them, POC_{Z2}-BTBTO_{x4} exhibited minimal self-quenching and maintained high photoluminescence efficiency, even in neat films, enabling its integration into OLED devices fabricated by spin-coating and inkjet-printing techniques.

Complementarily, *croconaine* (CR)-based materials were investigated as organic thermal additives of polymers to modulate the thermal properties of poly(L-lactic acid) (L-PLA). A benzoindolenine-based croconaine (CR-BI) with strong NIR absorption and high affinity with L-PLA chains was selected to realize L-PLA@CR-BI composite films with a uniform coloration by the CR-BI as a consequence of a homogeneous distribution of

the organic dye within the polymer matrix. Remarkably, even at a low loading (1%wt), CR-BI is able of increasing by more than 240% the thermal diffusivity and conductivity of PLA, acting as a very efficient thermal modulator and as a molecular plasticizer that improves chain mobility and crystallinity. These features open new opportunities for thermal energy management and storage applications in sustainable building materials.

Overall, the integration of BTBT/BTBTO_{x4}-based semiconductors and PLA@CR-BI composites exemplifies a multidisciplinary approach to the design of *functional organic materials* capable of combining optical emission, charge transport, and tunable thermal behavior. The synergistic study of these two classes of organic platforms lays the groundwork for the next generation of responsive, energy-saving, and environmentally friendly smart building technologies.

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CHAPTER I

Introduction

1.1 The Role of Organic Materials in Energy-Saving Technologies and Smart Buildings

Over the past decade, the urgency to reduce carbon dioxide (CO₂) emissions has become central in climate policy, sustainable design, and material science. Buildings—both in their construction (embodied emissions) and operation—are among the largest contributors to global greenhouse gas emissions. According to recent studies, about 30-40% of worldwide CO₂ emissions are associated with buildings, with energy use during building operation and the life-cycle of building materials being major contributors [1]. The global pursuit of energy efficiency and sustainability has spurred intensive research into innovative materials and technologies [2,3]. Among the most promising directions is the use of organic materials for energy-saving applications, particularly within the rapidly evolving domain of smart buildings. As cities grow and the demand for energy-efficient infrastructure intensifies, organic materials offer a unique combination of tunability, flexibility, low environmental impact, and cost-effectiveness, making them highly attractive for next-generation energy technologies. Organic materials stand in contrast to their inorganic counterparts, such as metals, ceramics, and semiconductors like silicon. While inorganic materials often provide excellent mechanical strength and thermal stability, they tend to be rigid, heavy, resource-intensive, and less sustainable in terms of production and end-of-life disposal. Organic materials, on the other hand, are lightweight, chemically versatile, often biodegradable, and can be synthesized from renewable resources. These characteristics make them particularly suitable for integration into smart, adaptable, and sustainable architectural solutions. These are structures that use advanced technologies to monitor, optimize, and reduce energy consumption in real time. Smart buildings rely on integrated systems that respond to environmental conditions and user behaviors, and organic materials play a central role in enabling such dynamic and responsive functionalities.

Among the most notable applications of organic materials in this context are:

- Electrochromic devices (Figure 1A): These systems can modulate their transparency or colour in response to electrical stimuli, thereby controlling the amount of light and heat entering a building. Organic electrochromic materials, such as conjugated polymers, are particularly advantageous due to their low operating voltage, flexible form factors, and customizable optical properties. Used in smart windows (Figure 1B), these materials can significantly reduce the need for artificial lighting and air conditioning, leading to substantial energy savings [4-6].
- Thermal energy storage systems (TESS): Organic phase change materials (PCMs) are increasingly being explored for thermal energy storage applications due to their ability to absorb, store, and release substantial amounts of latent heat during phase transitions, typically between solid and liquid states. During the melting process, the material absorbs thermal energy (endothermic reaction) without a significant rise in temperature, while during solidification, the stored energy is released (exothermic

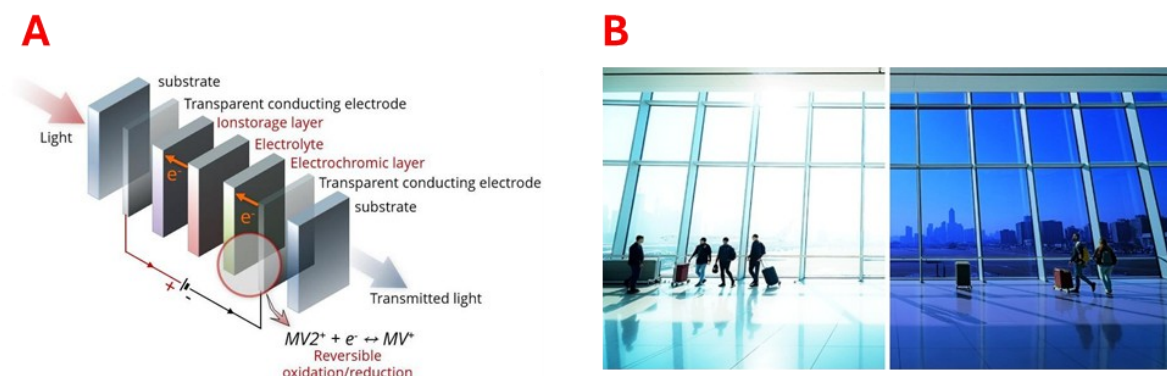


Figure 1. A) Schematic diagram of an electrochromic device; B) Example of smart windows.

reaction), thereby helping to regulate temperature fluctuations. These characteristics make organic PCMs highly suitable for integration into building envelopes, wallboards, ceiling panels, and HVAC (Heating, Ventilation and Air Conditioning) systems to stabilize indoor temperature profiles, reduce peak thermal loads, and enhance occupant thermal comfort. Compared to inorganic PCMs such as salt hydrates, organic materials, including paraffinic hydrocarbons and fatty acid derivatives, exhibit several advantages: they possess better thermal cycling stability (typically >1000 cycles without degradation), exhibit negligible phase segregation, have low corrosion tendencies toward encapsulation materials, and display minimal or no supercooling (often <1–2 °C). Their melting temperature range can be tuned (usually between 18–30 °C for building applications) by adjusting chain length or blending compositions. However, their relatively low thermal conductivity (typically 0.2–0.4 W m⁻¹ K⁻¹) can limit heat transfer rates; hence, enhancement strategies such as the incorporation of high-conductivity additives (e.g., graphite, carbon nanotubes, metal foams) or microencapsulation are often employed. Generally, organic PCMs represent a promising class of thermal storage media for passive and active energy management in buildings (Figure 2), contributing to reduced energy demand and improved system efficiency through load shifting and peak shaving mechanisms [7-9].

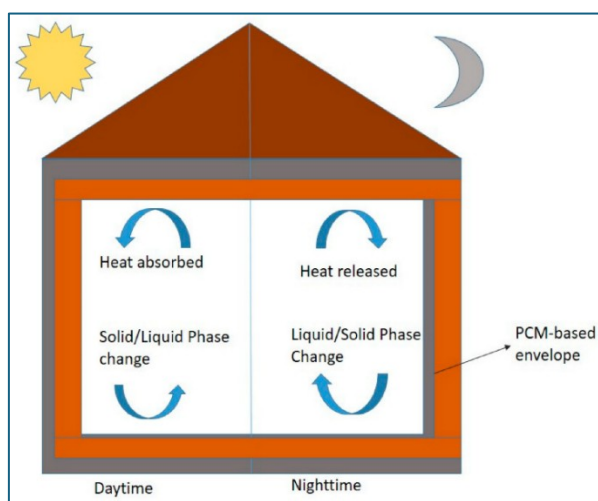


Figure 2. PCM-incorporated building envelope.

- Organic photovoltaics (OPVs): They are an emerging class of solar cells that use organic semiconductors, such as polymers or small molecules, as the light-absorbing layer instead of traditional crystalline silicon. While their power conversion efficiency (PCE) is generally lower than silicon-based cells—commercial modules typically range from 4–10%—OPVs offer unique features that make them particularly suitable for building-integrated photovoltaics (BIPV) (Figure 3). These include lightweight construction, flexibility, semi-transparency, tunable color, and potential for low-cost, large-scale fabrication through solution-processing techniques such as roll-to-roll printing and coating.

The combination of these properties enables OPVs to be integrated into building façades, windows, skylights, canopies, or interior surfaces without imposing significant structural loads. Semi-transparent OPV films in insulating glass units (IGUs) can provide daylighting while simultaneously generating electricity, offering both energy and aesthetic benefits. Flexible OPV modules can conform to curved or irregular surfaces, expanding architectural possibilities beyond what is feasible with rigid silicon panels. Additionally, OPV coatings can filter near-infrared (IR) radiation, reducing cooling loads while harvesting energy, thus improving overall building energy efficiency. In summary, OPVs offer a versatile and aesthetically adaptable solution for on-site renewable energy generation in the built environment. Their unique combination of lightweight, flexible, and semi-transparent characteristics allows architects and engineers to transform building envelopes into active, energy-generating surfaces, enhancing energy efficiency and contributing to the development of sustainable and smart buildings. While technical challenges related to efficiency, stability, and lifetime remain, continued material and manufacturing innovations are rapidly advancing the feasibility of OPVs as a practical BIPV solution [10,11].



Figure 3. An example of building-integrated photovoltaics (BIPV).

- Sensors and actuators: Organic semiconductors and conductive polymers are increasingly employed in the development of flexible and lightweight sensors capable of monitoring a wide range of environmental parameters, including temperature, humidity, light intensity, and air quality. These materials, such as polyaniline (PANI), poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS), and organic small-molecule semiconductors, offer key advantages over traditional inorganic sensors: they can be processed at low temperatures, deposited on flexible substrates, and integrated directly into building materials, paints, or coatings. Embedded into walls, ceilings, floors, or furniture, these sensors can form part of an IoT (Internet of Things) ecosystem that continuously collects data on indoor environmental conditions. When combined with actuators—such as thermochromic films, electrochromic windows, or HVAC control modules—this system can actively respond to changes in the environment. For example, light sensors can adjust window shading or artificial lighting levels; temperature and humidity sensors can optimize heating, ventilation, and air conditioning; and air-quality sensors can trigger ventilation or filtration systems to maintain healthy indoor conditions. The flexible and printable nature of organic sensors allows for conformable designs that can be applied to irregular surfaces, laminated into transparent panels, or incorporated into wearable devices for building occupants. Moreover, conductive polymers often exhibit biocompatibility, mechanical robustness, and chemical tunability, enabling long-term operation and adaptation to various environmental conditions [12,13].

In conclusion, organic materials are emerging as a versatile and sustainable solution in the field of energy-efficient construction and building management. Their unique properties enable a wide range of smart applications that go beyond traditional building materials. As research advances and commercialization grows, organic materials are expected to play an increasingly central role in shaping the smart buildings of tomorrow structures that are not only intelligent and responsive but also deeply aligned with the principles of environmental sustainability and circular economy. Among the most promising categories within this field are functional organic materials, a class of compounds specifically designed to exhibit tailored electrical, optical, thermal, and in general chemico-physical properties. These materials are particularly well-suited for smart building technologies due to their tunability, responsiveness to external stimuli, and compatibility with flexible, lightweight substrates. Whether used in electrochromic windows, thermal energy storage systems, organic photovoltaics, or embedded sensors, functional organic materials enable dynamic building components that adapt to environmental conditions and user needs, significantly enhancing energy efficiency and occupant comfort.

Within this class, donor–acceptor–donor (D–A–D) compounds are of particular interest, thanks to their well-defined electronic structure and tunable energy levels which allow for enhanced features, making them ideal candidates for use in applications such as electrochromic windows, organic photovoltaics, and thermal energy regulation systems.

The idea of the present doctoral project was born with the aim of investigating the potential of two specific classes of D–A–D compounds: croconaines, known for their strong and tunable near-infrared absorption, as well as the ability to convert luminous energy in heat and benzothieno[3,2-b]benzothiophene (BTBT)-based molecules, which offer excellent fluorescent and charge transport properties. These two molecular classes will be explored for their suitability in enabling responsive, energy-saving functionalities in the next generation of smart building materials.

1.2 Functional Organic Materials

Functional organic materials are a class of carbon-based compounds with semiconductor properties specifically designed to exhibit useful electronic, optical, or magnetic properties. Unlike traditional organic molecules used in structural or passive roles, these materials are "functional" because they actively participate in processes like charge transport, light emission, or energy conversion.

They typically feature π -conjugated systems, alternating single and double bonds, that allow delocalization of electrons across the entire molecule. This delocalization enables interactions with light and electrical fields, making them suitable for applications such as organic photovoltaics (OPVs), organic light-emitting diodes (OLEDs), organic field-effect transistors (OFETs), sensors, electrochromic devices, bioimaging and phototherapy.

Their key advantages include lightweight structure, flexibility, solution processability, and tunability through synthetic chemistry. Functional organic materials include both polymers and small molecules. Among these, **donor–acceptor–donor (D–A–D)** molecules represent a particularly important subclass due to their tunable optoelectronic properties, symmetric architecture, and strong intramolecular charge transfer.

1.2.1 D-A-D-Type Functional Organic Compounds

D-A-D-type functional organic compounds (Donor–Acceptor–Donor) are a class of molecules characterized by a molecular structure in which two electron-donating groups (D) are connected to a central electron-accepting group (A) (Figure 4). This **Donor–Acceptor–Donor (D–A–D)** architecture plays a crucial role in tuning the electronic and optical properties of the compound, making these systems highly attractive for a variety of advanced technological applications.



Figure 4. D-A-D Structure.

1.2.1.1 History and Progress of D–A–D Small Molecules

Over the past three decades, small-molecule D–A–D architectures have progressively evolved—from early conceptual symmetric charge-transfer units to meticulously engineered planar and organometallic scaffolds.

The progression includes the chemico-structural evolution of both the acceptor core (benzocycloheptene, benzothiadiazole, cyanothiophene, Ethylendioxybenzene-Imide (EBI), Thieno[3,4-c]pyrrole-4,6-dione-based diketopyrrolopyrrole/Naphthalenetetracarboxylic diimide (TDPP/NT), phenylene-linked benzothiadiazole), the donor unit diversification (phenylthio, thiophene, 3,4-Ethylenedioxythiophene (EDOT), dithienopyrrole, bithiophene, benzofuran, fluorenyl, Triphenylamine-OMe (TPA-OMe), dihydroacridine), the synthetic strategies and the solid state aggregation, i.e. symmetric assembly, planarity optimization, morphology optimization, etc.

The evolution of donor–acceptor–donor (D–A–D) small molecules has been marked by significant milestones since the early 1990s, reflecting their growing importance across various scientific fields (Table 1). Initial studies focused on fundamental photophysical properties and nonlinear optical behaviours of stilbene-based D–A–D push–pull systems, establishing the foundational understanding of intramolecular charge transfer (ICT) [14]. During the late 1990s and early 2000s, the incorporation of thiophene and benzothiadiazole units in D–A–D architectures expanded their utility in organic electronics, particularly in enhancing charge transport in organic field-effect transistors (OFETs) and tuning band gaps for optoelectronic applications [15–18]. Progressing into the 2010s, perylenediimide (PDI)-based D–A–D triads and D–A–D dyes found application in organic photovoltaics (OPVs), leveraging their excellent electron-accepting properties to improve device efficiency and morphology control [19]. The late 2010s and early 2020s witnessed a surge in computational design and high-throughput screening, facilitating targeted synthesis of D–A–D molecules with tailored optoelectronic properties for enhanced photovoltaic performance and biosensing [20–22]. More recently, from around 2022 onwards, D–A–D architectures have gained prominence in biomedical applications, particularly through the development of near-infrared II (NIR-II) emissive and photothermal agents for advanced imaging and cancer phototherapy [23–26]. The most recent advances in 2024 demonstrate the integration of D–A–D luminophores with benzothiadiazole cores in organic light-emitting diodes (OLEDs), highlighting their potential in next-generation electroluminescent devices through mechanisms such as thermally activated delayed fluorescence (TADF) and in electrochromic and electroluminescent devices [27,28].

Overall, the D–A–D molecular motif exemplifies a versatile and evolving platform, with its intrinsic tunable electronic properties continuing to drive innovation across energy, electronics, and biomedical fields.

1.2.1.2 Electron and Molecular Structure of D-A-D Compounds

In a D–A–D molecule, two electron-rich donor (D) units symmetrically flank a central electron-deficient acceptor (A). Donor units are typically **electron-rich** moieties with a high electron density. They tend to have lone pairs (e.g., nitrogen in triphenylamine or carbazole) or electron-donating substituents (e.g., alkyl or alkoxy groups) that facilitate **electron donation**. These donors are a **source of electrons** during the photoexcitation

Table 1. Milestones of the D–A–D small-molecules.

Year	Study Focus	Key Application	Reference
1993	ICT in 4-(dialkylamino) stilbenes; structure–photophysics correlation	Intramolecular charge transfer (ICT) analysis	[14]
2007	Dithienylbenzothiadiazole-based n-type semiconductors	OFETs (organic field-effect transistors), light emission	[16]
2010	Benzobisthiadiazole-based D– π –A– π –D systems	Low-band-gap polymers and chromophores for OPVs	[15]
2012	Fluorinated benzothiadiazole small molecules	Solution-processed organic solar cells (OPVs)	[18]
2014	Perylenediimide-based D–A–D dyads/triads; self-assembly	Organic photovoltaics (OPVs); morphology control	[19]
2015	Heteroannulated benzothiadiazole acceptors	Donor–acceptor systems in organic electronics	[17]
2017	EBI-based small molecule semiconductors	Organic solar cells (OPVs)	[20]
2021	D–A–D monomers (DFT/TDDFT) for electronic properties	Polymer solar cells (OPVs), theoretical modeling	[21]
2021	Substituent effects on D–A–D small molecules	Organic semiconductors (DFT study)	[22]
2022	D–A–D nanoparticles with synergistic photothermal/photodynamic effects	Biomedical applications (theranostics)	[23]
2023	D–A–D molecules for multimodal imaging and therapy	Fluorescence, photoacoustic imaging, photothermal therapy	[24]
2024	Benzothiadiazole and dimethyldihydroacridine D–A–D compounds	Electrochemistry, photophysics (experimental + theoretical)	[27]
2024	Fluorene-linked D–A–D BT derivatives with thiophene units	Electrochromic and electroluminescent devices	[28]
2025	Oligothiophene-based D–A–D photosensitizers	Photodynamic therapy, push–pull tuning	[26]
2025	Bright NIR-II D–A–D aggregates for imaging and therapy	Fluorescence bioimaging, photothermal therapy	[25]

or charge transfer processes. They are characterized by high highest occupied molecular orbital (HOMO) energy levels, which facilitate hole transport and provide sites for oxidation. Additionally, when conjugated with acceptor units, they contribute to strong light absorption. The most common donor moieties in a D-A-D molecules are carbazole (3,6- or 2,7-Carbazole Units) [29], thiophene and its derivatives such as EDOT (3,4-

ethylenedioxythiophene) [26,30,31], dithienopyrrole [32], and triphenylamine [33,34] (Figure 5). On the other hand, acceptor units are **electron-poor** groups that easily **accept electrons** from donors. They usually contain electronegative units (e.g., C=N, CN, C=O, SO₂, etc.) or conjugated systems that stabilize the added electron density. As a result, they exhibit low lowest unoccupied molecular orbital (LUMO) energy levels, making them efficient electron acceptors. Acceptor units function as electron sinks, stabilizing the excited state and favouring the electron transport. When combined with donor groups, they also contribute to reducing the band gap of the overall molecule [35]. Among the widely used acceptor groups there are pyrazine [36-38], benzothiadiazole (BT) [26,27], diketopyrrolopyrrole (DPP) [39], and benzobisthiadiazole (BBT) [40]. Isoindigo is a rarer but very effective acceptor in D–A–D polymers with excellent results in electrochromic and photovoltaic devices, thanks to a reduced band-gap and stable performance in the NIR region [41] (Figure 5).

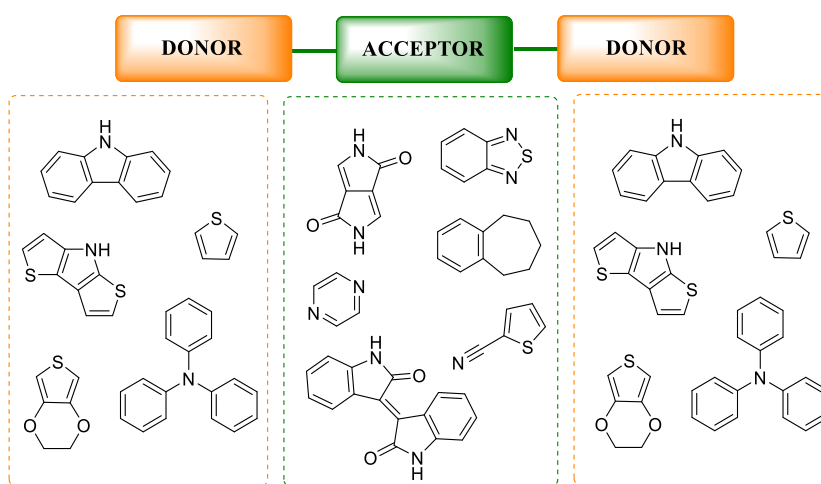


Figure 5. Common Donor and Acceptor Moieties in D–A–D Molecules.

When connected through π -conjugated linkers, donor and acceptor units arrange a push–pull system that exhibits several important features. One of the key phenomena is **intramolecular charge transfer (ICT)**: upon photoexcitation, electrons are promoted from the donor's highest occupied molecular orbital (HOMO) to the acceptor's lowest unoccupied molecular orbital (LUMO), resulting in a charge-separated excited state. This electron density shift from donor to acceptor reduces the effective electronic band gap of the molecule, often leading to strong absorption in the visible or near-infrared region [42]. The **band gap** itself can be **modulated** by tuning the strength of the donor and acceptor units as well as by modifying the π -conjugated bridge between them. These changes directly influence the HOMO–LUMO gap, thereby allowing for precise control over the **optical and electronic properties** of the material, which is crucial for applications such as organic photovoltaics, OLEDs, and chemical sensors. Additionally, the π -conjugated system promotes **electron delocalization** across the molecule, enhancing charge mobility and improving photophysical characteristics such as fluorescence intensity and charge separation efficiency.

Spectroscopic evidence supports these behaviours, particularly through UV-Vis absorption and fluorescence measurements. D–A–D molecules typically exhibit red-shifted and intense absorption bands compared to

isolated donor or acceptor units—clear evidence of efficient intramolecular charge transfer (ICT). In fact, red shifts in absorption are attributed to enhanced π -conjugation and stronger electron-donating capabilities in ICT molecules [43]. The ICT absorption band corresponds to electronic transitions from the HOMO (localized on the donor) to the LUMO (localized on the acceptor), and its onset wavelength provides a reasonable estimate of the optical band gap [21,44,45]. In fluorescence spectra, these molecules often display a pronounced Stokes shift, which reflects structural relaxation and charge redistribution in the excited state. Moreover, measurements of photoluminescence quantum yield (PLQY) and fluorescence lifetime offer valuable insight into the efficiency of the ICT process and the rigidity or flexibility of the molecular structure—also corroborated by solvent-dependent behavior and PLQY trends [46].

As a consequence, the chemico-structural engineering of the D-A-D systems play a key role in addressing the potential applications of these materials. Hacıfendioğlu et al. [47] proposed design guidelines based on the analysis of more than 50 acceptor units used in polymers with a D-B-A-B (D, donor; A, acceptor; B, bridge) structure. They highlighted how planarity, π -conjugation and hyperpolarizability of the system influence the band gap, the HOMO and LUMO energy levels and in general the overall electronic properties—parameters that are fundamental for applications in organic electronics. A theoretical study of the same research group, based on density functional theory (DFT) of 60 donor units shows that dihedral angles, bond order and specific chemical substructures play a critical role in determining planarity, electronic delocalization, and thus the band gap. It is essential to choose donor units that promote planar and extended conjugated structures to optimize electronic performance in organic devices [48]. Sundar et al. [49] describe rational strategies to modulate the conjugation length, the donor and acceptor strength and the planarity of the molecular framework through π -conjugated bridges, fused rings, and variable substituents—such as $-\text{CH}_3$, $-\text{OH}$, $-\text{NH}_2$ (as donors), and $-\text{CF}_3$, $-\text{CN}$, $-\text{NO}_2$ (as acceptors). The result is a broad tuning range of the optical band gap, from approximately 0.7 eV to 3.7 eV, which is crucial for tailoring material properties in optoelectronic applications.

Others recently studies highlight the importance of the geometry and planarity of D-A-D compounds in determining the electronic, optical, and charge transport properties, especially in materials designed for **organic electronics, photovoltaics, OLEDs, and sensors**.

Planarity plays a crucial role in enhancing π -conjugation and intramolecular charge transfer (ICT) in donor–acceptor (D–A) systems. A planar molecular backbone facilitates efficient orbital overlap between the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), promoting charge delocalization and reducing the optical band gap, which in turn improves light absorption in the visible and near-infrared (NIR) regions. Hashemi et al. [50] demonstrated through DFT studies that planar geometries in D–A polymers result in stronger donor–acceptor interactions and better alignment of frontier molecular orbitals, enhancing electronic properties. In contrast, non-planar geometries caused by large dihedral angles—often due to steric hindrance—can disrupt conjugation, localize frontier orbitals, and reduce ICT efficiency. As shown by Casey et al. [51], structural modifications such as cyano substitution can influence planarity and significantly affect organic photovoltaic (OPV) performance. The cyano substitution systematically lowers the

LUMO without significantly affecting the HOMO, resulting in enhanced open-circuit voltage (V_{OC}) and overall improved performance in organic photovoltaic (OPV) devices. Furthermore, molecular rigidity, often achieved through fused rings or constrained π -systems, suppresses internal rotations and enhances photoluminescence quantum yield, charge mobility and environmental stability. In contrast, flexible backbones tend to promote non-radiative decay and lower optoelectronic performance. This relationship was highlighted by Zaier and Ayachi [52], who reported improved nonlinear optical (NLO) responses and emission stability in rigid, coplanar systems.

1.2.1.3 Symmetric and Asymmetric Small D–A–D Molecules

Within this class, a fundamental design distinction lies in the symmetry of the donor groups: molecules can be either symmetric, containing identical donors flanking the acceptor unit, or asymmetric, where the two donors differ in structure or electronic character. This seemingly simple structural variation leads to important differences in molecular behavior, packing, and optoelectronic performance.

Symmetric D–A–D molecules are characterized by balanced molecular structures that promote uniform charge distribution and consistent orbital alignment across the conjugated backbone. This symmetry often translates into strong π – π stacking and high crystallinity in the solid state—properties that are favorable for charge transport and film stability, as proven by most of investigations cited so far.

In contrast, asymmetric D–A–D' molecules—where the two donor units differ—break molecular symmetry and introduce new functionalities. This asymmetry often results in enhanced intramolecular charge transfer (ICT), leading to broader and red-shifted absorption spectra, smaller optical band gaps, and richer electrochemical behavior. Additionally, asymmetric molecules tend to have higher dipole moments, which can influence intermolecular interactions and packing motifs in the solid state. Despite the risk of reduced crystallinity, such structural variation can be advantageous: for instance, introducing asymmetric side chains or donor groups can improve solubility, optimize film morphology, and even enhance device performance when properly engineered [53-55].

In summary, symmetric D–A–D small molecules offer advantages in terms of easy of synthesis, planarity and solid-state organization, making them suitable for applications requiring high crystallinity and balanced charge transport. On the other hand, asymmetric D–A–D' molecules, despite a greater synthetic and structural complexity, can provide enhanced optical and electronic tunability, better absorption profiles, and greater structural flexibility—features that are particularly valuable in next-generation optoelectronic devices. The choice between symmetric and asymmetric architectures ultimately depends on the targeted application and the desired balance between molecular order and functional diversity.

1.2.1.4 Properties and Applications of D–A–D Compounds

As already anticipated, the versatility of D–A–D compounds derives from their highly adjustable structure–property relationships, which can be adapted to meet the needs of different optoelectronic, electrochemical and

photocatalytic technologies. D–A–D small molecules have found uses in diverse areas, such as organic photovoltaics, photocatalysis, OLEDs, and even biomedicine (imaging and therapy).

Organic Solar Cells (OSCs)

One of the most prominent applications of D–A–D compounds is in **organic solar cells (OSCs)** [56]. Here, their ability to absorb across the visible and near-infrared spectrum enhances light harvesting and photocurrent generation. For example, many high-performing non-fullerene acceptors (NFAs) and small-molecule donors feature D–A–D motifs, which improve energy level alignment and facilitate efficient charge transport in bulk heterojunction blends, as demonstrated by Chen et al. [57]. Yassin et al. [32] instead presented a preliminary evaluation of the potential of the symmetric donor–acceptor–donor D–A–D system, built by connecting two dithienopyrrole donor blocks to a central electron acceptor obtained by dimerization of 3-alkoxy-4-cyanothiophene in massive heterojunction solar cells. These compounds combined high photoluminescence efficiency with a broad solid-state absorption spectrum and a band gap of 1.70 eV. D–A–D frameworks have also been employed as small molecule semiconductors. Le Borgne et al. [20] in their study reported EBI-based D–A–D small molecules—wherein an ethane-1,2-diylidene bis(indolin-2-one) acceptor core was flanked by thiophene, bithiophene, or benzofuran donors. When incorporated into bulk heterojunction (BHJ) solar cells, one derivative (EBI-2T, 2T=bithiophene) delivered a maximum power conversion efficiency (PCE) of 1.92%, with performance linked to its planar conformation and optimized blend morphology. In 2014, D–A–D small molecules, especially those using diketopyrrolopyrrole (DPP) as the acceptor and triphenylamine (TPA) or thienothiophene (HTT) as donors, have been developed as solution-processable donor materials. One of this reached a power conversion efficiency (PCE) of ~1.5% under standard illumination in the bulk-heterojunction OSCs [39]. Very interesting are D–A–D molecules based on isoindigo with benzofuran and dithienopyrrole donors (Figure 6) that show tunable optoelectronic properties; preliminary OSC testing indicates promising outcomes depending on substitution at the indigo nitrogen [58].

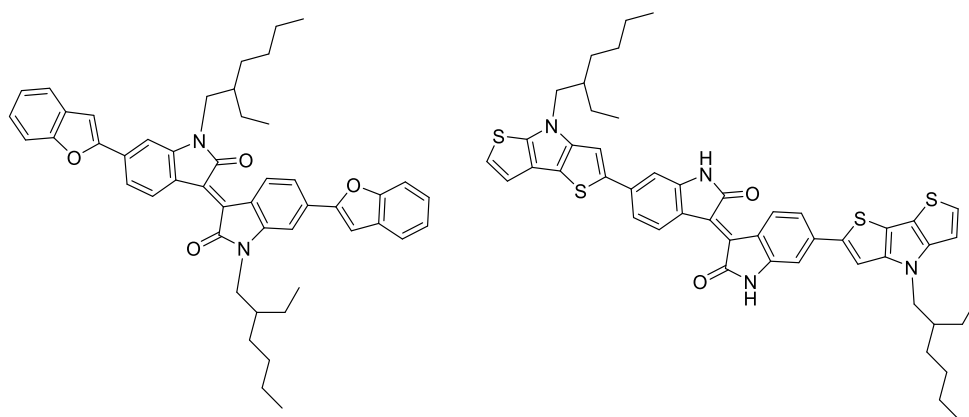


Figure 6. D–A–D molecules based on isoindigo (blue) with benzofuran (left) and dithienopyrrole (right) donors [58].

Finally, four D–A–D type donor molecules with TPA, thiophene, and thiazolothiazole were designed and analyzed using DFT and TD-DFT methods. Among them, one showed the lowest band gap (4.73 eV), broadest absorption (455.3 nm), and best charge mobility with the lowest electron reorganization energy ($\lambda_e = 0.0177$).

It also exhibited the highest predicted Voc (2.04 V), making it one promising candidate for high-performance organic solar cells [59].

Organic Field-Effect Transistors (OFETs)

D–A–D molecules have also shown promise in **organic field-effect transistors (OFETs)** (Figure 7) due to their tunable energy levels and improved π – π stacking interactions, enabling ambipolar charge transport and enhanced device stability. In the pursuit of high-performance OFETs, recent research has focused on designing novel semiconducting materials with tailored donor–acceptor (D–A) architectures to enhance charge transport, stability, and functionality.

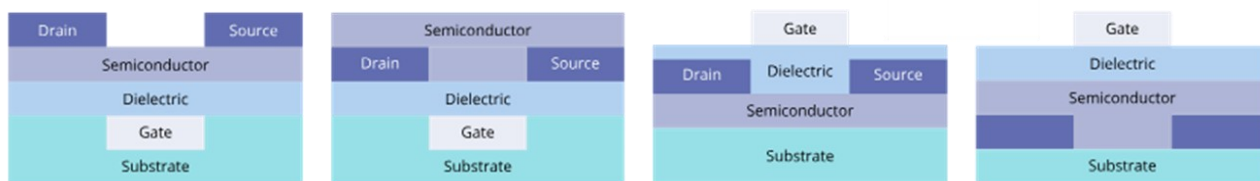


Figure 7. OFET Device Architecture.

One promising approach involves the development of n-type and light-emitting FETs using strongly electron-accepting units such as benzothiadiazole and trifluoromethylphenyl groups. These components effectively lower LUMO energy levels, thereby improving electron mobility and on/off ratios. Dithienylbenzothiadiazole derivatives, in particular, have demonstrated strong fluorescence and narrow band gaps, making them ideal candidates for light-emitting n-type OFETs due to their efficient charge transport and optoelectronic properties [16]. Further structural and electronic optimization was explored through D–A–D molecules featuring benzochalcogenodiazole (BDO, BDT) cores symmetrically linked to heteroaromatic units such as furan, thiophene, and selenophene. Single-crystal X-ray diffraction and theoretical calculations confirmed their near-planar geometries and revealed extensive non-covalent interactions (e.g., $\pi \cdots \pi$, chalcogen $\cdots \pi$) that govern their solid-state packing and enhance charge transport. Notably, several of these molecules formed ordered crystallites during thin film processing, contributing to effective charge mobility. OFETs fabricated with these materials achieved hole mobilities up to $0.08 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and Ion/Ioff ratios of 10^4 , demonstrating their strong potential for flexible and solution-processable organic electronics [60]. Expanding on this D–A–D molecular design, two benzocarbazole-based semiconductors—BCDPP and BCPzDP (Figure 8)—were synthesized and evaluated. Both materials integrate donor end-capping units with different electron-deficient cores: diketopyrrolopyrrole (DPP) for BCDPP and dipyrrolopyrazinedione (PzDP) for BCPzDP. The nature of the acceptor core was found to significantly influence the charge transport behavior. BCDPP exhibited unipolar p-type characteristics, while the more electron-deficient BCPzDP demonstrated ambipolar transport, enabling both hole and electron mobility in OFET devices. This highlights the critical role of acceptor tuning in modulating semiconductor performance [61]. In addition, also D–A–D oligomers and polymers (e.g., bithiophene-benzothiazole or DPP-based structures) exhibit ambipolar charge transport in OFETs, with hole mobilities up to $\approx 9.7 \times 10^{-4} \text{ cm}^2/\text{V}\cdot\text{s}$ and on/off ratios around 10^4 [62].

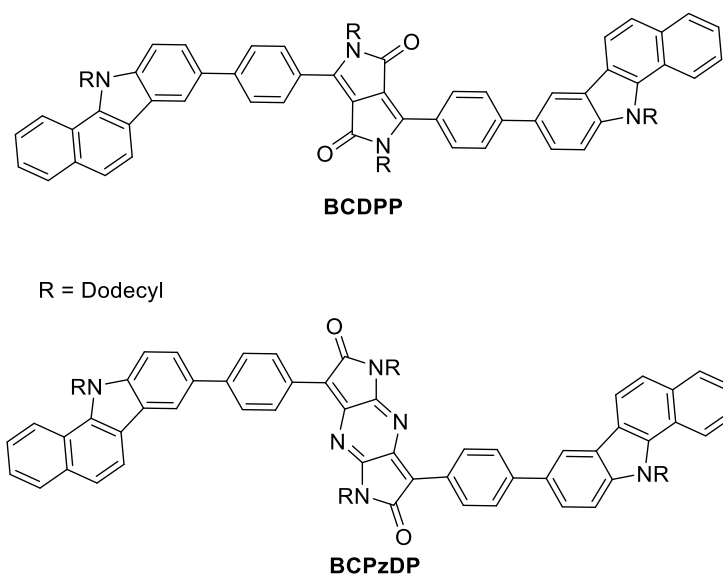


Figure 8. Chemical structures of BCDPP and BCPzDP.

Organic Light-Emitting Diodes (OLEDs)

D–A–D compounds, thanks to their tunable redox and optical properties, have been heavily explored as luminophores in **organic light-emitting diodes (OLEDs)**. In the field of **OLEDs**, D–A–D structures are used to develop emitters with efficient **thermally activated delayed fluorescence (TADF)** and **hot exciton mechanisms**, allowing for high external quantum efficiency (EQE) and narrow emission bandwidths [63-65].

A landmark experimental case involves a 2024 study of D–A–D compounds composed of a benzothiadiazole acceptor with 9,9-dimethyl-9,10-dihydroacridine donors attached via phenylene linkers. These compounds were thoroughly characterized, revealing narrow ionization potentials (~5.28–5.33 eV), enhanced electron affinities, solvent-dependent photoluminescence in the orange–red region, solid-state fluorescence efficiency improvements, and indicators of reverse intersystem crossing (RISC)—suggesting potential for thermally activated delayed fluorescence (TADF) and hot-exciton emission in OLEDs [27].

In this work (Sec. 4.2), a new family of organic luminescent materials was developed, featuring thermally activated delayed fluorescence (TADF), for organic light-emitting diodes devices (OLEDs). These materials are based on a donor–acceptor–donor molecular design, where the central electron-accepting unit is a benzothienobenzothioephene-tetraoxide (BTBTO_{x4}) core. Three different electron-donating groups (phenothiazine (PTz), dimethoxydiphenylamine (MPA) and a carbazole derivative (POCz)) were attached to this core using a straightforward and efficient microwave-assisted efficient microwave-assisted Buchwald-Hartwig reaction [66].

Electrochromic Devices

Donor–acceptor–donor (D–A–D) structured materials have emerged as promising candidates for electrochromic applications due to their tunable electronic and optical properties. By incorporating electron-

rich donor units and electron-deficient acceptor cores, D–A–D systems enable precise control over bandgap, redox behavior, and color modulation. This design allows for improved coloration efficiency, high optical contrast, and faster switching speeds, all essential features for high-performance electrochromic devices exploitable in smart windows and displays. Additionally, the structural versatility of D–A–D molecules supports the development of materials with enhanced stability and multi-state color switching. Recent studies have shown that both small molecules and polymers with D –A– D architecture exhibit more excellent electrochromic performance than many inorganic counterparts, with considerably greater color tunability, potentially lower costs, flexibility, and light weight [28,46,67-69]. However, organic materials also face challenges: long-term stability, possible self-quenching or aggregation, limited contrast, or slow response times. Engineering molecular structure is a key tool to addressing these issues.

Electrochromic materials are one of the arguments of this doctoral thesis. The topic will be explored in depth in the Section 4.4.

Organic Photocatalysis

Beyond electronic devices, D–A–D compounds have also proven effective in **photocatalytic applications** [70], including **solar-driven hydrogen evolution**. Their strong light absorption, favorable excited-state dynamics, and long-lived singlet excitons allow them to act as efficient molecular photocatalysts under visible light [71]. For the same purpose, a novel imine-linked covalent organic framework (DABT-Py-COF, Figure 9) was synthesized by combining a D–A–D type monomer with a pyrene-based amine under solvothermal conditions. The resulting COF features a donor–acceptor architecture that enhances charge separation and suppresses recombination. Under visible-light irradiation (AM 1.5), DABT-Py-COF demonstrated excellent photocatalytic performance, achieving a high hydrogen evolution rate of $5458 \mu\text{mol g}^{-1} \text{h}^{-1}$ [72]. Jin et al. [73] integrated pyrazole–benzothiadiazole–pyrazole organic molecule bearing a donor–acceptor–donor conjugated π -system (Figure 10) into metal organic frameworks (MOFs) to afford a more efficient heterogeneous photocatalyst. Under visible-light irradiation, three aerobic oxidation reactions involving different oxygenation pathways were achieved with the obtained MOFs (Figure 10).

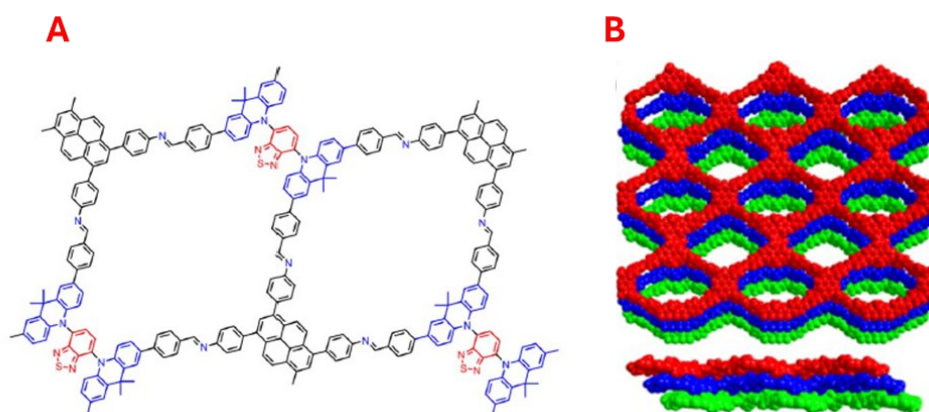


Figure 9. A) DABT-Py-COF molecular structure; B) Top and side views of the space-filling models of DABT-Py-COF in slipped AA stacking mode [72].

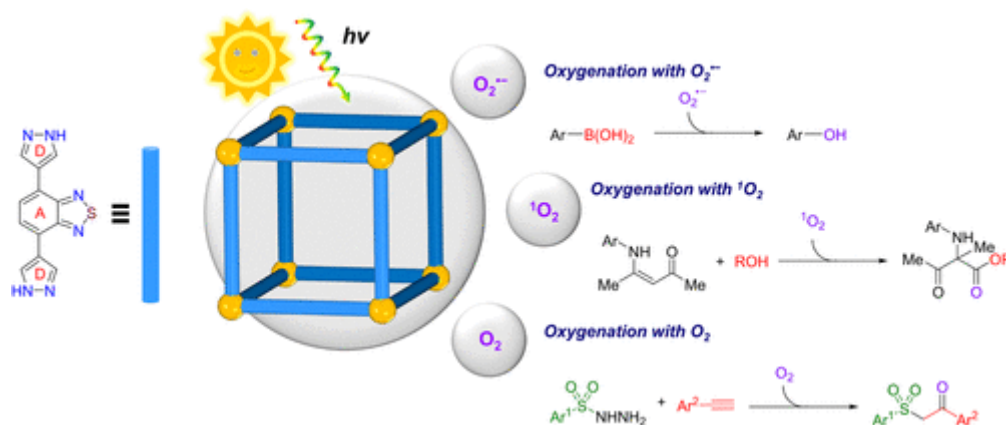


Figure 10. D-A-D molecular structure of the molecule integrated into MOF and schematic illustration of MOF used as photocatalyst for aerobic oxygenation under visible-light irradiation [73].

D-A-D compounds have also been used as metal-free photocatalysts for the light-driven reduction of CO_2 . Wang et al. [74] in their study, synthesized and tested under solar simulation four naphthalene diimide (NDI)-based D-A-D molecules (NDI-2T, NDI-TT, NDI-4T, and NDI-6T) with varying numbers of thiophene units. Among them, NDI-4T (Figure 11) showed the best performance, achieving a CO_2 yield of $168.6 \mu mol g^{-1} cat^{-1} 24 h^{-1}$ using water as the electron donor, without any sacrificial agent or cocatalyst. This was attributed to its balanced redox potential, low charge-transfer resistance and strong photocurrent response.

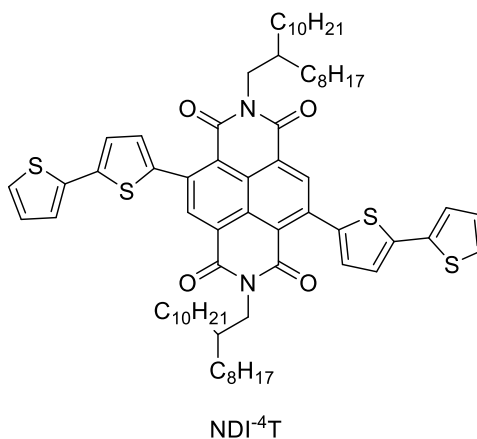


Figure 11. Chemical structure of NDI-4T.

Biomedical Applications

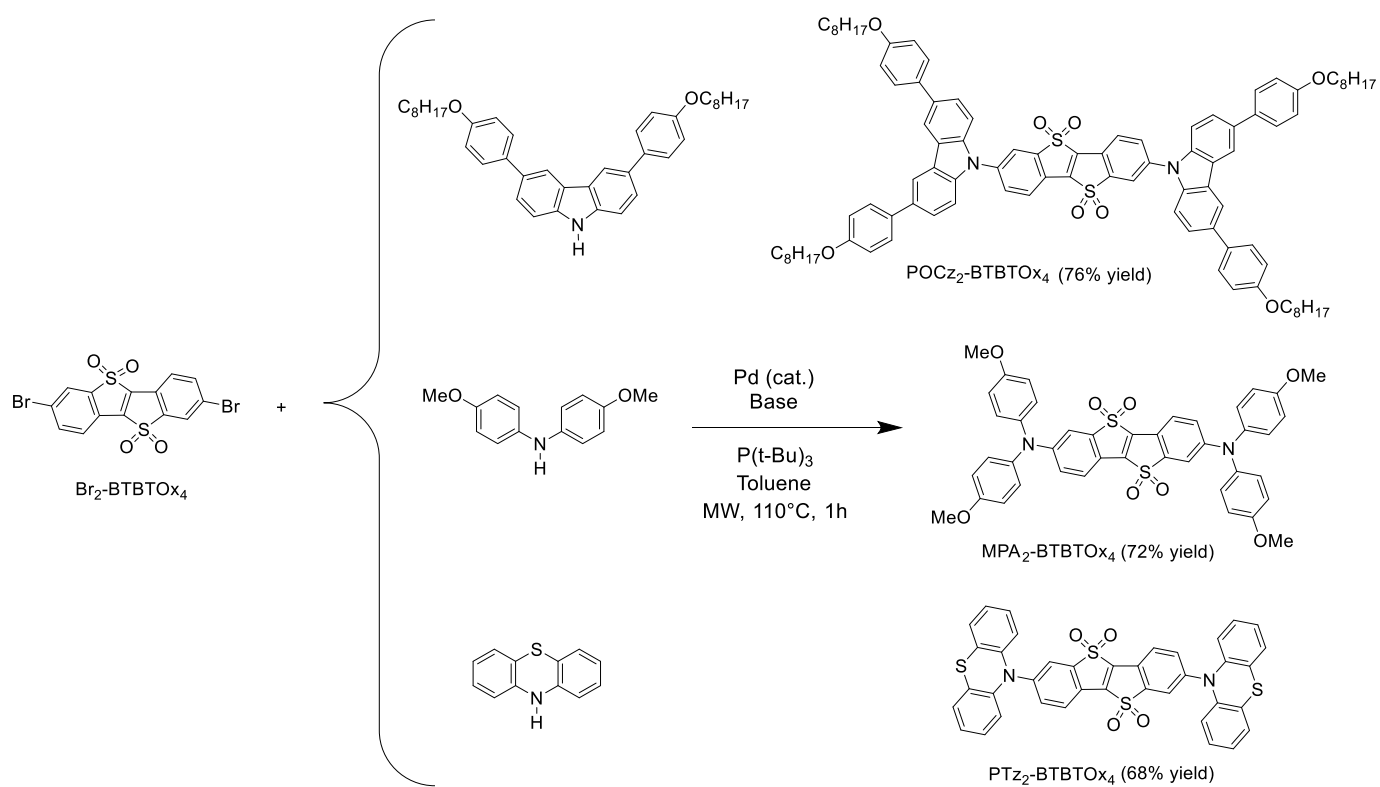
From ~2022 onwards, the design of NIR-II emissive and photothermal D-A-D molecules records a growing trend in medical application [23-26,75,76]. D-A-D systems such as squaraines and croconaines have shown utility in biological sensing, fluorescent imaging, photodynamic and thermodynamic therapy, thanks to their high fluorescence quantum yields and environmental sensitivity [75,77].

1.2.1.5 Synthesis of D-A-D Compounds

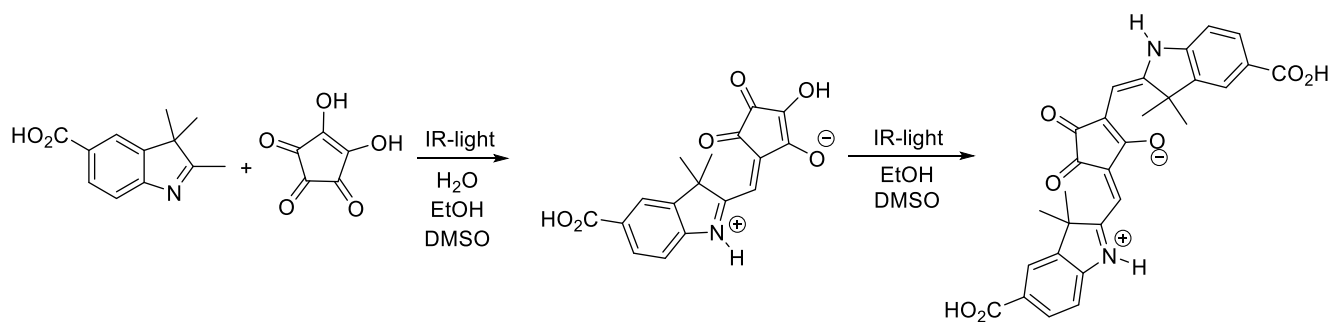
Over time, the synthesis of donor–acceptor–donor (D–A–D) small molecules has moved from relatively simple donor–acceptor combinations toward more sophisticated synthetic methods that allow fine control over the electronic properties, the conjugation length, and structural geometry. Early works often used classical cross-coupling methods (Suzuki, Stille, etc.) [39], but with increasing demand for strong donor groups, complex acceptors, and tunable absorption/emission properties, synthetic strategies have shifted to include powerful C–N bond-forming reactions such as the Buchwald–Hartwig amination. The Buchwald–Hartwig reaction allows attachment of aromatic or heterocyclic amine “donor” units onto halogenated acceptor cores under Pd catalysis, offering good yields, broad substrate scope, and tolerance to wide functional groups. Recently, a Buchwald–Hartwig double amination (i.e. two donor units attached to an acceptor via two C–N bonds formation) has been employed to build symmetrical D–A–D TADF materials with desired emission color, high external quantum efficiency and small singlet–triplet gap [78]. In this work we used a straightforward synthetic protocol based on Buchwald–Hartwig cross-coupling to prepare D-A-D molecules according to the Scheme 1 [66].

More recently, synthetic routes have also prioritized one-pot or cascade reactions, as well as dehydrogenative coupling, to reduce steps and improve atom economy; for example, Mondal et al. [79] used acceptorless dehydrogenative coupling to build pyrimidine-ferrocene D-A-D systems. Alongside synthetic refinements, design has embraced more structural complexity—twisted geometries, non-planar donors, longer conjugated spacers—to balance donor-acceptor charge transfer, minimize recombination, and maximize light harvesting [27]. This evolution reflects a shift from simply achieving D-A-D architectures to controlling fine structural, electronic, and morphological parameters to optimize performance in applications like solar cells, fluorescence sensors, and photocatalysis.

Alternative heat sources have also been used to prepare D-A-D compounds by optimizing reaction times and temperatures. For examples, in our work [66] we exploited microwave-assisted Buchwald–Hartwig cross-coupling to prepare D-A-D molecules with significant reduction of reaction time and energy consumption. Furthermore, a solvent-free method to carry out the synthesis of indolenine-based squaraines and croconaines was developed. Different protocols of condensation reactions based on conventional thermal heating, mechanochemical milling, and IR-light activation were compared. The most performing alternative protocol was the irradiation of the reaction mixture with an IR lamp (Scheme 2), which promotes the condensation reactions leading to the synthesis of both croconaines and squaraines in solvent-free conditions, with considerable shorter reaction times (from a few minutes to 1 h) and reduced energy consumption [80].



Scheme 1. Synthesis of $\text{PTz}_2\text{-BTBTOx}_4$, $\text{MPA}_2\text{-BTBTOx}_4$, $\text{POCz}_2\text{-BTBTOx}_4$.



Scheme 2. Condensation reaction based on IR-light activation.

1.2.1.6 Polymers-based on D-A-D Monomers

Conjugated **donor–acceptor–donor (D–A–D)** molecules serve as highly versatile building block for constructing polymers with finely tunable properties. By alternating electron-rich donor units and electron-deficient acceptor units, D–A–D building block enable precise modulation of the polymer's band gap, HOMO/LUMO energy levels, color, and charge-carrier characteristics, making them attractive for applications in organic electronics, electrochromic devices, photovoltaics, and photocatalysis [81-85].

For instance, Sendur et al. synthesized an unsymmetrical D–A–D monomer comprising benzothiadiazole with asymmetric donor arms (EDOT and thiophene) and found that its electrochemically polymerized product exhibited a low band gap of 1.18 eV along with ambipolar doping characteristics, outperforming corresponding symmetrical analogues [82]. Later, Singhal et al. [83] developed D-A-D copolymers using 3,4-ethylenedioxythiophene (EDOT) as the donor unit, applying electropolymerization techniques to tune optical and electrochromic performance, including contrast ratio and switching time. Kaya et al. [84] introduced a novel light-induced step-growth polymerization method for thiophene-based D-A-D building block, offering a more controlled and milder route for producing electroactive polymers. In the same year, Xia et al. [85] advanced this concept by designing D-A-D-A-D-type oligomers from simpler D-A-D small molecules, significantly improving molecular packing and charge mobility, thereby enhancing the efficiency of organic photovoltaic devices. Furthermore, small D–A–D structured conjugated trimers, such as those based on EDOT–benzothiadiazole–EDOT (E-B-E), have recently been shown to exhibit outstanding photophysical and photocatalytic properties—including long-lived emissive excitons and high photocatalytic hydrogen-evolution activity—highlighting the potential of well-defined molecular D–A–D structures as efficient photocatalysts [71].

1.3 D-A-D Croconic Acid-based Compounds: Croconaines

D-A-D croconic acid-based compounds in general, and croconaines (CRs) in particular, are an important class of functional organic materials based on the croconic acid unit (Figure 12). The central core of CRs is the croconate anion, with the general formula of $(C_5O_5)^{2-}$ (Figure 13).

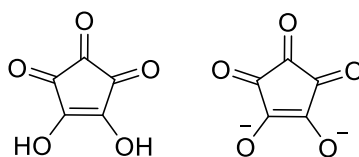


Figure 12. Croconic acid (left) and croconate anion (right).

It possesses interesting structural features such as high symmetry, cyclic planar structure, extensive π -electron delocalization, and aromatic character [86]. Moreover, the croconate anion displays **good acceptor ability** and its crystal lattice is stabilized by strong H-bonds and π - π interactions between adjacent layers, giving rise to extended supramolecular 3D structures. These are key characteristics to determine and address optical and

electric properties in solid-state material chemistry. Generally, CRs consisting of 2 donor moieties connected to 2 and 5 positions of the central 5-member croconate ring, with a D–A–D structure [87].

1.3.1 Properties and Applications

As typically in D-A-D compounds, the D-A-D structure ensures extended π -conjugation and gives CRs semiconductor properties. By an accurate choice of the donor units, it is possible to modulate the HOMO and LUMO energy levels and then the band gap, addressing electrical and optical properties for specific applications. CRs show features such as high absorption extinction coefficient, high photostability, and narrow and intense absorption bands in the NIR region (absorption even at a wavelength longer than 1100 nm) [88]. Furthermore, they display intriguing electro-optical, photoacoustic and photothermal properties that can be exploited for the realization of high technology devices and bio-medical applications.

1.3.1.1 NIR Absorption Capability and Photothermal Properties

The NIR absorption capability of CRs was initially attributed to the strong donor–acceptor molecular charge transfer. Recently it has definitively been attributed to the biradical character [89]. The electronic structure of the molecule can be considered as the result of two resonance contributions, that of the mesoionic form and that of the biradical form (Figure 13). These two electroisomers are in equilibrium; but by acting on the geometry and substitutions of the conjugated skeleton, the structure can be stabilized either in the mesoionic form or in the biradical form. Computational studies demonstrate that the CRs exhibit strong tendency towards the biradical form [90].

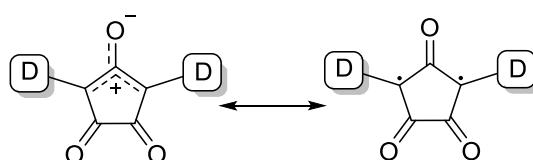


Figure 13. Resonance structures in CRs: mesoionic (left) and biradical (right) forms.

The small band gap is also a feature favouring the formation of open-shell singlet or triplet states and, therefore, the enhancement of the diradical character. Since the energies of the singlet and triplet states are related to the biradical character of the ground state, which may be tuned by chemical structure modifications, the final properties of the molecule can be tuned by a proper chemical design [91]. Maeda et al. [92] have recently investigated two compounds, shown in the Figure 14, using various techniques including $^1\text{H-NMR}$, ESR, X-ray crystallography, and DFT calculations, confirming the diradical character previously theorized by Fabian and Zahradnik [93].

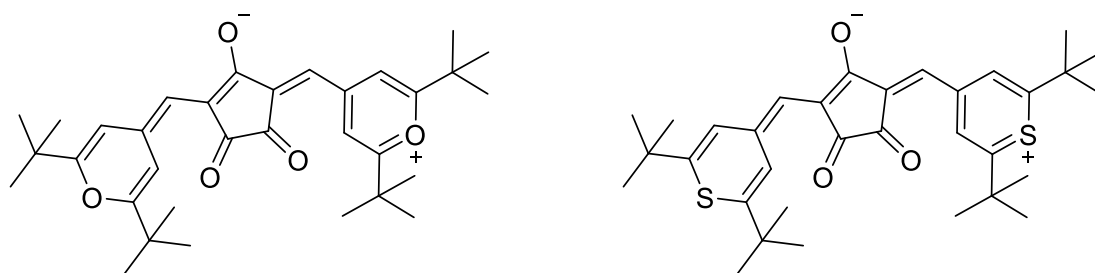


Figure 14. CRs studied by Maeda research group.

ESR and ^1H -NMR spectra provided spectroscopic evidence of singlet and triplet states in these diradicals. In singlet diradicaloids, electrons are only partially coupled, and this degree of coupling can be expressed by the diradical character. The singlet diradicaloids exhibit intriguing functionalities such as electric conductivity, optical nonlinearity including TPA, and singlet fission.

The NIR absorption capability was one of the most studied early features of CRs. A singular application of NIR-absorbing CRs was proposed in a 2001 patent [94], where they, together with other infrared absorbing compounds such as phthalocyanines, 2,3-naphthalocyanines and squaraines, were used to improve the reheat rate of a container preform. The container preform was composed of a polymer suitable to produce a stretch blow molded bottle and, at least, one organic NIR-absorbing material able to absorb at least twice as much light in the range 700-1200 nm as in the range 400-700 nm. The NIR-absorbing component being present in sufficient amount to improve the reheat rate of the container preform. This property known as photothermal heating capability was explored some years later by Smith's research group that can be considered the pioneer of the studies of laser-induced photothermal heating capability of CRs [95]. Pang et al. [96] reported a photothermal conversion efficiency (PCE) of 77% for TCR (Figure 15) upon 735 nm laser irradiation, while Tang et al. [97,98] reported PCEs of 72.7% and 79.5% for CR-DPA-T and CR-TPE-T (Figure 16), respectively, upon 808 nm laser irradiation. In their work, Tang et al. [97] exploited the light harvesting ability and high photothermal conversion efficiency of CR-DPA-T, to fabricate a self-healing flexible film with poly-(dimethylsiloxane). The small molecule CR-TPE-T was investigated for highly efficient utilization of solar energy, showing excellent photothermal performance in the aggregated state. NIR-absorbing photothermal CRs also find application as mesogenic calamitous materials.

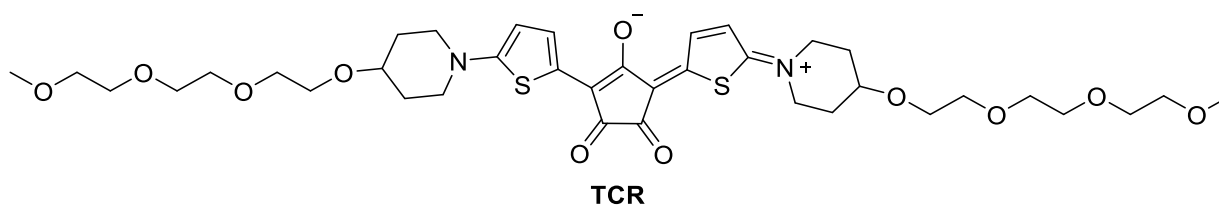


Figure 15. Chemical structure of TCR.

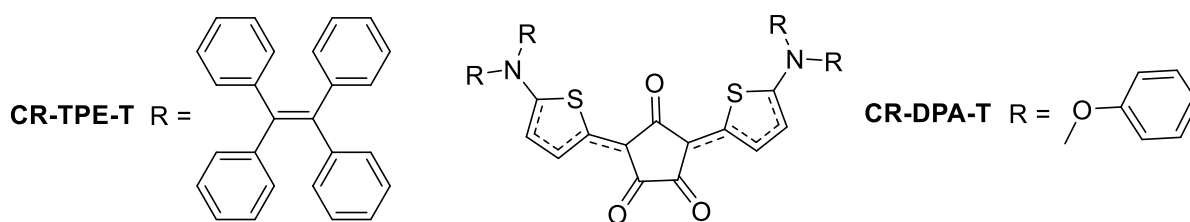


Figure 16. Chemical structure of CR-TPE-T and CR-DPA-T.

Yang et al. [99] explained how, thanks to the photothermal heating effect induced by the CR, YHD796 (Figure 17), well dispersed in a LCE (liquid crystalline elastomer) matrix, the composite film obtained performs a completely reversible contraction/expansion response towards the NIR light stimulus. They reported the first example of a NIR-absorbing mesogenic organic magnet.

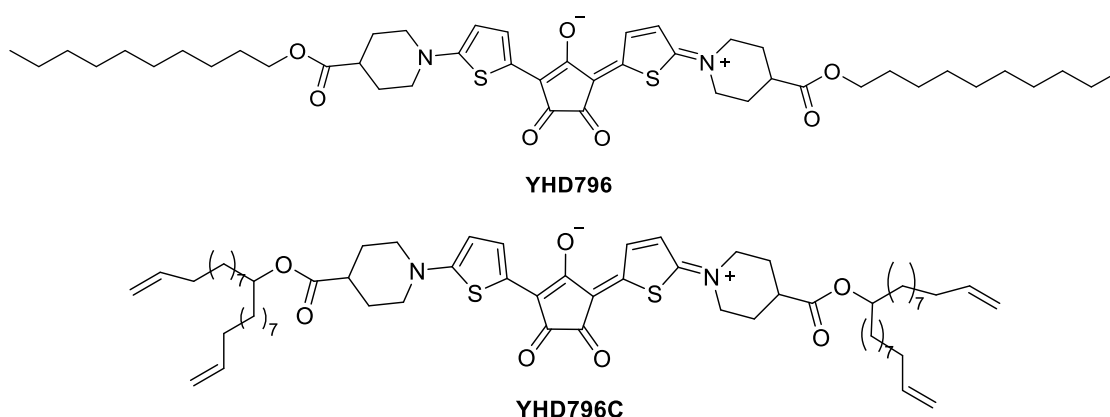


Figure 17. Chemical structure of YHD796 and YHD796C.

In 2017, Liu et al. [100] exploited the NIR absorbing YHD796C chromophore (Figure 17) as a soft actuator material able to increase the local temperature from 18 to 260 °C in 8 s and lift up weights 5600 times heavier than its own weight, under 800 nm NIR irradiation. The NIR absorbing chromophore YHD796C was designed with cross-linkable functional groups (four alkenyl-tailed groups) and submitted to in situ acyclic diene metathesis polymerization with a LC monomer to fabricate a uniaxial aligned main-chain LCE soft actuator material, in which the NIR chromophore is chemically bonded in the LCE material.

The resulting soft actuator material exhibited an ultrafast photoresponsive speed and superior mechanical property, easily lifting up heavy loads, even up to 5680 times heavier than their own weight. Following this, Nie et al. [101] prepared a photothermally responsive liquid crystal elastomer using the same YHD796 (Figure 17) as the photothermal agent in order to produce single-faced Mobius strip actuators capable of producing continuous in situ rotation under NIR irradiation. A 2014 patent [102] reports the use of CRs as additives to plastics to facilitate laser welding of these materials. Dyes usually used as laser absorbers must meet certain requirements: (a) intense absorption at the wavelength of the laser used; (b) heat resistance during the welding process; and (c) neither the dye nor the decomposition products shall be toxic when used together with foodstuffs and the like. These CRs are easy to adapt to plastic materials, in fact, by changing the substituents on the amino nitrogen, it is possible to modulate the solubility, while, through an appropriate selection of the

aromatic or heteroaromatic group, it is possible to set the absorption profile of the dye. In 2019 [103], another patent disclosed a new NIR-absorbing CR suitable for use in NIR laser welding methods of plastic materials. In the same year, another patent describes the use of CRs as photothermal dyes to be mixed with thermoplastic PEEK polymers for the purpose of creating articles by 3D printing [104]. Very recently, in 2024, Xu et al. [105] reported the use of a CR to functionalize the surface of polypropylene with a CR-functionalized polymer acting as an antifouling and NIR-light-mediated photothermal sterilizing agent. The CR was designed with a reactive functional group (alkyl bromide) suitable for polymerization and used to prepare various amphiphilic block polymers acting as antibacterial coatings of polypropylene substrates.

In the biomedical field, near-infrared (NIR) croconaines have shown great potential as phototherapeutic agents for synergistic photothermal and photodynamic cancer therapy, guided by NIR fluorescence imaging [106,107]. The photothermal properties have also suggested the possibility of using CRs as organic agents for photoacoustic (PA) or optoacoustic (OP) imaging, an emerging technique in the field of high-performance molecular imaging, which is very useful in the biomedical field [108-110].

Nowadays, the photothermal properties of CRs are highly researched and widely exploited in biomedical applications. Therefore, we thought of broadening the field of application, exploiting the photothermal properties of croconaines in a completely new field.

1.3.1.2. CRs as Organic Photothermal Additive

We used a photothermal benzoindolenine-based croconaine, labelled as CR-BI, (Figure 18) as a filler in a highly versatile biopolymer, polylactic acid (PLA) (Figure 18), to improve its thermal properties. PLA was the most widely produced bioplastic in the past year. According to the latest market data compiled by European Bioplastics in collaboration with the Nova-Institute, PLA accounted for 37.1% of the 2.47 million tons of bioplastics produced globally in 2024 [111]. PLA is also considered one of the most promising biopolymers on the market, thanks to its broad range of applications—from food packaging and biodegradable bags to disposable tableware, non-woven fabrics, and biomedical uses. Moreover, it is an excellent material for 3D printing applications [112]. Recently, the applications of PLA have been extended to other fields. PLA is expected to become an ideal and universal support matrix for high-performance bio-based phase change materials (PCMs), used as latent heat storage materials in cutting-edge building technologies like the latent heat thermal energy storage (LHTES) systems [113,114].

PLA as a plastic matrix offers a unique combination of lightweight, transparency, moisture stability, easy processability, printability, good corrosion-resistance. Despite its many strengths, it has a major limitation: its low intrinsic thermal conductivity. This makes it unsuitable for electronic components that require efficient heat conduction/dissipation, especially in high-power and high-frequency electronic devices. Currently, to address this critical issue, the most popular route exploited in practical industrial production is to introduce into polymer matrices highly thermally conductive inorganic fillers, such as boron nitride nanosheets [115], aluminium nitride [116], silicon carbide [117], carbon nanotubes [118], graphene and graphene oxide [119],

etc. However, these types of fillers, being not related to the polymer matrix, are randomly distributed within it, making necessary a high additive amount to achieve an efficient thermally conductive networks inner polymer matrix. On the other hand, the increase of the fillers content in the polymer matrix negatively impacts processing operations and mechanical properties. To face and solve these problems, the research has proposed some strategies, including prefabricated thermal conductive networks [120] and electrospinning methods [121], aiming to obtain an ordered arrangement of thermally conductive fillers inner polymer matrix. Despite these methods results effectively to promote thermally conductive networks inner polymer composites, there are some drawbacks, such as complex processes, expensive production equipment and long production cycles. An elected strategy should include alternative additives able to promote their uniform distribution within the polymer matrix, ensuring, at the lowest possible concentration, an adequate thermal conductivity of the final composite. This would allow to minimize the negative effect of fillers on the mechanical properties of polymer matrix, while ensuring the required thermal conductivity characteristics. Moving in this direction, we addressed our attention to this intriguing class of organic functional materials, the Croconaines (CRs), to be investigated as photothermal additives for PLA.

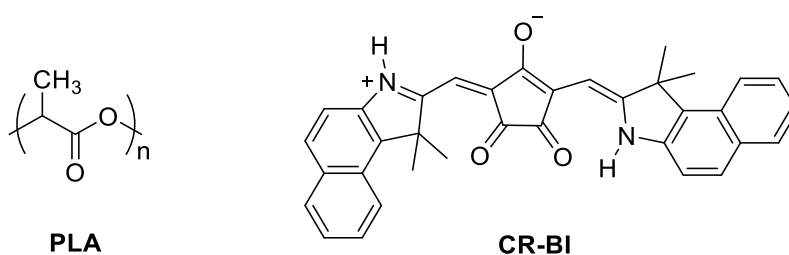


Figure 18. Chemical structure of PLA and Croconaine CR-BI.

These two organic components can be tailored to have a good mutual affinity to make homogeneous solid mixtures giving solid-state layers with a uniform distribution of the CR additive in the PLA matrix. To this end we have prepared three PLA composite films that incorporated varying amount of CR-BI (from 0.1 g to 1 g) and characterized them by UV-Vis and FTIR Spectroscopy and Thermal and Photothermal measurements. The results demonstrated that this new approach offered an efficient and scalable strategy to fine-tune PLA's properties, making it highly suitable for thermal management and energy-storage systems useful in sustainable building technologies.

1.4 D-A-D Compounds with BTBT Acceptor Core

The BTBT core, formally [1]benzothieno[3,2-b][1]benzothiophene, is a polycyclic heteroaromatic system composed of two thienyl rings fused to a central benzene unit (Figure 19). It is known for its high planarity, good π - π stacking, strong intermolecular interactions in the solid state, and excellent hole (p-type) mobility in organic semiconductors. These features have made BTBT and its derivatives important building blocks in organic field-effect transistors (OFETs) [122-124], DSSC solar cells [125], sensors, etc. This moiety can be obtained in high yield with a simple synthetic protocol suitable for large-scale production. At the same time, the two thienyl rings can be easily oxidized to yield the S,S tetraoxide derivative (BTBT O_{x4}) (Figure 19),

converting the molecule into an electron-acceptor unit that is potentially useful in D–A–D high-performing electronic devices [126]. The oxidation of the sulfur atoms in the thienyl rings that converts them into sulfone groups (thiophene-S,S-dioxide), lowers the frontier molecular orbital (FMO) energy levels (especially the LUMO), changing the electron affinity, and can alter crystal packing, thermal stability, and emission properties.

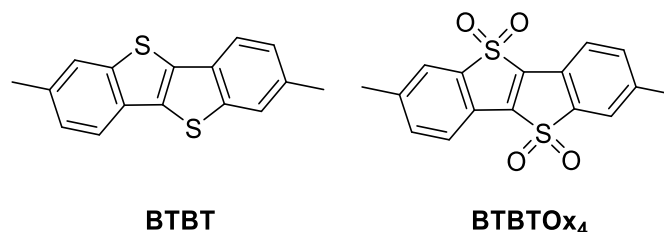


Figure 19. Chemical structure of [1]benzothieno[3,2-b][1]benzothiophene (BTBT) (left) and [1]benzothieno[3,2-b][1]benzothiophene S,S-tetraoxide (BTBT O₄) (right).

D–A–D compounds based on BTBT (or oxidized BTBT) as acceptor core, flanked by donor units, are relatively recent but promising molecules. The development of [1]benzothieno[3,2-b][1]benzothiophene (BTBT)-based materials has progressed significantly over the past two decades, with early studies primarily focusing on charge-transport applications. In 2006, Takimiya et al. [122] introduced 2,7-diphenyl-BTBT as a highly promising organic semiconductor for air-stable organic field-effect transistors (OFETs), demonstrating hole mobilities up to $2.0 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. This was followed by Ebata et al., [123] who reported highly soluble BTBT derivatives suitable for high-performance, solution-processed OFETs, and by further investigations into the solid-state molecular ordering and its influence on device performance. In parallel, BTBT derivatives found application in dye-sensitized solar cells, where their extended π -conjugation and favorable photophysical properties were exploited for light-harvesting efficiency [125]. A significant shift occurred with the recent work by Rzewnicka et al. [126], who demonstrated how oxidation of the sulfur atoms in BTBT could effectively tune its electronic properties, enabling the design of acceptor units for optoelectronic applications. Complementary work on anthracene–BTBT dyads and triads further highlighted the potential of BTBT-based D–A–D architectures for ambipolar transport and phototransistor applications [127]. Altogether, the evolution of BTBT-based compounds from semiconducting cores in OFETs to functional D–A–D emitters in advanced optoelectronic devices demonstrates their exceptional structural tunability and broad application potential.

Building on this strategy, we developed new D–A–D compounds incorporating fully oxidized BTBT (BTBT-tetraoxide) as the central acceptor core. These molecules exhibited thermally activated delayed fluorescence (TADF) (Figure 20A) and were successfully implemented in self-hosted, solution-processed third generation OLEDs (Figure 20B), achieving external quantum efficiencies exceeding 1% [66].

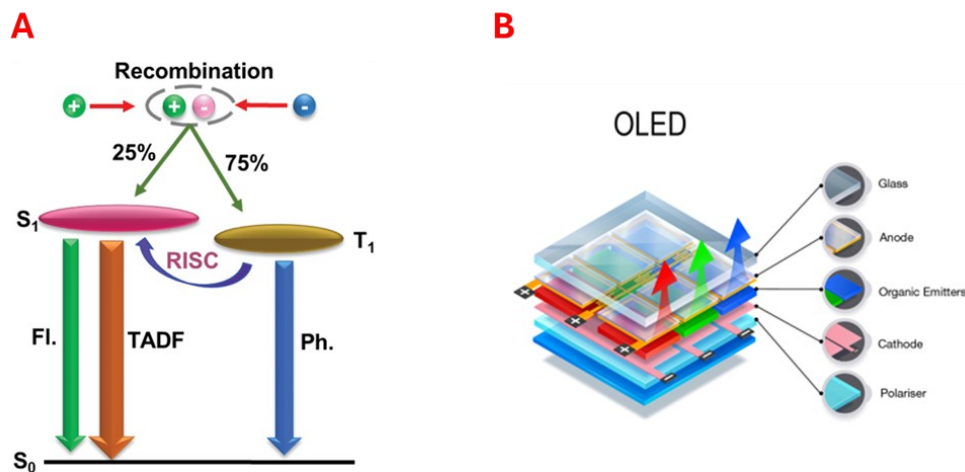


Figure 20. A) TADF emission mechanism; B) Third generation OLED device architecture.

The well-established properties of both oxidized and non-oxidized BTBT acceptor cores have motivated further investigation into this highly promising unit. The inherent versatility and tunability of BTBT and BTBTO_{x4}-based systems make them attractive not only for OLEDs but also as potential candidates for electrochromic applications, where balanced charge transport and stable conductivity are crucial for achieving efficient performance and long-term operational stability. To better understand and optimize these materials, we carried out a systematic study of their electrochemical behavior, electronic molecular structures, and charge carrier mobilities.

CHAPTER II

Work Goal

This PhD research was carried out at the Organic Chemistry Laboratory of the Department of Chemistry at the University of Bari and at the ArCoD Department of the Polytechnic of Bari, in collaboration with CNR-Nanotec of Lecce, CNR-IPCF of Bari, and CNR-ITC of Padua. The main goal of this doctoral work was the development of new functional organic materials for various energy-related applications, ranging from energy saving to energy storage, with particular focus on the building sector and the management of high energy-efficiency buildings.

The work was divided into several stages:

1. Preliminary study of scientific literature regarding functional organic materials;
2. Synthesis and characterization of organic π -conjugated materials based on the BTBTOx₄ acceptor unit;
3. Synthesis and characterization of organic π -conjugated materials based on the BTBT acceptor unit;
5. Synthesis of organic materials based on the croconic acid acceptor unit;
4. Preparation and characterization of new polymeric organic composite films;
5. Application of the above-mentioned materials in organic electronic devices.

CHAPTER III

Materials and Methodology

3.1 Materials

L-Polylactic acid (L-PLA) ($M_w = 64700$ amu, $M_n = 32100$ amu, $PDI = M_w/M_n = 2.1$, commercial source) was used to prepare the L-PLA@CR-BI composite films in the present study.

For the synthesis of PTz₂-BTBT, MPA₂-BTBT, POCz₂-BTBT, PTz₂-BTBT-Ox₄, MPA₂-BTBT-Ox₄, POCz₂-BTBT-Ox₄ all reagents and solvents of ACS purity were purchased from commercial sources and used without further purification. All reactions sensitive to air were carried out under a nitrogen atmosphere with anhydrous solvents, distilled immediately prior to use. Toluene was distilled from sodium/benzophenone. Column chromatography was performed using silica gel 60, 40-63 μ m. Silica gel 60 F254 aluminium sheets were used for analytical TLC.

3.2 Methodology

3.2.1 Preparation of L-PLA@CR-BI Composite Films

Three solutions of L-PLA@CR-BI composite were prepared by dissolving in each 100 mg of L-PLA in 5 mL of CHCl₃ and 0.1 g, 0.5 g and 1 mg of CR-BI (0.1, 0.5 and 1 %wt of CR-BI with respect to L-PLA), respectively. The samples were labelled as PLA@CR-BI*0.1, L-PLA@CR-BI*0.5, LPLA@ CR-BI*1. A solution of neat L-PLA (20 mg/ml) in CHCl₃ was used as the reference. Films of neat L-PLA and L-PLA@CR-BI*0.1, L-PLA@CR-BI*0.5, L-PLA@CR-BI*1 composites on glass and ITO were obtained by casting from solution and annealed at 50°C for 72h (Figure 21). The thickness of films of the order of tens microns was measured by a micrometre.

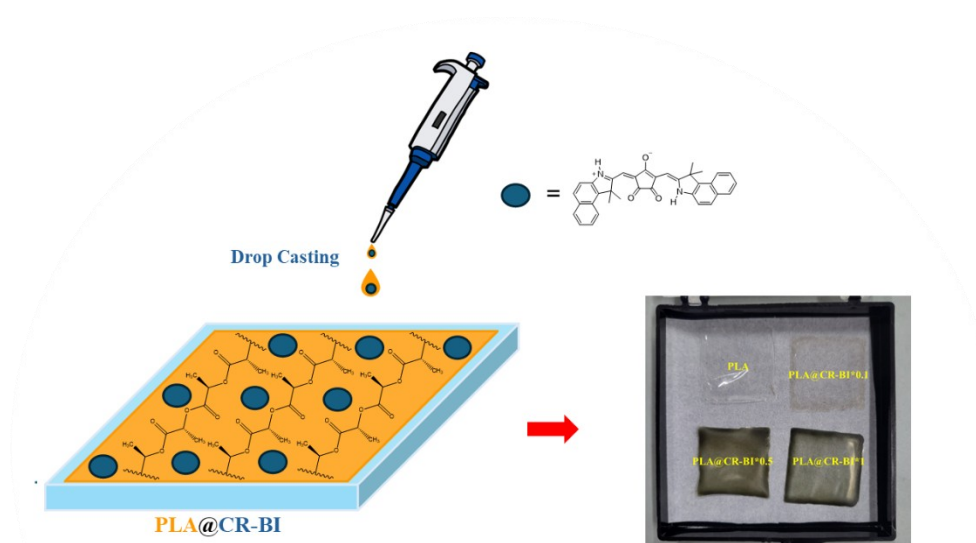


Figure 21. Preparation of L-PLA@CR-BI composite films.

3.2.2 Synthesis of CR-BI

(1,1-Dimethyl-1,3-dihydro-2H-benzo[e]indol-2-ylidene)methyl-5-((1,1-dimethyl-1H-benzo[e]indol-3-io-2-yl)methylene)-3,4-dioxocyclopent-1-en-1-olate (CR-BI) was synthesized according to the literature procedure reported in a previous work of Prof. Capozzi et al. [128,80]. We have used infrared (IR) light as an alternative energy source (Figure 22A, 22B). Infrared light provides a form of thermal energy that can be precisely controlled and directed to specific reaction sites. IR light can penetrate deeper into materials than traditional heating methods, allowing for more uniform and efficient heating. By using infrared heat incandescent lamp, the optimal reaction conditions required for CR-BI synthesis can be achieved at lower temperatures (until 120° C) and with greater energy efficiency, making the process more sustainable and cost-effective as already demonstrated in our previous works [80].

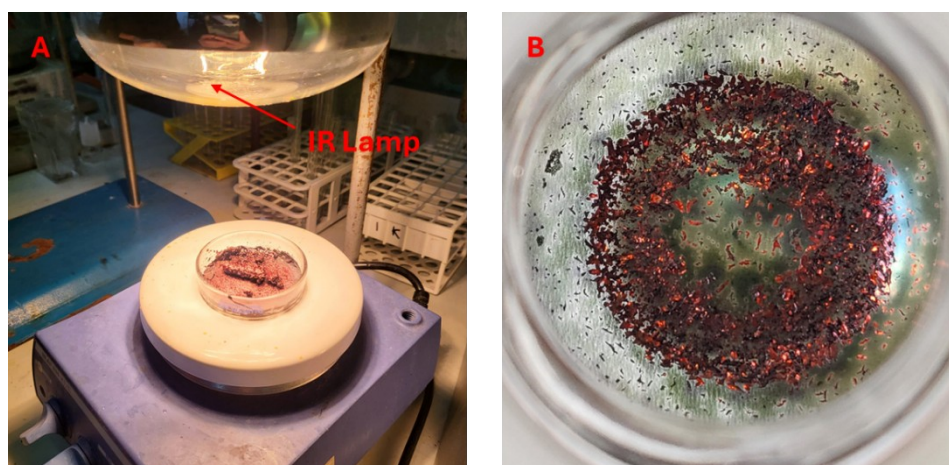


Figure 22. A) Experimental setup for CR-BI synthesis; B) CR-BI produced: brown metallic solid.

3.2.3 UV-Vis and FTIR Measurements of L-PLA@CR-BI Composite Films

Absorption spectra were recorded on a UV-Vis Spectrophotometer, in the range 200-1000 nm, in CHCl_3 solution for the neat L-PLA and in thin film for the L-PLA@CR-BI composites. UV-vis absorption measurements (scan mode) were collected using a Cary 300 double beam spectrophotometer using rectangular 10 mm path length quartz cuvettes from Hellma, at 25°C. The absorption spectra were collected with concentrations in the range 10-20 mM (total volume 10 mL volumetric flask).

FTIR spectra were recorded on a FTIR spectrophotometer using dry KBr pellets, with the scan range 400-4000 cm^{-1} . The analysis was performed on L-PLA@CR-BI composite films, prepared by casting from solution onto KBr disks (the films were dried under vacuum for 1h).

3.2.4 TGA and DSC Measurements of L-PLA@CR-BI Composite Films

Thermal stability, decomposition temperature, and char yield of L-PLA and L-PLA@CR-BI composite films were investigated by a Thermogravimetric Analyzer (TGA-Perkin Elmer Pyris 1) as reported by Rizzi et al. [129]. The glass transition temperature and the melting/crystallization behaviour of samples were evaluated by differential scanning calorimetric measurements using a DSC-Q200 – TA Instruments. Samples weighing 2-3 mg in an aluminium pan were equilibrated at 30°C and heated to 200°C. After an isotherm of 3 min at 200°C, the samples were cooled to -10°C, held at that temperature for 3 min, and reheated to 200°C. All cooling and heating scans were carried out with a heating rate of 10°C/min under a nitrogen atmosphere with a flow rate of 50 mL/min to avoid thermo-oxidative degradation. Crystallinity degree has been calculated by the eq. (1) as in ref. [130].

$$C(\%) = \frac{\Delta H_m - \Delta H_{c.c.} - \Delta H_{pre-m.c.}}{\Delta H_m^\circ (1 - \alpha)} \quad \text{eq. (1)}$$

where ΔH_m is the melting enthalpy, $\Delta H_{c.c.}$ is the cold crystallization enthalpy, $\Delta H_{pre-m.c.}$ is the pre-melt crystallization enthalpy and ΔH_m° is the melting enthalpy of 100% crystalline form of PLA (93,6 J/g) and α is the weight fraction of CR-BI.

3.2.5 Thermophysical Experiments on L-PLA@CR-BI Composite Films

L-PLA and L-PLA@CR-BI composite films are prepared and analysed as previously detailed. Density was measured via buoyancy method by means of a Sartorius balance. The thermal diffusivity was measured by Laser-Flash [131] equipment THETA Instrument on the same disc, after gold was sputtered on both sides, in order to prevent the laser light (1064 nm) used in the equipment from heating the sample and passing through it. Moreover, the DSC Setaram Microcalvet equipment, was used to evaluate the specific heat capacity. The combination of the above measurements gives the thermal conductivity, according to eq. (2):

$$\lambda = \alpha \cdot \rho \cdot C_p \quad \text{eq. (2)}$$

Where λ [W m⁻¹ K⁻¹] is the thermal conductivity, α [m² s⁻¹] is the thermal diffusivity, ρ [Kg m⁻³] is the density and C_p [J Kg⁻¹ K⁻¹] is the specific heat capacity. Given the very low concentration of CR-BI (1% maximum) into the L-PLA, density and specific heat capacity of L-PLA@CR-BI composite samples furnished the same results of neat PLA sample, as expected by the rule of mixture. On the contrary, a noticeable increase of thermal conductivity was observed, as reported below. All thermophysical properties were measured at room temperature.

3.2.6 Photothermal Experiments on L-PLA@CR-BI Composite Films

The four films, L-PLA, L-PLA@CR-BI*0.1, L-PLA@CR-BI*0.5 and L-PLA@CR-BI*1 were leaned on a table and lit by a flash lamp Bowens Traveller 3000G, emitting a pulse of light, discharging the battery pack of 3 kJ electrical energy. The colour temperature of the light is 5500 K. The duration of the light pulse is shorter than 5ms. The IR camera FLIR X6981sc SLS, 7.5–12.0 μ m wavelength interval of response, 640 X 512 pixels,

at 1 kHz, collected a sequence of images of the surface temperature. Some images are collected before the flash, averaged and subtracted to the images after the flash. The light produced by the flash lamp, passing through the sample is absorbed according to the Beer-Lambert law [132]:

$$I_{abs} = I_i(1 - e^{-\varepsilon L}) \quad \text{eq. (3)}$$

where I_{abs} [J m^{-2}] is the energy absorbed by the sample, I_i [J m^{-2}] is the energy of the incident light, L [m] is the thickness of the sample and ε [m^{-1}] the extinction coefficient, eventually depending on the CR-BI concentration: the greater the concentration the greater the absorption, the thicker the sample the greater the absorption. The light absorption, in a broad spectrum, can be measured by a bolometric technique, that is, by measuring the temperature rise of the sample after photothermal transformation of light energy in heat [133]. The temperature rise of a slab depends on the absorbed light, its thermophysical properties and the thickness:

$$\Delta T = \frac{I_{abs}}{\rho C_p L} \quad \text{eq. (4)}$$

the thicker the sample the lower the temperature rise. Table 1 reports the thickness of each sample. The thickness varies among the samples and within each sample from border to centrum. Such differences, together with the opposite role the thickness plays in the numerator and the denominator of eq. (4), leads to assume one simplifying assumption. Considering the low thickness of the samples it is convenient to linearize eq. (3). Therefore, the ratio between the temperature rise in each LPLA@ CR-BI sample and that in the pure L-PLA can be given with a good degree of approximation by eq. (5):

$$\frac{\Delta T_x}{\Delta T_0} = \frac{\varepsilon_x}{\varepsilon_0} \quad \text{eq. (5)}$$

where the subscript “0” stand for the pure L-PLA and $x = [0.1, 0.5, 1]$ %. It was also assumed that the incident light I_i is the same for each sample, and density and specific heat capacity do not significantly change with the addition of CR-BI, given its low concentration.

3.2.7 Charge Carrier Mobility on L-PLA@CR-BI Composite Films

The photo-CELIV technique was used to probe the electrical conductivity of L-PLA@CR-BI composite layers. MIS-CELIV devices were fabricated with an architecture of glass/ITO/SiO₂/organic layer/Al. A 30 nm SiO₂ film was deposited via e-beam on precleaned ITO substrate. A 200 nm L-PLA@CR-BI composite film was then spin coated (2000 rpm) onto the SiO₂ from chloroform solution (60 mg/mL) and further thermal annealed at 100 °C for 10 min. Finally, 100 nm Al was evaporated on the top of the organic layer as a cathode.

3.2.8 Synthetic Procedure of PTz₂-BTBTOx₄, MPA₂-BTBTOx₄, POCz₂-BTBTOx₄

Scheme 3 shows the retrosynthetic procedure followed to prepare the final emitting materials (PTz₂-BTBTOx₄, MPA₂-BTBTOx₄, and POCz₂-BTBTOx₄). The synthesis was accomplished by the Hartwig–Buchwald amination of Br₂-BTBTOx₄ with two equivalents of the corresponding donor units, *i.e.* phenothiazine (PTz) for PTz₂-BTBTOx₄, 4,4'-dimethoxydiphenylamine (MPA) for MPA₂-

Dimethoxydiphenylamine is a strong donor unit widely used in D- π -D molecular semiconductors [125,136,137], characterized by a non-planar and less rigid structure than the phenothiazine. The carbazole derivative POCz, bis-3,6-(4-octyloxyphenyl)-carbazole, was designed as the donor unit with a more complex molecular structure, combining the carbazole with two octyloxyphenyl units able to enhance the electron donor power of carbazole and at the same time to modulate, by steric effects of aliphatic chains, the aggregation properties in the solid state of the final emitting material.

3.2.9 Structural/chemical Analysis of PTz₂-BTBTO_x, MPA₂-BTBTO_x, POCz₂-BTBTO_x

FT-IR spectra were measured on a spectrophotometer using dry KBr pellets, with the scan range 4000–400 cm⁻¹. ¹H and ¹³C NMR spectra were recorded in CDCl₃ on a 400 spectrometer at 400 MHz and 100 MHz, respectively. The residual signals at $\delta = 7.24$ and $\delta = 77.0$ (CDCl₃) ppm were used as the standard for ¹H NMR and ¹³CNMR spectra, respectively. MS spectra were recorded on a mass spectrometer. MALDI-TOF spectrum was recorded on a MALDI TOF spectrometer in negative mode, by dithranol as the matrix. Elemental analyses were done by an Elemental Analyzer. The melting points were recovered in glass capillaries by a Gallenkamp apparatus and are uncorrected.

3.2.10 Photophysics Analysis of PTz₂-BTBTO_x, MPA₂-BTBTO_x, POCz₂-BTBTO_x

UV-vis absorption measurements (scan mode) were collected using a Cary 300 double beam spectrophotometer using rectangular 10 mm path length quartz cuvettes from Hellma, at 25°C. The absorption spectra were collected with concentrations in the range 10-20 μ M (total volume 10 mL volumetric flask). For all the solvents, dilutions were made from a stock solution in chloroform at 1 mg/mL. Fluorescence spectroscopic studies were performed with an Edinburg FLS980 spectrometer equipped with a peltier-cooled Hamamatsu R928 photomultiplier tube (185-850 nm), at 25°C. The studies in solutions were performed in a diluted solution with absorbance lower than 0.1 a.u. by using as holder a rectangular 10 mm path length quartz cuvettes from Hellma. For the analysis in solid state the materials were dispersed in rigid polymer matrix (Poly(methyl methacrylate) (PMMA) and Zeonex, Figure 23) at different concentration and deposited on quartz substrates. Corrected spectra were obtained *via* a calibration curve supplied with the instrument.

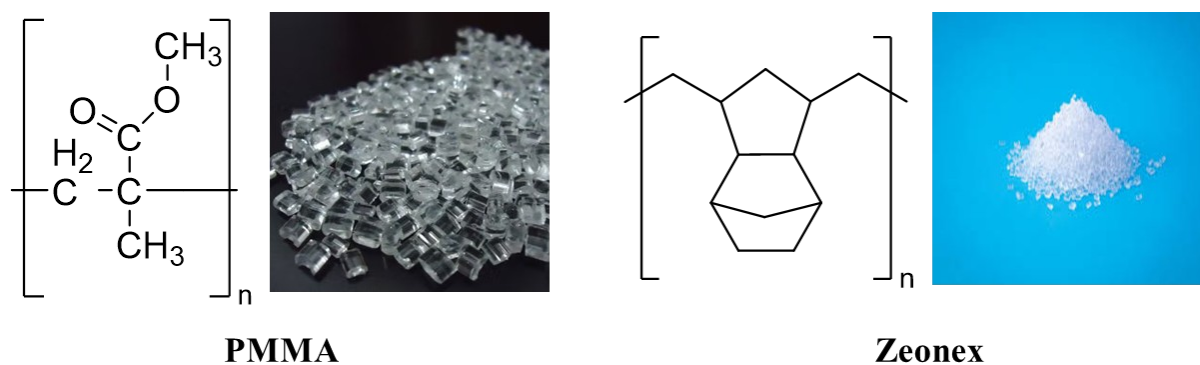


Figure 23. Rigid polymer matrix, PMMA and Zeonex, used as support for molecules.

For the excitation and emission spectra, the slits widths were adjusted between 1-5 nm, integration time 0.1 s, 1 nm step. The relative photoluminescence quantum yields (PLQY ϕ_{PL}) in solution were determined at 25°C, from corrected emission spectra using quinine sulfate in 0.1 M HClO₄ as the standard. For each QY measurements, slit width, excitation wavelength, scan rate, integration time and emission range were kept identical for the reference and the sample. The fluorescence QY was determined thanks to the following formula:

$$\phi_{PL} = \phi_R * \frac{Abs_R}{Abs_S} * \frac{\eta_S^2}{\eta_R^2} * \frac{I_S}{I_R} \quad \text{eq. (6)}$$

Where: ϕ_{PL} = Fluorescence quantum yield, Abs = absorbance of the solution, η = refractive index of the solvent, I = Integrated fluorescence intensity of the emitted light, and subscripts “R” and “S” refer to the reference and sample, respectively. For all solid films, PLQYs were calculated by corrected emission spectra obtained from an apparatus consisting of a barium sulfate coated integrating sphere (4 or 6 inches), a 450 W Xe lamp (λ_{exc} = tunable by a monochromator supplied with the instrument) as light sources, and a R928 photomultiplier tube as signal detectors, following the procedure described by De Mello et al [138]. Time-resolved experiments were performed in solution using 10 mm path length quartz cuvettes or directly using solid-state samples deposited on a quartz substrate. Decay transients in the ns- μ s range were determined by the time-correlated single-photon counting (TCSPC) technique using Edinburgh FLS980 spectrometer equipped with two different laser diodes as excitation sources (for ns- μ s range: EPL 1 MHz, λ_{exc} = 407 nm) and a peltier-cooled Hamamatsu R928 photomultiplier tube as detector. Delayed fluorescence decay was measured using single photon counting multichannel scaling (MCS) with a variable pulse length diode laser (VPL-375) as the excitation source. Delayed fluorescence decays in the μ s-ms range have been measured using single photon counting multichannel scaling (MCS) with a variable pulse length diode laser (VPL-375) as the excitation source. MCS is a complementary time-resolved technique to the more widely used TCSPC and is the method of choice for measuring delayed fluorescence. In MCS the detection window is split into time intervals and all photons that arrive within a specified time interval are counted, then the photons in the next interval are counted and so on until the entire time range is covered. This multiple stop mode detection enables higher detection count rates to be used than in TCSPC, reducing the acquisition time for longer decays. The pulse length of the VPL laser can be adjusted from 100 ns to 1000 μ s, which allows the pulse length to be optimised to the type of emission being measured. For our decays, the pulse length of the VPL was set to 100 ns which is sufficient to deliver sufficient power to the sample without obscuring the delayed fluorescence. Analysis of the luminescence decay profiles vs time was accomplished with the DAS6 Decay Analysis Software provided by the manufacturer. The quality of the fit was estimated by visual inspection of the weighted residuals and calculation of χ^2 . The first method to record the spectra of the prompt and delayed fluorescence (PF and DF) components is a time-resolved emission scan (TRES). In a TRES measurement, the fluorescence decay is measured as a function of the emission wavelength to construct a three-dimensional time-resolved spectrum. The VPL is ideal for TRES

measurements of delayed fluorescence as its high intensity and repetition rate allow rapid acquisition, with the TRES profile measured in less than 15 minutes. To obtain the emission spectra of the prompt and delayed components, the TRES profile is integrated using the FLS980's Fluoracle software to obtain the spectra in a specified time window. Experimental uncertainties are estimated to be $\pm 8\%$ for lifetime determinations, $\pm 20\%$ for emission quantum yields, ± 2 nm and ± 5 nm for absorption and emission peaks respectively. The second method of recording time-resolved spectra (from 400 ps to 1 s) is by nanosecond gated luminescence using the third harmonics of a high-energy pulsed Nd:YAG laser emitting at 355 nm (EKSPLA). The emission is focused onto a spectrograph and detected on a sensitive gated iCCD camera (Stanford Computer Optics) with sub-nanosecond resolution. The use of the iCCD camera and spectrograph allows individual spectra to be recorded at specific time delays (TD) with given integration times (IT) after pulsed laser excitation. This technique allows the simultaneous construction of decay curves with associated spectral data by collecting multiple spectra with exponentially increasing TD and IT. The results are collected under vacuum at 295 K and under a nitrogen flow at 77K.

3.2.11 Cyclic Voltammetry of PTz₂-BTBTO_{x4}, MPA₂-BTBTO_{x4}, POCz₂-BTBTO_{x4}

Cyclic voltammetry (CV) was performed at room temperature, in CH₂Cl₂ solution using tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M) as the supporting electrolyte and referenced against the ferrocene/ferrocenium (Fc/Fc⁺) redox couple. The CV curves were recorded in a potential window between + 0.0 and + 1.4 V vs Ag/AgCl.

3.2.12 Crystallographic Data of PTz₂-BTBTO_{x4}, MPA₂-BTBTO_{x4}, POCz₂-BTBTO_{x4}

***Ab-initio* structure determination by X-ray powder diffraction (XRPD)**

All the steps of the *ab-initio* structure solution by XRPD data (*i.e.*, indexing, space group determination, integrated intensities extraction, structure solution and Rietveld refinement) were carried out by *EXPO* [139]. The main outcomes are reported below:

- **Indexing.** The unit cell parameters were determined by *N-TREOR09*, *i.e.*, the default indexing program implemented in *EXPO*, exploiting the information on 38 experimental intense diffraction peaks lying in the 2θ range 7.5°-28.5°. The most plausible cell found by *N-TREOR09* was monoclinic [cell parameters $a=12.0101(16)$ Å, $b=13.5470(17)$ and $c=11.3074(16)$ Å, $\alpha = \gamma = 90.0^\circ$, $\beta = 101.574^\circ$ (11), $V=1802.3(4)$ Å³], characterized by an M20 de Wolff figure of merit [140] equal to 43 and no unindexed lines.

- **Space group determination.** The prior information on the unit cell parameters and atomic content was used to determine the space group by carrying out: a) the integrated intensities extraction in *P2/m* (*i.e.*, the space group with the largest Laue symmetry compatible with the geometry of the monoclinic unit cell and no extinction conditions); b) a statistical analysis on the suitably weighted integrated intensities, to detect the systematic absences and calculate a probability value for each extinction symbol compatible with the monoclinic crystal system (*i.e.*, 14 extinction symbols) [141]. *EXPO* correctly identified the most probable

extinction symbol (*i.e.*, $P\ 1\ 21/c\ 1$) and the corresponding space group $P21/c$ that was graphically selected to continue the *ab-initio* structure solution pathway.

- **Full pattern decomposition.** The extraction of the integrated intensities of reflections was performed by applying a not default procedure [142] to reduce the errors on the integrated intensities estimates and improve the results of the structure solution process.

- **Structure solution**

This step was carried out by applying two different approaches based on Direct Methods [143] and Simulated Annealing [144], working in reciprocal and direct space, respectively; the two procedures provided very similar structure models, enhancing the confidence on the correctness of the outcomes.

a) Structure solution by Direct Methods (DM). The integrated intensities were processed by DM, that determined twenty different sets of phases of reflections. For each set of phases, *via* an automatic procedure, *EXPO* performed a structure model optimization, obtaining twenty structure models that were ranked according to increasing values of *RF* (*i.e.*, the agreement factor between observed and calculated structure factor moduli). The most plausible structure model (*i.e.*, that one with the lowest *RF* value) was automatically selected by *EXPO* and consisted of 26 non-H atoms. The missing atom bonded to the sulphur atom was located by a careful analysis of an electron density map based on difference Fourier synthesis.

b) Structure solution by Simulated Annealing (SA). To solve the crystal structure, the SA approach in *EXPO* exploited the prior information on unit cell parameters, space group and trial starting model (H atoms included), built using ACD/ChemSketch [145] program and optimized by *EXPO* by Molecular Mechanics force fields. Twenty independent SA runs were carried out; the corresponding twenty final candidate structure models were ranked according to increasing values of the *Rwp* default cost function (the weighted profile reliability factor, *i.e.*, the weighted sum of the squared differences between observed and calculated profile). The degrees of freedom (*DOFs*) were automatically detected and varied by *EXPO* in each SA run, to find the best configuration corresponding to the minimum of the cost-function hypersurface. The total number of *DOFs* for **MPA₂-BTBTO_x** was thirteen, six of them describing the position and the orientation of the center of mass (external *DOFs*) and seven of them were torsion angles describing the molecular conformation (internal *DOFs*). At the end of the SA procedure, the most plausible structure model (*i.e.*, that one corresponding to the lowest *Rwp* value) was automatically selected by *EXPO*; its non-H atoms positions were compared with the corresponding positions of the crystal structure determined by DM; the root mean square deviation (RMSD) of the two structure models (non-H atoms) was 0.596 Å, where $\text{RMSD} = \sqrt{\sum i d_i^2 / N_{\text{au}}}$, *i.e.*, the square root of the averaged squared distances between couples of corresponding atoms in the two compared models; *N_{au}* is the number of atoms in the asymmetric unit. The two structure models were similar, emphasizing the reliability of the structure solution results.

- **Rietveld refinement**

The best SA structure model, H-atoms included, was further optimized by Rietveld [146] refinement. The structure refinement was carried out by applying restraints on bond distances and angles and constraints on the thermal isotropic factors of non-H atoms. The H atoms were refined according to the riding model. The rest of refined parameters was: unit cell parameters, background, full width at half maximum of the peak shape, peak asymmetry and zero-shift; the total number of refined parameters was 117. The refined SA structure model was even more overlapping with the structure model positioned by DM and the RMSD value of the two structure models (non-H atoms) lowered to 0.356 Å.

3.2.13 DFT Calculations of PTz₂-BTBTOx₄, MPA₂-BTBTOx₄, POCz₂-BTBTOx₄

We use density functional theory (DFT) and time-dependent DFT (TD-DFT) as well as the quasi degenerate perturbation theory (QDPT) with zeroth-order regular approximation (ZORA) [147] implemented in Orca 5.0.3 [148] in order to gain an additional insight into the luminescence mechanisms of the studied molecules. Ground state (S₀) and singlet excited state (S₁) geometries were optimised at the PBE0/def2-SVP level of theory which was found to be the most optimal for this task. All molecular orbital (MO) iso surfaces were visualised using Gabedit 2.5.0 [149]. All geometries were verified to be true energy minima by a frequency calculation. All optimisations were performed with tight self-consistent field (SCF) and geometry convergence criteria. Excited state energy of TD-DFT states was calculated using the S₁ geometry. In this case relativistically corrected triple-zeta basis set with ZORA was used: ZORA-def2-TZVP22 [150] alongside a range-separated CAMB3LYP functional. Spin-orbit coupling (SOC) calculations were performed as implemented in the ORCA software. SOC matrix elements (SOCME) were computed using the same settings as for the TD-DFT states. The RI-SOMF(1X) setting was used to accelerate SOC calculations.

3.2.14 OLEDs Devices with PTz₂-BTBTOx₄, MPA₂-BTBTOx₄, POCz₂-BTBTOx₄

For the fabrication of OLEDs, pre-patterned ITO-coated glasses were used as substrates. A UV-ozone treatment was performed for 20 minutes to enhance surface wettability. The pedot:PSS (CleviosAI4083) was deposited by spin coating at 2500 rpm, followed by annealing at 150°C for 20 minutes. The polyvinylcarbazole (molecular weight 1,100,00) was then spin-coated at 7000 rpm and annealed at 110°C for 10 minutes, starting from a solution with a concentration of 3 mg/ml in chloroform/chlorobenzene (volume ratio 95/5). The solutions for spin coating the emitting layers were prepared by dissolving the three active materials (**PTz₂-BTBTOx₄**, **MPA₂-BTBTOx₄** and **POCz₂-BTBTOx₄**) in toluene, each with a concentration of 10 mg/ml. They were then spin-coated at 2000 rpm and annealed at 100°C for 10 minutes to promote the evaporation of the residual solvent. In contrast, the solution for printing the **POCz₂-BTBTOx₄** layer was prepared by dissolving the material in a solvent mix of chloroform/toluene/o-dichlorobenzene in a volume ratio of 28/1/1, with a final concentration of 0.25 mg/ml. The **POCz₂-BTBTOxx₄**-based solution was then printed using a custom-made inkjet printer equipped with a single nozzle with a diameter of 300 µm. The nozzle moves at 1m min⁻¹ over the fixed glass substrate and ejects drops with a volume of ≈15 nL from a height of 7 mm above the substrate. The individual circular drops are separated by a distance of 1 mm (center to center). The final printed layer has a size of ≈3 cm². The printed layer was dried for 1 min at room temperature and then annealed at 110 °C for 5

min. Subsequently, 50 nm of TPBi, 1 nm of LiF, and 100 nm of Al were deposited by thermal evaporation at rates of 0.5 Å/s, 0.1 Å/s, and 1 Å/s, respectively, in high vacuum condition (10⁻⁷ mbar). The optoelectronic characteristics were acquired using an Optronics OL770 spectrometer coupled to the OL610 telescope unit and connected to a Keithley 2420 current–voltage source meter. Exciton utilization efficiencies (EUE, η_r) for each device were calculated from the equation:

$$\eta_r = \frac{EQE}{\Phi_{PL} \eta_{out} \gamma} \quad \text{eq. (7)}$$

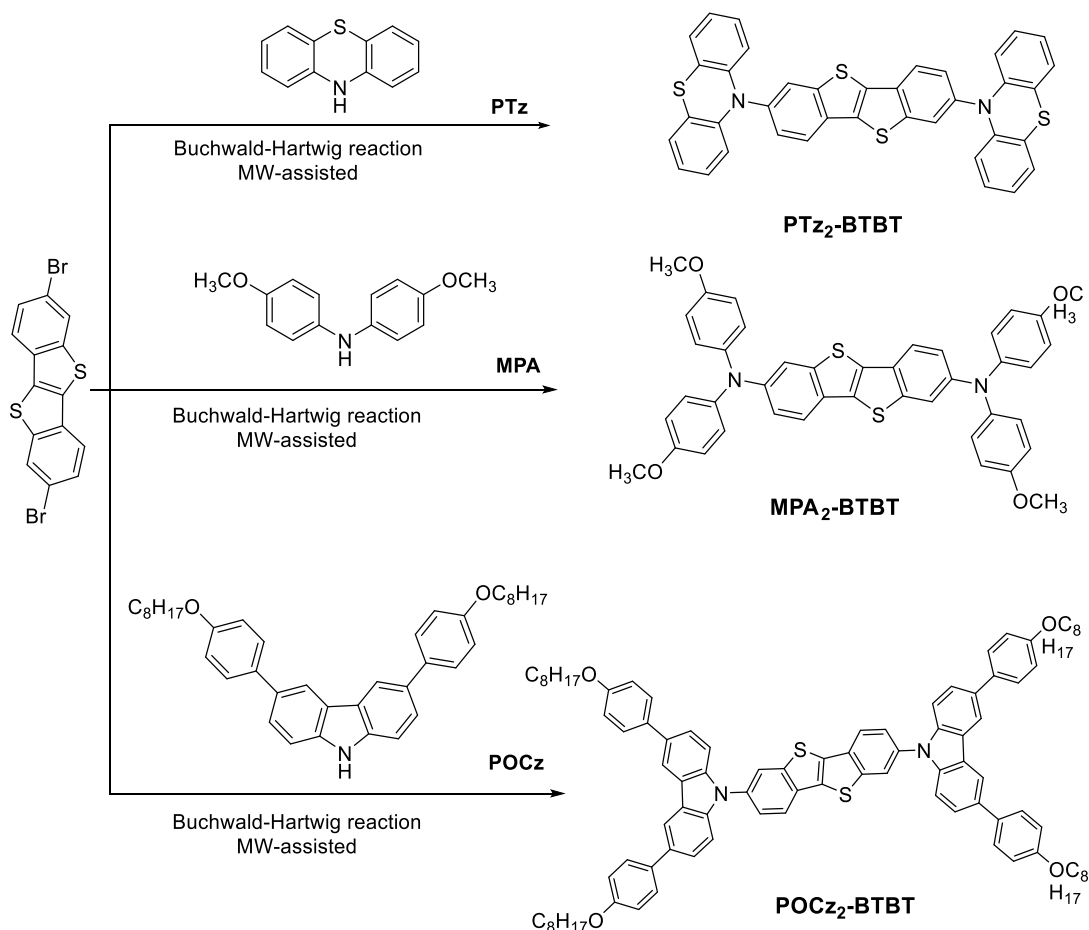
where EQE is the external quantum efficiency, η_{out} is the outcoupling efficiency (typically 0.2), γ is the carrier recombination efficiency (1 for an optimized device) and Φ_{PL} is the EML photoluminescence quantum yield.

3.2.15 Synthetic Procedure of PTz₂-BTBT, MPA₂-BTBT, POCz₂-BTBT

The key synthetic process is very simple and versatile and is based on the microwave-assisted amination of Buchwald-Hartwig, carried out starting from the reagents BTBT-Br₂, coupled with the donor units PTz, MPA and POCz (Scheme 4). The reaction was carried out in toluene as the solvent, at 110 °C and it is complete in about 1h. All synthetic details are reported in the Experimental Part (CHAPTER V).

3.2.16 Measurements of PTz₂-BTBT, MPA₂-BTBT, POCz₂-BTBT and MPA₂-BTBTOx₄, PTz₂-BTBTOx₄ and POCz₂-BTBTOx₄

FT-IR spectra were measured on a spectrophotometer using dry KBr pellets, with the scan range 4000–400 cm⁻¹. ¹H and ¹³C NMR spectra were recorded in CDCl₃ on a 400 spectrometer at 400 MHz and 100 MHz, respectively. The residual signals at $\delta = 7.24$ and $\delta = 77.0$ (CDCl₃) ppm were used as the standard for ¹H NMR and ¹³CNMR spectra, respectively. Elemental analyses were done by an Elemental Analyzer. The melting points were recovered in glass capillaries by a Gallenkamp apparatus and are uncorrected.



Scheme 4. Schematic synthetic route to PTz₂-BTBT, MPA₂-BTBT, POCz₂-BTBT.

3.2.17 Electrochemical Characterization of PTz₂-BTBT, MPA₂-BTBT, POCz₂-BTBT and MPA₂-BTBT₄, PTz₂-BTBT₄ and POCz₂-BTBT₄

Electrochemical characterization of dyes was carried out by cyclic voltammetry (CV) using an Autolab PGSTAT302N (Metrohm) potentiostat. A typical three-electrode cell was assembled with a glassy carbon disk-working electrode, a Pt-wire auxiliary electrode, and an Ag/AgCl non-aqueous reference electrode. Cyclic voltammograms were acquired at scan rate 50 mV s⁻¹, on 1 mM dye solutions prepared in the electrolyte solution, which consisted of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in dichloromethane (CH₂Cl₂). All the solutions were previously degassed with N₂. The CV of the Ferrocenium/Ferrocene (Fc⁺/Fc) couple (1 mM) was also recorded in the same condition used for all compounds solutions and used as external reference for potential calibration.

3.2.18 DFT Calculations of PTz₂-BTBT, MPA₂-BTBT, POCz₂-BTBT and MPA₂-BTBTOx₄, PTz₂-BTBTOx₄ and POCz₂-BTBTOx₄

We use density functional theory (DFT) and time-dependent DFT (TD-DFT) implemented in Orca 5.0.3 [151,152] in order to gain an insight into the electronic levels of the studied molecules. Ground state (S_0) geometry was optimized at the PBE0/def2-SVP [153] level of theory. All geometries were verified to be true energy minimum by a frequency calculation with no imaginary frequencies found. All optimizations were performed with tight self-consistent field (SCF) and geometry convergence criteria. A range-separated CAM-B3LYP functional and the def2-SVP basis set were used for single point energy calculations. All molecular orbital (MO) iso surfaces were visualized using Gabedit 2.5.0 [154].

3.2.19 MIS-CELIV Measurements of PTz₂-BTBT, MPA₂-BTBT, POCz₂-BTBT and MPA₂-BTBTOx₄, PTz₂-BTBTOx₄ and POCz₂-BTBTOx₄

3.2.19.1 Device Fabrication

MIS-CELIV devices were fabricated with an architecture of glass/ITO/SiO₂/organic layer/Al. A 30 nm SiO₂ film was deposited via e-beam on precleaned ITO substrate. A 200 nm organic film was then spin coated (2000 rpm) onto the SiO₂ from chloroform solution (60 mg/mL) and further thermal annealed at 100 °C for 10 min. Finally, 100 nm Al was evaporated on the top of the organic layer as a cathode (Figure 24).

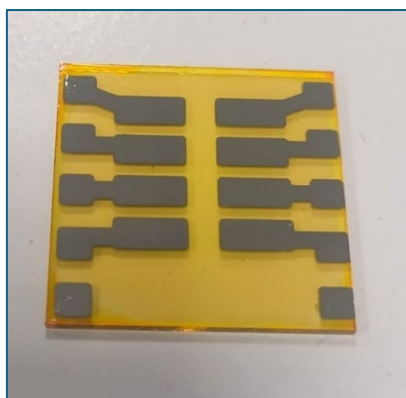


Figure 24. MIS-CELIV device made using MPA₂-BTBTOx₄.

3.2.19.2 MIS-CELIV Technique

After preparation, the devices were placed into a cryostat (Oxford Optistat DNV), evacuated to 10^{-5} mbar, and disconnected from the vacuum pump. Holes' mobility was measured by negatively biasing (offset) the ITO electrode while optically pumping the sample using a short (7 ns) laser pulse from a tunable pulsed laser (Opolette 355). The photogenerated holes drift towards the negatively biased electrode resulting in the

accumulation of holes at the SiO₂/semiconductor interface, while electrons are swept away from the Al contact. Then, a linearly increasing voltage, from a function generator (Agilent 33220A), extracts the accumulated holes back to the Al contact. Meanwhile, for electrons mobility measurements, the Al electrode was negatively biased (offset), while optically pumping the sample, which resulted in the accumulation of photogenerated electrons at the SiO₂/semiconductor interface, while holes are swept away from the same contact. As the Al electrode becomes positively biased, during the ramp voltage, electrons drift towards the Al contact from which they are collected. Collected charges give rise, across an external series resistance, to time-dependent extraction current density given by $J(t) = J_0 + \Delta J(t)$, recorded via a storage oscilloscope (Tektronix DPO3054). The very first initial current step J_0 :

$$J_0 = \frac{\varepsilon_0 A}{\frac{d_s + d_i}{\varepsilon_s + \varepsilon_i}} \quad \text{eq. (8)}$$

is caused by the geometric capacitance of the sample. Here $A = dU/dt \text{ Vs}^{-1}$ is the voltage ramp rate, ε_0 is the vacuum permittivity, whereas ε_s (ε_i) and d_s (d_i) are the relative permittivity and thicknesses of the organic semiconductor layer (insulator layer), respectively. The time-dependent extraction current $\Delta J(t)$, the area above J_0 , is the extracted photo-generated carrier concentration (photo-MIS-CELIV), in addition (eventually) to the equilibrium charge carrier concentration, meanwhile it gives only the amount of equilibrium charge carriers in the case of dark-MIS-CELIV. A schematic picture is shown in Figure 25.

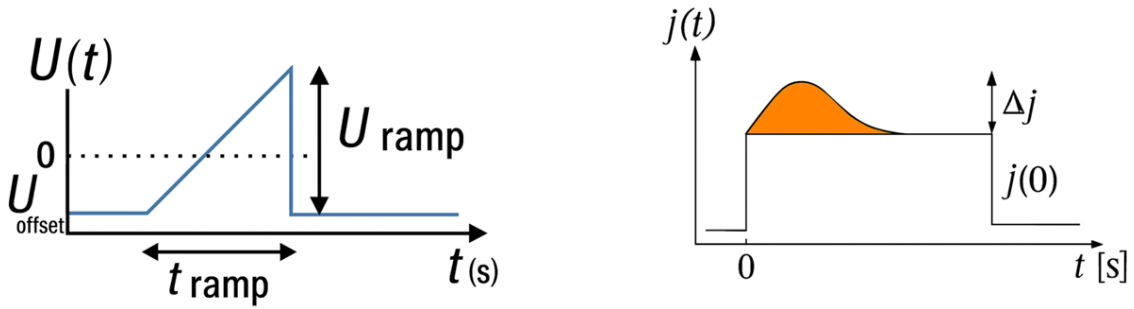


Figure 25. Schematic of the applied voltage (offset + ramp) and current transient response.

The time it takes for the transient to reach the maximum extraction point is defined as the transit time ($t_{\max}$), hence it is possible to calculate the mobility from the following equation [155-157]:

$$\mu = \frac{2d_s^2}{At_{\max}^2} \left(1 + \frac{\varepsilon_s d_i}{d_s \varepsilon_i} \right) \quad \text{eq. (9)}$$

3.2.20 Electrochemical Analysis: MPA₂-BTBT Vs MPA₂-BTBTO_{x4}

Electrochemical characterization of compounds was carried out by cyclic voltammetry (CV) using an Autolab (Metrhom Mod.) potentiostat. A typical three-electrode cell was assembled with a glassy carbon disk working electrode, a Pt-wire auxiliary electrode, and an Ag/AgCl nonaqueous reference electrode. Cyclic voltammograms were acquired at different scan rate, from 50 to 100 mV/s, on 1 mM compound solutions prepared in the electrolyte solution, which consisted of 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in dichloromethane (CH₂Cl₂). All the solutions were previously degassed with N₂. The CV of the Ferrocenium/Ferrocene (Fc⁺/Fc) couple (0.1 mM) was also recorded in the same condition and used as external reference for potential calibration.

3.2.21 Electrochromic Device Fabrication

The EC polymer gels were prepared with 2% (w/w) of the anodic specie, the 2% (w/w) of ethylviologen doperchlorate, the 40% (w/w) of PVF, and 56% (w/w) of NMP. The two electrochromic active species were first dissolved in NMP at room temperature and then mixed with the polymer under continuous stirring at 120 °C for 30 min. ITO/EC gel/ ITO devices were assembled by drop casting of the hot EC mixture onto a ITO-coated glass support (Visiontek Systems Ltd. with a sheet resistance of 25 Ω sq⁻¹ and a thickness of 1 mm) with a second ITO electrode used to create a sandwich with active area of about 1.5 × 1.5 cm². The cell gap was controlled by inserting cylindrical spacers with mean base diameter of 30 × 10⁻⁶ m. Standard cyclic voltammetry of the electrochromic polymer gel (EC gel) was performed with an Amel Instruments 7050 model potentiostat on the ITO/EC gel/ITO cell in which the two ITO plates worked as working and counter electrodes. Spectroelectrochemical experiments were performed, on the two-electrode device, with the Vertex 80 (Bruker) spectrophotometer. The potential was supplied by means of an Autolab (Metrhom Mod.) potentiostat. Measurements were performed at 25 °C. (Figure 26)

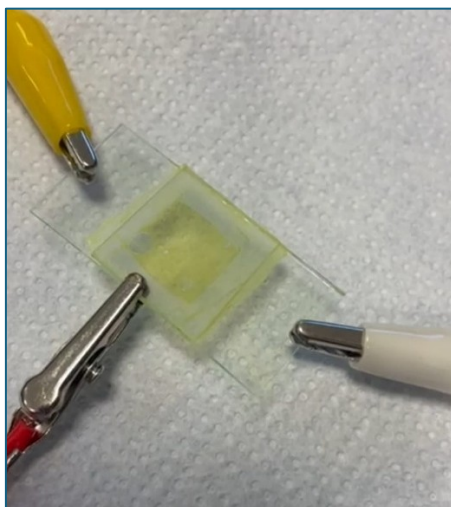


Figure 26. Electrochromic device made using MPA₂-BTBT.

CHAPTER IV

Results and Discussion

4.1 D-A-D Compounds for Thermal Energy Storage Applications: CR-BI as Photothermal Filler

In order to broaden the application field of the CRs and investigate their potential use of CRs in thermal energy storage applications, we explored the effect of the addition of the CR-BI on the thermophysical properties of L-PLA. We prepared three different solutions of L-PLA and CR-BI in chloroform, containing 20 mg/ml of LPLA and 0.1%wt, 0.5%wt and 1%wt of CR-BI, respectively (L-PLA@CR-BI*0.1, LPLA@CR-BI*0.5 and L-PLA@CR-BI*1). The three solutions were deposited by casting on glass and ITO supports. Films with a homogeneous distribution of CR-BI in the L-PLA matrix were obtained, proving a good affinity between the two organic components. On glass the L-PLA@CR-BI composite films display a very good adhesion, while on ITO they detach easily from the surface giving stable and resistant plastic films.

The L-PLA@CR-BI films were characterized by UV-Vis and FTIR spectroscopy, TGA and DSC measurements, photothermal and thermophysical experiments.

4.1.1 UV-Vis Spectroscopy

UV-Vis spectra confirm the presence of the organic additive in the polymer matrix, showing CR-BI characteristic absorption peak. CR-BI has a strong absorption in the NIR region ($\lambda_{\text{max}} = 810$ nm, molar extinction coefficient $\epsilon = 5.04 \times 10^4$). Its absorption spectrum is reported in Figure 27 (inset), together with that of L-PLA@CR-BI films. All spectra show the characteristic absorption profile of CR-BI, thanks to a homogeneous dispersion of CR-BI in the PLA matrix behaving as a solid solution (Figure 27).

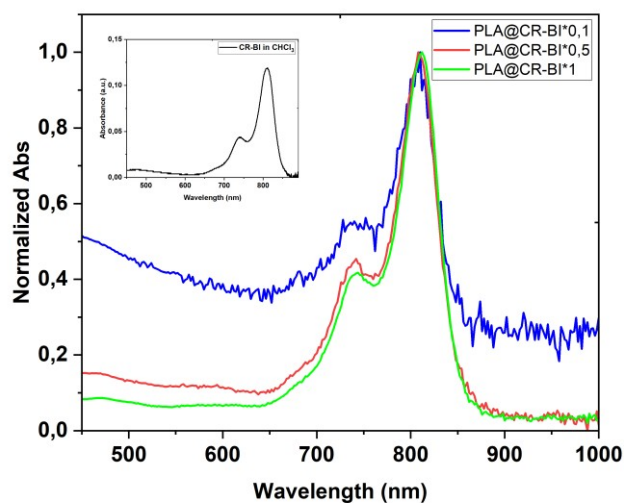


Figure 27. Absorption spectra of L-PLA@CR-BI composite films: a) L-PLA@CR-BI*0.1 (blue); b) LPLA@ CR-BI*0.5 (red) and c) L-PLA@CR-BI*1 (green). In the inset the absorption spectrum of CR-BI in CHCl₃ (2.36 μ M).

4.1.2 FTIR Spectroscopy

Pure L-PLA and CR-BI (KBr pellets) were analysed for comparison and their FTIR spectra are reported in Figure 28, while in Figure 29 are reported the FTIR spectra of pure L-PLA and L-PLA@CR-BI*1 composite film. Due to the low quantity of CR-BI dispersed in the PLA matrix, the FTIR spectra of L-PLA@CR-BI composite samples are very similar and show substantially the signals of L-PLA (Table 2). For clarity of figure, are reported for comparison only the FTIR spectra of L-PLA and L-PLA@CR-BI*1 (Figure 29).

Table 2. Peak band assignments for PLA IR.

Assignments	Peak position, cm^{-1}
-CH- stretch	2996 (asym.), 2933 (sym.)
-C=O carbonyl stretch	1760
-CH ₃ bend	1454
-C=O bend	1266
-CO- stretch	1188, 1130, 1093
-OH bend	1047
-C-C stretch	869

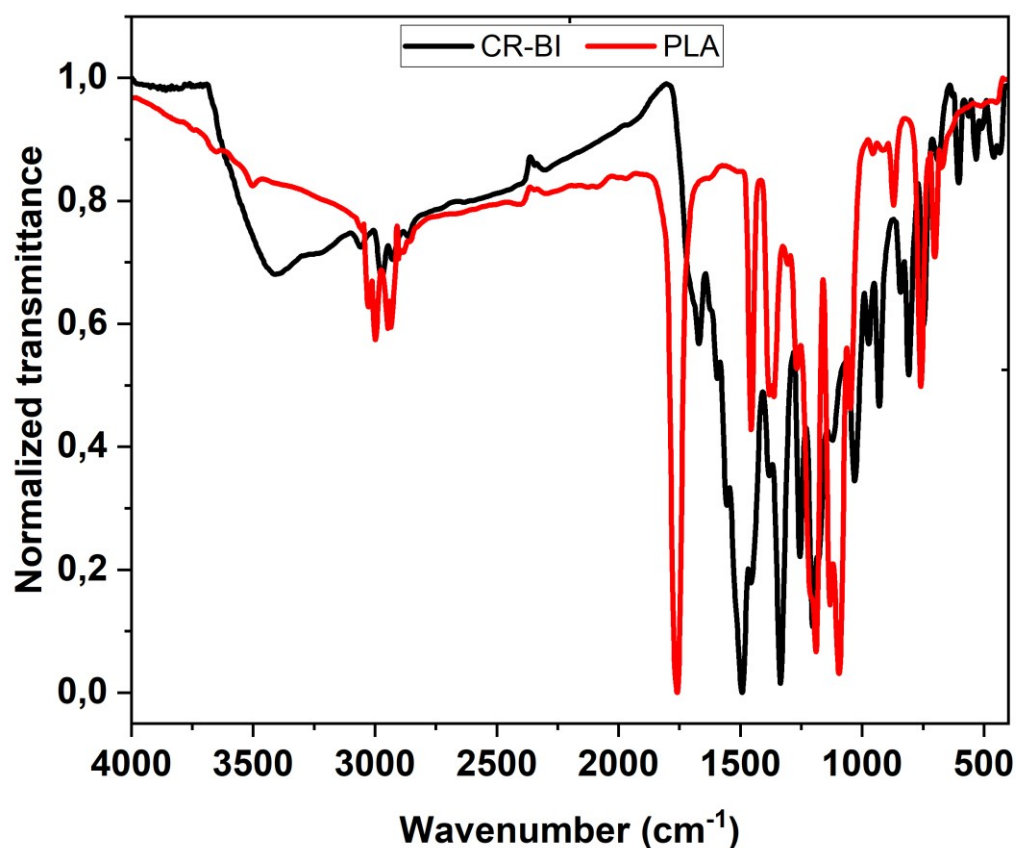


Figure 28. FTIR spectra of L-PLA (KBr pellet, red) and CR-BI (KBr pellet, black).

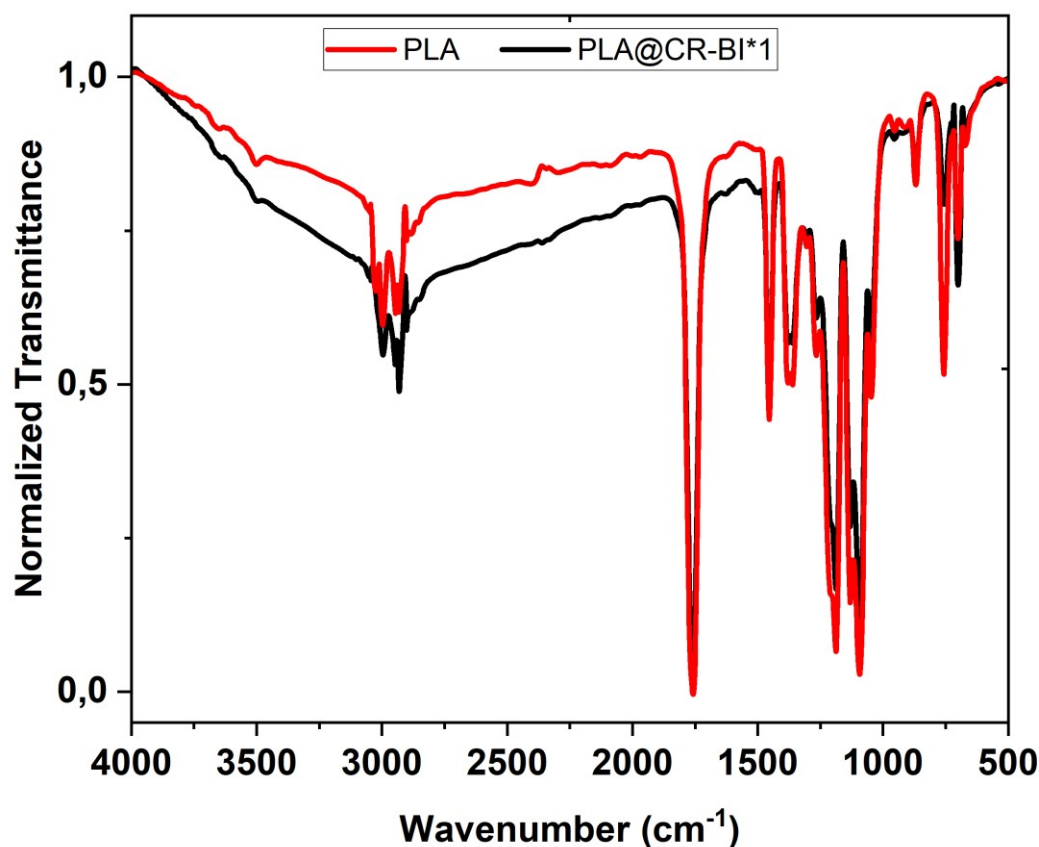


Figure 29. FTIR spectra of pure L-PLA (KBr pellet, red) and L-PLA@CR-BI*1 composite film (black).

4.1.3 TGA and DSC Measurements

To investigate the effect of CR-BI on the thermal properties of PLA in L-PLA@CR-BI composite solid layers, thermal analysis was performed by recording the thermograms of both neat L-PLA and L-PLA@CR-BI composite films, as shown in Figure 30. The thermograms are very similar across all samples. An initial weight loss of approximately 7% is observed in each case, with a maximum degradation rate at 68 °C, attributed to residual solvent used for the film preparation process. Following this initial loss, all samples - regardless of CR-BI content - exhibit a single-step degradation process occurring within the 240-390 °C temperature range, with a maximum decomposition rate at an average temperature of 364 ± 3 °C. The only noticeable effect of CR-BI incorporation in the PLA matrix films is a slight increase in char yield, which correlates with the increasing CR-BI content and is attributed to the higher thermal stability of CR-BI itself (see inset in Figure 30). The char yields are 0,5% for neat L-PLA, 0,5% for L-PLA@CR-BI*0.1, 1,1% for LPLA@ CR-BI*0.5 and 1,7% for L-PLA@CR-BI*1. These results indicate that the incorporation of CR-BI into the PLA matrix, even up to a concentration of 1%, does not significantly alter the thermal stability of the resulting composite films. This observation is consistent with previously reported findings of other additives [158].

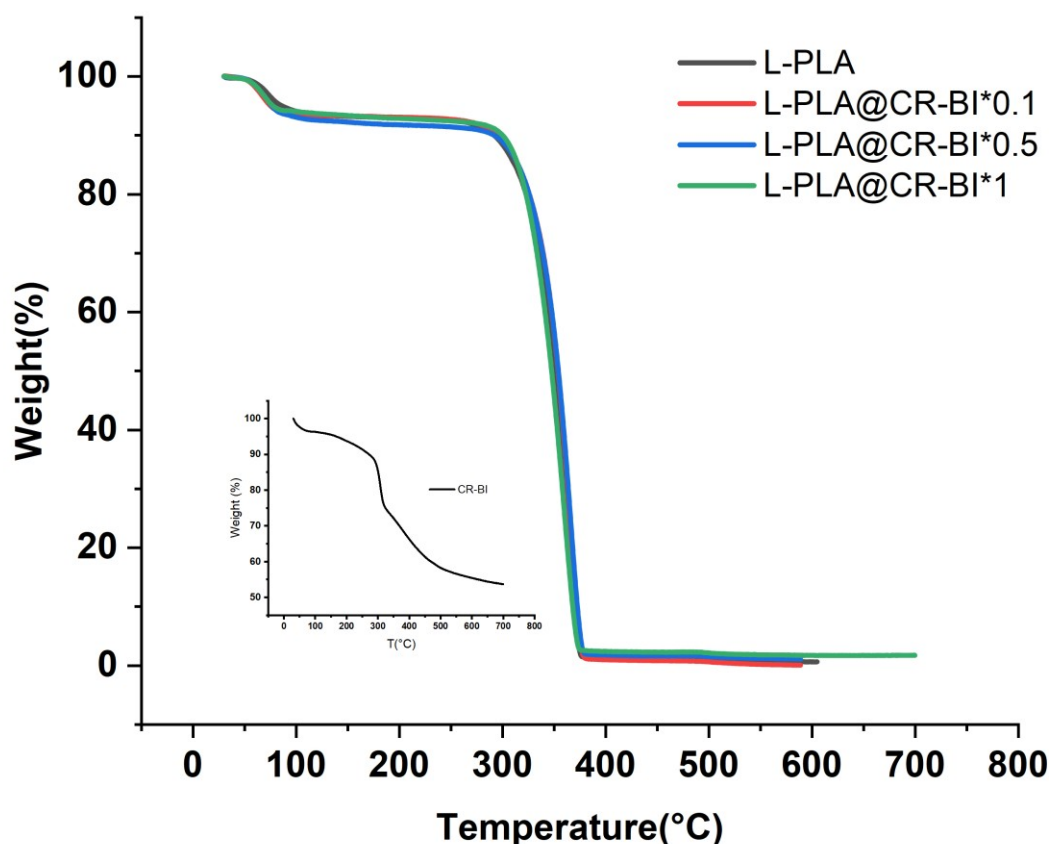


Figure 30. Thermograms of L-PLA (black), and L-PLA@CR-BI*0.1 (red), L-PLA@CR-BI*0.5 (blue), L-PLA@CR-BI*1 (green) samples. Thermogram of CR-BI in the inset.

Following the thermogravimetric (TG) analysis, which indicated no significant decomposition below 200 °C, differential scanning calorimetry (DSC) measurements were conducted on neat L-PLA and L-PLA@CR-BI composite films over the temperature range of -10 to 200 °C. Figure 31 presents the DSC curves obtained during the second heating cycle for both neat L-PLA and L-PLA@CR-BI composite films. The first heating scan (not shown) was performed to eliminate the influence of prior thermal history. All cooling thermograms, provided in the “Experimental Part” (CHAPTER V) display both crystallization and a glass transition event. The thermal parameters associated with the crystallization process are summarized in Table 3. Due to partial overlap with the crystallization peak, the glass transition temperature (T_g) could not be accurately determined from the cooling scans.

Table 3. DSC parameters of samples from the cooling scan.

Sample	T_c (°C)	$T_{onset/c}$ (°C)	ΔH_c (J/g)
L-PLA	104.9	112.6	36.5
L-PLA@CR-BI*0.1	101.4	112.9	32.0

L-PLA@CR-BI*0.5	98.7	111.8	23.3
L-PLA@CR-BI*1	94.5	110.9	23.0

The incorporation of increasing amounts of CR-BI leads to a marked reduction in the crystallization enthalpy, accompanied by a progressive shift of the peak crystallization temperature towards lower values. A similar downward trend is observed for the onset temperature of crystallization, although the shift is less pronounced compared to that of the peak temperature. This behaviour suggests that, in the presence of CR-BI, the crystallization process becomes less reversible. As a result, only a portion of the original crystalline structure is recovered upon cooling, while the remainder transforms into a supercooled amorphous phase. This is further supported by the presence of a cold crystallization event observed during the subsequent heating scan. Specifically, the DSC thermograms recorded during the second heating cycle reveal an exothermic cold crystallization peak occurring between the glass transition and a pre-melting exothermic crystallization event, immediately preceding the main endothermic melting transition (data are reported in Table 3). This thermal behaviour is consistent with previous reports in the literature [159].

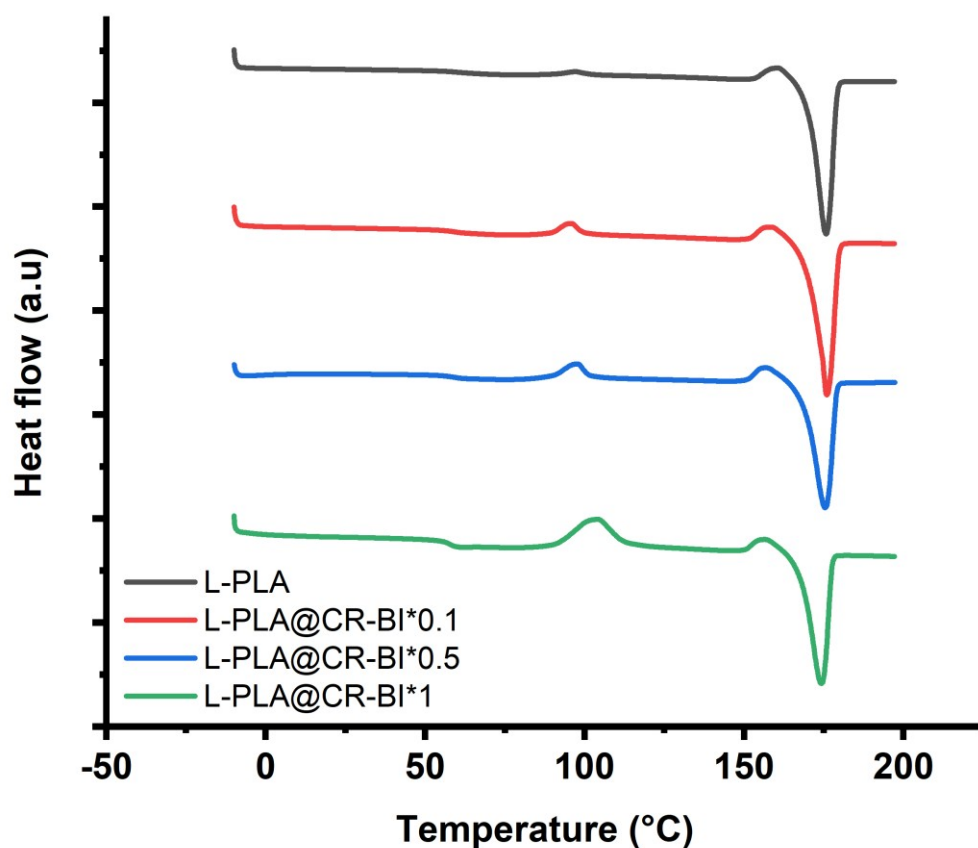


Figure 31. DSC curves of L-PLA (black), L-PLA@CR-BI*0.1 (red), L-PLA@CR-BI*0.5 (blue) and L-PLA@CR-BI*1 (green) samples

Literature data indicated that the glass transition temperature (T_g) of neat L-PLA films is influenced by the preparation method [160,161]. The T_g value obtained in this study, 60.4 °C, is consistent with that reported by Wang et al. [162]. The incorporation of CR-BI results in a slight reduction of T_g , suggesting that CR-BI acts as a plasticizer by increasing polymer chain mobility and thereby facilitating the transition from a disordered to a more ordered state. Furthermore, an increase in both the enthalpy and the temperature of cold crystallization is observed with increasing CR-BI content, while the onset temperature of cold crystallization has not significant change. This trend indicates that CR-BI interacts with the polymer chains in a manner that promotes their crystallization upon heating, enabling the release of energy previously stored in the supercooled amorphous state. Conversely, the nearly constant enthalpy associated with pre-melting crystallization across all samples suggests the presence of polymer chain segments that are not significantly influenced by CRBI. These segments require higher thermal energy – close to the melting enthalpy – to undergo crystallization. This behaviour is consistent with the low concentration of CR-BI and the relatively constant melting enthalpy values, which includes contributions from both the initial crystalline domains formed during film preparation and those formed during the cold and pre-melting crystallization events. The degree of crystallinity (C) calculated using the enthalpies of melting, cold crystallization and pre-melting crystallization according to Equation (1) (Sec. 2.2.4), shows that – except for the sample containing 0.1% CR-BI – the presence of CR-BI leads to an increase in the amorphous fraction. In summary, TG and DSC analyses reveal that, in the framework of the amounts used, CRBI does not significantly alter the thermal stability of the films but does lead to a reduction in crystallinity during the film formation process. Additionally, the observed changes in T_g and cold crystallization enthalpy further support the conclusion that CR-BI enhances polymer chain mobility in heated L-PLA films, thereby facilitating the release of the thermal energy through the formation of new crystalline domains. These characteristics suggest that such materials could also be of interest for thermal energy storage applications [163].

4.1.4 Thermal and Photothermal Measurements

Thermal properties of neat L-PLA have been measured as reported in Sec 2.2.5. Moreover, the experiment for the assessment of thermal diffusivity (by Laser Flash method) have been done maintaining the laser light as low as possible to avoid sample damage. Furtherly, the signal to noise ratio was improved by averaging 128 tests. Thermal conductivity results from the combination of the afore-mentioned measurements as in eq. (2) (Sec. 2.2.5). The results are reported in Table 4.

Table 4. Thermal data of L-PLA and L-PLA@CR-BI*1 composite

	Density (Kg/m ³)	Specific heat (J/KgK)	Thermal Diffusivity (mm ² /s)	Thermal Conductivity (W/m K)
L-PLA	1200	1300	0.0998	0.16
L-PLA@CR-BI*1	1200	1300	0.349	0.55

Successively, the PLA@CR-BI composite with the higher content of CR-BI (L-PLA@CR-BI*1) was investigated to assess the effects of CR-BI as a filler inner L-PLA matrix on the thermal properties. The results are reported in Table 4 as well. The photothermal energy conversion capability of CR-BI in the L-PLA matrix by photothermal experiments was carried out on L-PLA@CR-BI composite films. The four films were mounted on a paper frame as shown in Figure 32A, while the picture of the experimental set up is shown in Figure 32B.

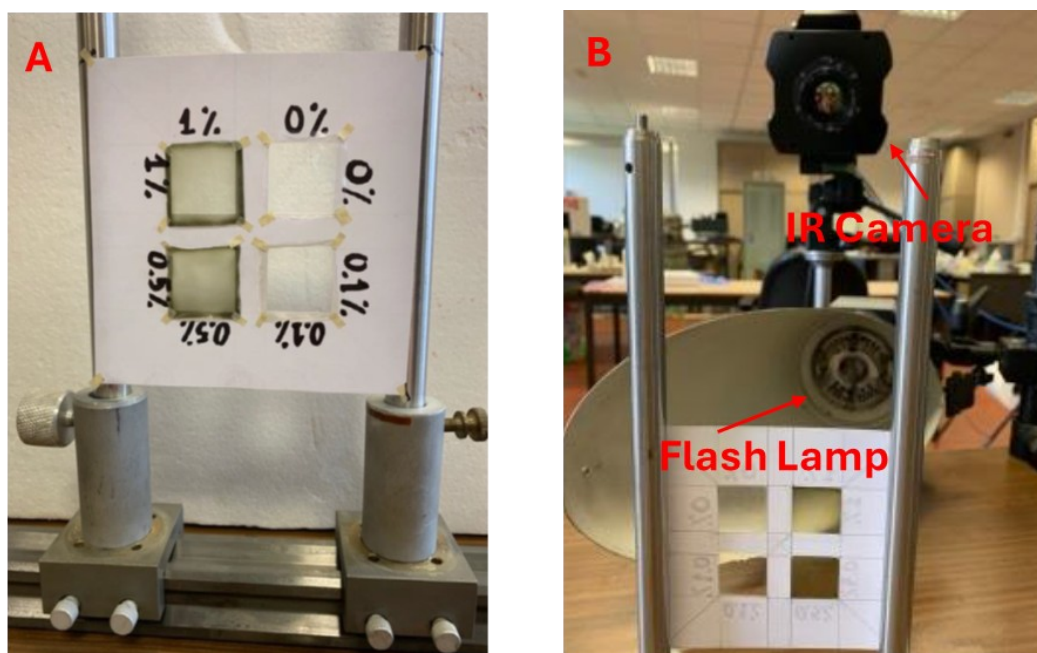


Figure 32. A) the four films mounted on the paper frame; B) the experimental lay out taken from the back of the paper frame.

By a photographic flash lamp (colour temperature 5500 K) a short pulse of light was directed to the surface of the samples. The test was done in *reflection mode*, that is, the camera and the flash stand on the same side of the samples. Figure 33A shows the infrared image after the flash pulse. Notice the hand drawing, indicating the CR-BI percentages, that heated up due to the absorption of light by the pencil graphite. The camera collected 500 images @ 1 KHz after the flash, plus 50 images before the flash to give the baseline to subtract from the successive images. The result is shown in Figure 33B for each sample. The effect of the photothermal energy conversion due to the CR-BI is qualitatively clearly visible and in the expected order: the higher the CR-BI concentration the higher the temperature rise. Twenty tests have been done to smooth possible variations in the lamp energy. Rotating the position of the four samples gave a further equalization for a possible inhomogeneity of the spatial light intensity. The results obtained by applying eq. (5) (Sec. 2.2.6) to the 20 tests are reported in Table 5.

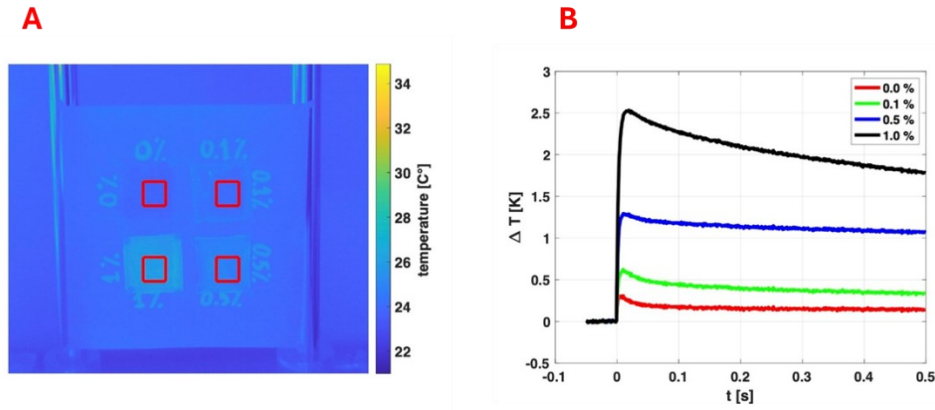


Figure 33. A) IR image of the samples after the flash pulse; B) the temperature profiles in time, collected averaging the pixels values inside the four red boxes of the IR image.

Table 5. Ratio of the extinction coefficients of each CR-BI sample against the neat L-PLA

L-PLA@CR-BI*0.1	L-PLA@CR-BI*0.5	L-PLA@CR-BI*1
2.3	4.6	9.1

The addition of croconaine CR-BI as a semiconductor filler inner L-PLA matrix strongly impact on the thermal diffusivity and then thermal conductivity of L-PLA. Despite the very low concentration of CR-BI (1%wt with respect to L-PLA) used to build up the L-PLA@CR-BI composite, an impressive increment of thermal diffusivity and conductivity is performed, that should be a consequence of a very uniform distribution of the filler inner L-PLA matrix, due to a high molecular affinity between L-PLA polymer chains and CR-BI. The high affinity allows to realize a very uniform and continuous filler networks inner L-PLA matrix, mimicking a solid solution and determining a strong impact on its thermal properties.

4.1.5 Photo-MIS-CELIV Measurements

Photo-MIS-CELIV measurements were performed on LPLA@CR-BI*1 samples to probe the electrical conductivity of the composite. Samples were optically pumped, from a tunable pulsed laser (Opolette 355), via a short laser pulse (7 ns) at a wavelength of 810 nm. Then, a linearly increasing voltage ($U(t)$), from a function generator (Agilent 33220A), was applied. The current signal (displayed in Figure 34) is caused by the geometric capacitance of the sample. Here $A = dU/dt$ [V/s] is the voltage ramp rate, ϵ_0 is the vacuum permittivity, whereas ϵ_s (ϵ_i) and d_s (d_i) are the relative permittivity and thicknesses of the composite layer (SiO_2 layer), respectively. No photocarriers transient was detected upon light excitation, indicating a complete conversion of light into thermal energy. This result confirms that upon light absorption the composite retains its insulating properties.

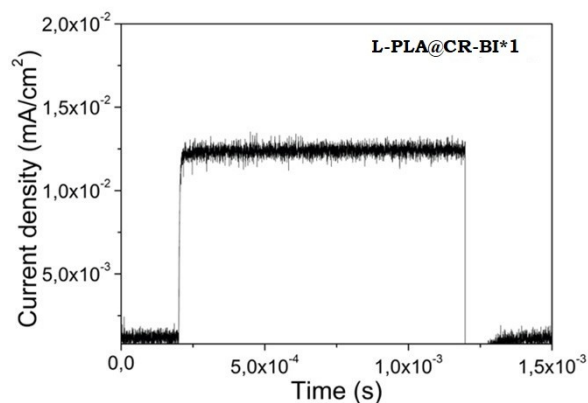


Figure 34. MIS-CELIV transient for composite L-PLA@CR-BI*1.

4.2 D-A-D Compounds with BTBT₄ Acceptor Core for OLED Devices

We report the results of our studies on three new TADF emitters with a D–A–D structure, based on [1]benzothieno[3,2b]benzothiophene-tetraoxide BTBT₄ as the electron-acceptor unit A and three different electron-donor units D (Figure 35). Phenothiazine, dimethoxyphenylamine and a carbazole derivative were selected as donor units D to prepare the final materials. New BTBT₄-based small molecules were prepared following a straightforward synthetic protocol based on the microwave-assisted Buchwald–Hartwig reaction. They were then characterized by cyclic voltammetry, photo-CELIV measurements, crystallographic analysis, and theoretical and photophysical studies. Photophysical studies revealed the TADF properties in this new class of organic emitting materials and as a proof of concept they were tested as neat emissive layers in solution-processed OLED devices.

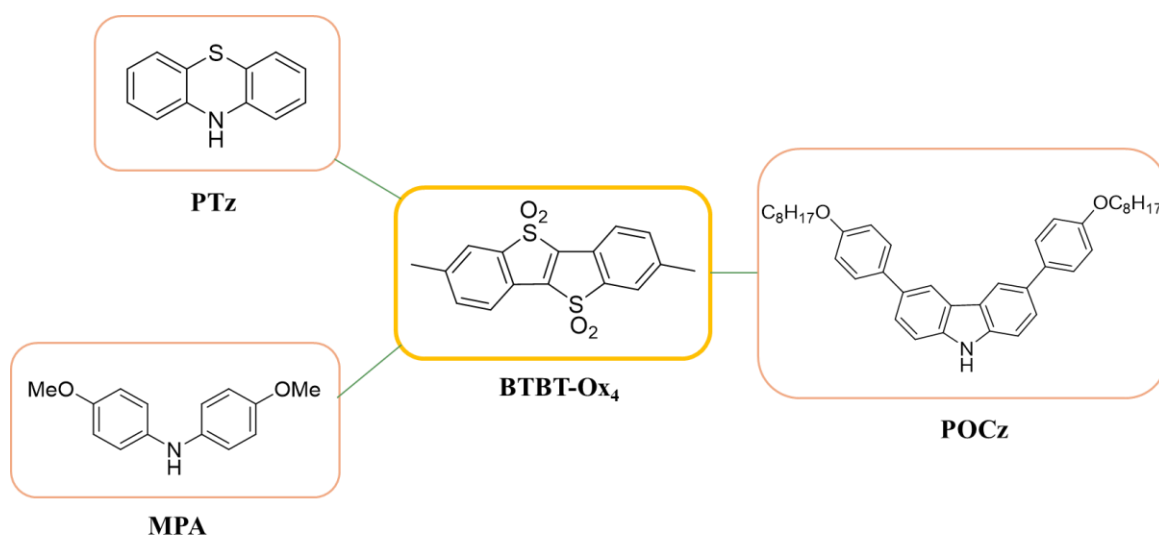


Figure 35. Donor groups: Phenothiazine, dimethoxyphenylamine and a carbazole derivative.

4.2.1 Cyclic Voltammetry

We investigated the electrochemical properties of the BTBTO_{x4}-based emitters BTBT by cyclic voltammetry (CV) measurements (Figure 36). All three compounds show two redox oxidation processes, and the values were found to be 1.00 and 1.06 V for POCz₂-BTBTO_{x4}, 0.80 and 0.92 V for PTz₂-BTBTO_{x4} and 0.73 and 0.97 V for MPA₂-BTBTO_{x4} vs. Ag/AgCl, respectively. The highest occupied molecular orbital (HOMO) energy levels were estimated to be -5.70, -5.42 and -5.35 eV for POCz₂-BTBTO_{x4}, PTz₂-BTBTO_{x4} and MPA₂-BTBTO_{x4}, respectively. The lowest unoccupied molecular orbital (LUMO) energy levels were calculated from the HOMO levels and the optical energy gaps, and found to be -3.04, -2.70 and -2.97 eV for POCz₂-BTBTO_{x4}, PTz₂-BTBTO_{x4} and MPA₂-BTBTO_{x4}, respectively. The data are reported in Table 6.

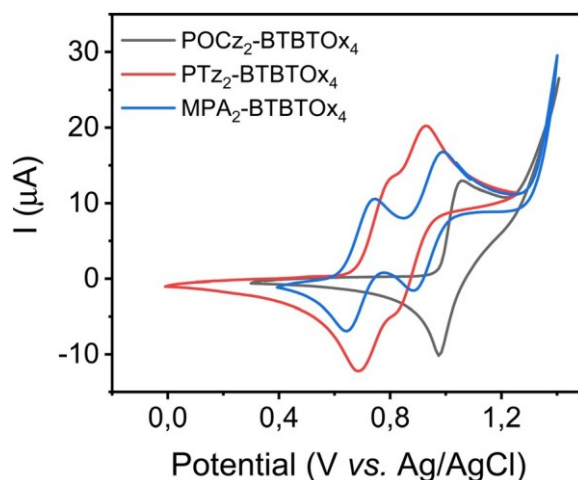


Figure 36. CV curves of organic emitting materials POCz₂-BTBTO_{x4}, PTz₂-BTBTO_{x4} and MPA₂-BTBTO_{x4}.

Table 6. Electrochemical properties and corresponding energy levels^a of POCz₂-BTBTO_{x4}, PTz₂-BTBTO_{x4} and MPA₂-BTBTO_{x4}

Compound	E _{1/2} (1) (mV)	E _{1/2} (2) (mV)	^c E _{HOMO} (eV)	^d E _{LUMO} (eV)	^e E _g ^{opt} (eV)
POCz ₂ -BTBTO _{x4}	566	627 ^b	-5.70	-3.40	2.67
PTz ₂ -BTBTO _{x4}	367	487	-5.42	-2.70	2.72
MPA ₂ -BTBTO _{x4}	296	536	-5.35	-2.97	2.39

^a c = 1*10⁻³ in CH₂Cl₂/TBAPF₆ (0.1 M), half-wave potentials calculated from the CVs of Fig. 28 and referenced to the Fc⁺/Fc couple (E_{1/2} = 434 mV) at 50 mV s⁻¹.

^b The potentials of POCz₂-BTBTO_{x4} were estimated by differential pulse voltammetry. DPV condition: modulation amplitude 5 mV; modulation time 0.05 s; interval time (Δt) 0.5 s; step potential (E_{step}) 0.005 V; scan rate n = E_{step}/Δt 0.01 V s⁻¹.

^c E_{HOMO} = -(E_{onset}^{ox} + 516) (eV).

^d E_{LUMO} = E_{HOMO} - E_g^{opt} (eV).

^e E_g^{opt} was estimated by absorption onset.

4.2.2 Charge Carrier Mobility

The photo-CELIV technique was developed and used for measuring the charge mobility of organic layers in the direction perpendicular to the film [164], which is the direction most relevant for photovoltaic applications or light emitting diodes [165]. In Figure 37 the photo-CELIV responses of an ITO/ POCZ₂-BTBTOx₄ or PTZ₂-BTBTOx₄ or MPA₂-BTBTOx₄/Al device are shown. Transients were acquired by optically pumping the sample at a wavelength of 450 nm and detected as a voltage drop by using an external load. A wavelength of 450 nm was chosen to provide a bulk photo-excitation for an accurate measurement of the mobility [166]. The time delay, maximum ramp voltage, pulse duration, and the external resistor were varied accordingly in order to optimize the signal to noise ratio [167]. The photo-CELIV response is characterized by a sharp increase, rectangular current transient (J_0), and a slowly growing current (ΔJ) whose maximum depends on the applied ramp voltage. By using peak time (t_{max}) values we were able to determine the carrier mobility according to the equation below, which is valid in the case of volume photogeneration and a drift current maximum (ΔJ) lower than the displacement current (J_0) [168]:

$$\mu = \frac{2d^2}{3At_{max}^2} \quad \text{eq. (10)}$$

where d is the sample thickness and A is the ramp speed (voltage/ramp duration). In the present case, the PTZ₂-BTBTOx₄ compound is characterized by the lower mobility value $5.2 \cdot 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, meanwhile both MPA₂-BTBTOx₄ and POCZ₂-BTBTOx₄ have similar mobility $1.1 \cdot 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, at a speed of around $2 \cdot 10^3 \text{ (V s}^{-1}\text{)}$. Regarding the latter case, we can clearly observe that the higher PLQY correlates with a good charge carrier mobility, making POCZ₂-BTBTOx₄ a suitable candidate for OLED applications.

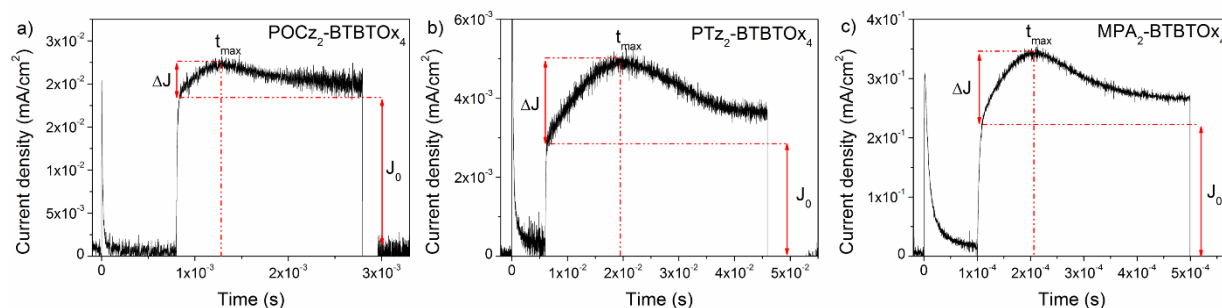


Figure 37. Photo-CELIV transients on ITO/ POCZ₂-BTBTOx₄ or PTZ₂-BTBTOx₄ or MPA₂-BTBTOx₄/Al devices. Measurements were performed in vacuum, at room temperature, at a ramp speed of around $2 \cdot 10^3 \text{ (V s}^{-1}\text{)}$.

4.2.3 X-ray Powder Diffraction (XRPD) Analysis

The diffraction pattern POCZ₂-BTBTOx₄ revealed the amorphous nature of the material, that, consequently, could not be characterized via an ab initio structure solution process. To check the novelty and phase purity of PTZ₂-BTBTOx₄ and MPA₂-BTBTOx₄, a qualitative analysis using the powder diffraction data was carried out

via the software QUALX2.0, aimed at identifying the presence of one (or more) known crystal phase stored in the POW_COD database. The qualitative analysis revealed that the two compounds were unpublished so far. For both, the structure solution process was attempted by EXPO; the full pathway (i.e., indexing, space group determination, extraction of the integrated intensities, structure solution and Rietveld refinement) was successful for $\text{MPA}_2\text{-BTBTOx}_4$ and did not succeed for $\text{PTz}_2\text{-BTBTOx}_4$ due to the lower quality and resolution of the diffraction data in this case. $\text{MPA}_2\text{-BTBTOx}_4$ crystallized in the centrosymmetric space group P21/c . The asymmetric unit, consisting of 27 non-H atoms (chemical formula $\text{C}_{21}\text{H}_{17}\text{NO}_4\text{S}$), was characterized by a planar core (including the aromatic ring C13-C14-C16-C18-C17-C15 and three additional atoms, i.e., S1, N1 and C21, Figure 38), and two out-of-plane methoxyphenyl groups (torsion angles C1-C2-N1-C13 and C13-N1-C7-C8 equal to -59° and 86° , respectively, see Figure 38).

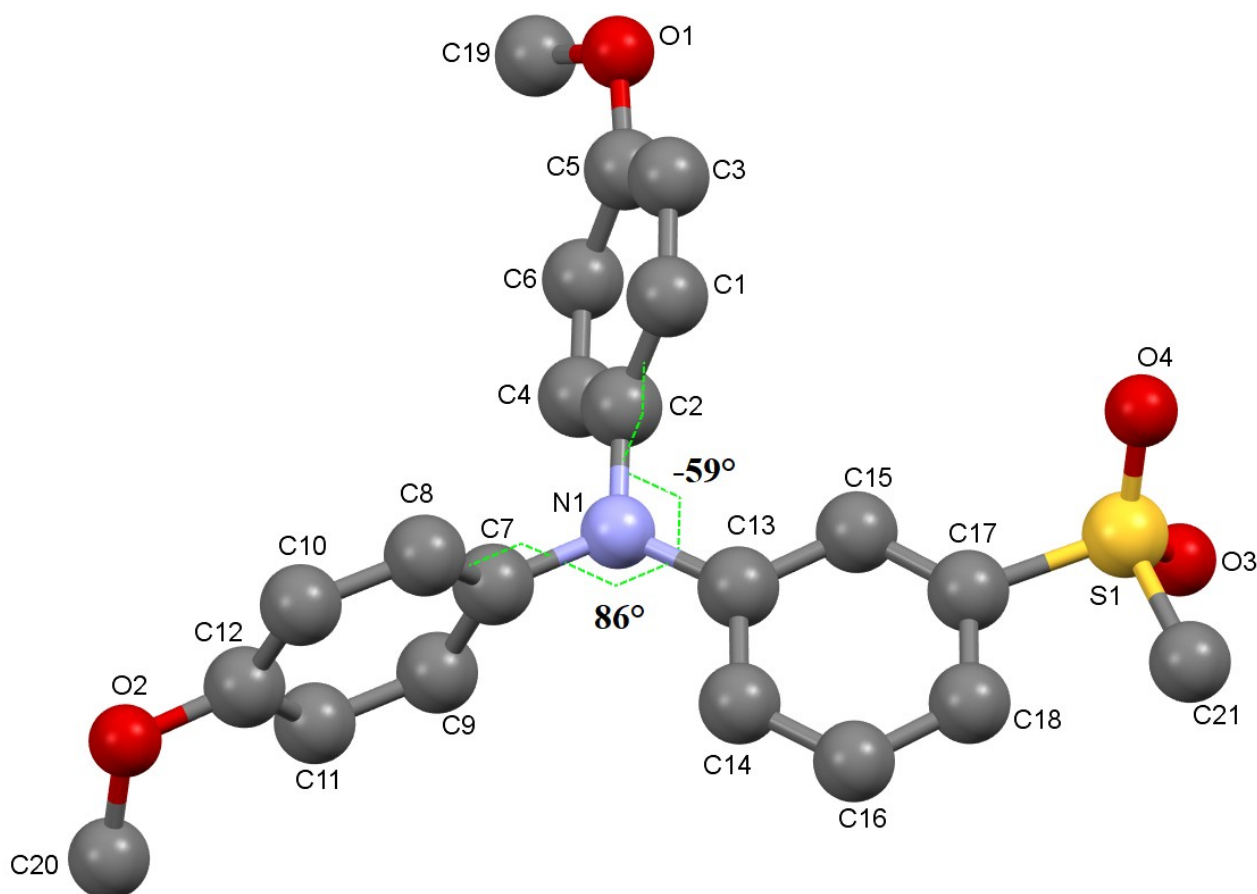


Figure 38. $\text{MPA}_2\text{-BTBTOx}_4$: A view of the asymmetric unit showing the atom-labelling scheme, the colour setting by atomic species (i.e., yellow, red, light blue and grey for S, O, N and C, respectively) and the values of two torsion angles (represented by broken green lines): C1—C2—N1—C13 (-59°) and C13—N1—C7—C8 (86°). H atoms have been omitted for clarity. Software used for molecular graphics: Mercury.

A view of the refined crystal structure determined by EXPO is provided in Figure 39, showing the asymmetric unit (i.e., half a molecule, colour setting by atomic species) and its symmetry equivalent unit (half a molecule, monochromatic blue colour) completing the butterfly-shape molecule.

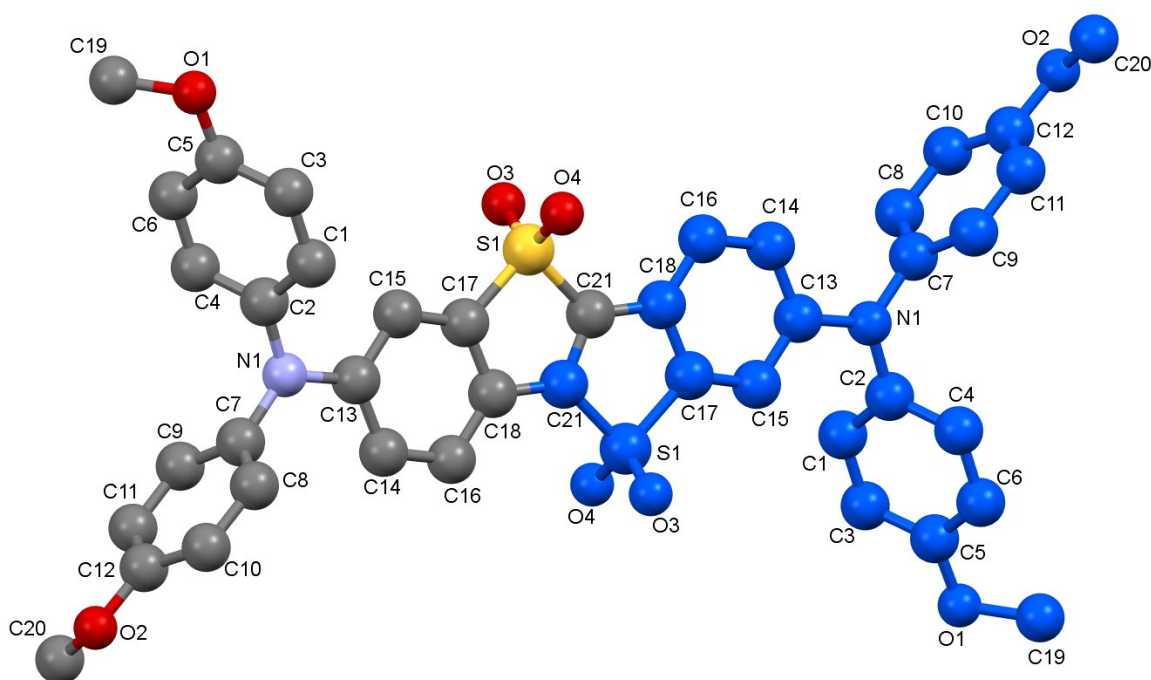


Figure 39. MPA₂-BTBTO_{x4}: a view of the asymmetric unit (half a molecule, drawn on the left hand side), showing the atom-labelling scheme and the colour setting by atomic species (i.e., yellow – S, red – O, light blue – N, and grey – C); the other half of the molecule is shown in blue and consists of symmetry equivalent atoms, whose labelling is identical to that of the corresponding symmetry independent atoms. H atoms are omitted for clarity. Mercury software was used to generate this graphic.

4.2.4 DFT Results

Density functional theory (DFT) and time-dependent DFT (TD-DFT) can provide useful insights for understanding of photophysical characteristics of luminescent molecules. In this work we study the ground (S_0) as well as the singlet (S_1) excited state geometries of for POCz₂-BTBTO_{x4}, PTz₂-BTBTO_{x4} and MPA₂-BTBTO_{x4}, to shed some light onto the delayed fluorescent properties of these luminophores. At first, we study the ground (S_0) and excited state (S_1) geometries of for POCz₂-BTBTO_{x4}, PTz₂-BTBTO_{x4} and MPA₂-BTBTO_{x4} (Figure 40). It is immediately apparent that the central acceptor core is flat, with the >SO₂ oxygen atoms being the only moieties out of plane. There are no fundamental structural differences between the S_0 and S_1 geometries, except perhaps for the relative orientation of donors with respect to the acceptor.

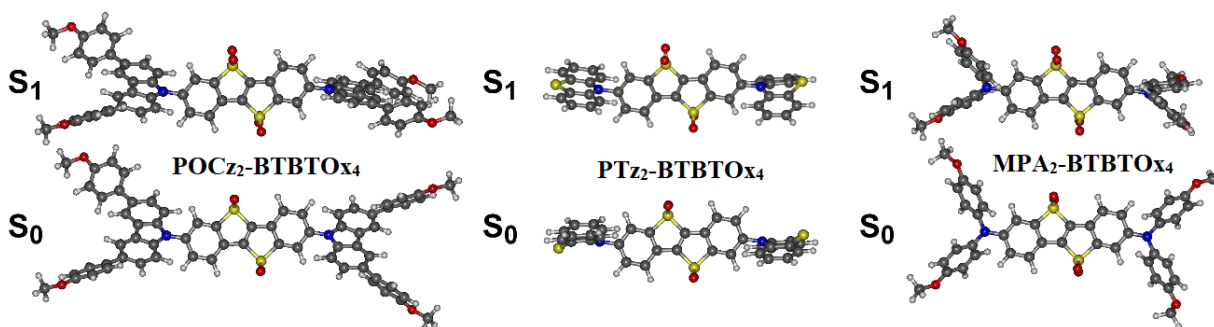


Figure 40. Comparison between calculated ground (S_0) and excited state (S_1) geometries.

At S_0 geometries both donors retain generally similar conformations against the acceptor core making them roughly equivalent. This equivalent function of donors is also reflected in the symmetric distribution of HOMOs in the ground state (Figure 41). This equivalence or symmetry is broken in the S_1 geometry, where the two donors show evidently different conformations from one to another: the first one retaining a relatively similar orientation to that in the ground state and the other being twisted around the C–N axis or deformed. In POC $_{Z2}$ -BTBTO $_{x4}$ and MPA $_2$ -BTBTO $_{x4}$, this is expressed by a larger D–A angle, leading to a more orthogonal configuration, and therefore a lower energy CT state (S_1) energy associated with this donor. A CT state associated with the other donor is also present at a higher energy (i.e. S_2). In the ground state geometry, the first singlet excitation ($S_0 \rightarrow S_1$) is dominated by the HOMO $\rightarrow$ LUMO transition and can be assigned a CT (PTZ $_2$ -BTBTO $_{x4}$) or hybridCT+LE (POC $_{Z2}$ -BTBTO $_{x4}$, MPA $_2$ -BTBTO $_{x4}$,) character. Interestingly, in PTZ $_2$ -BTBTO $_{x4}$ the configuration of both phenothiazines in the ground state is equatorial, while in the S_1 state one of the donors rearranges into a planar configuration. The said planar configuration serves as a stronger donor and contributes to the formation of the S_1 state, while the other phenothiazine unit in the equatorial configuration contributes to the S_2 . In both configurations however the D–A form a roughly orthogonal arrangement. Donor–acceptor systems featuring phenothiazine are notorious for displaying dual emissive behaviours [169,170].

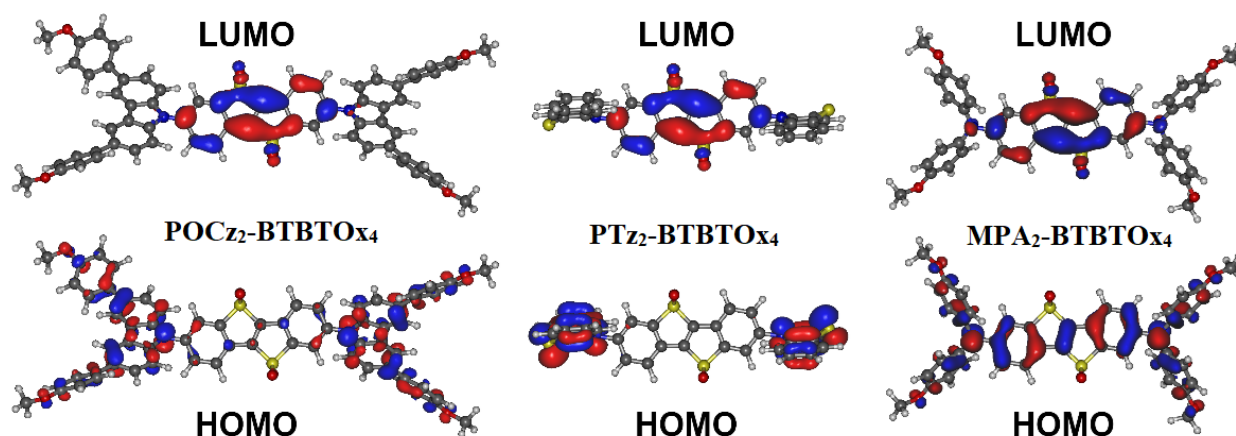


Figure 41. HOMO and LUMO isosurfaces calculated at the S_0 geometry of POC $_{Z2}$ -BTBTO $_{x4}$, PTZ $_2$ -BTBTO $_{x4}$ and MPA $_2$ -BTBTO $_{x4}$.

In the case of PTZ $_2$ -BTBTO $_{x4}$ two conformers of phenothiazine, equatorial and planar, coexist in one S_1 geometry giving rise to distinctive singlet CT excited states associated with either one of the two donors, as mentioned above. We hypothesize that this evident potential to switch between equatorial and planar geometries in the excited state may give rise to dual emissive behaviour in PTZ $_2$ -BTBTO $_{x4}$. Although the phenothiazine donors in PTZ $_2$ -BTBTO $_{x4}$ are shown to both be in their quasi-equatorial configuration in the S_0 this does not preclude higher energy conformers from being present, such as the quasi-axial forms. TD-DFT singlet and triplet excitation energies and the respective orbital pairing calculated at the S_1 geometry are shown in Figure 42 for PTZ $_2$ -BTBTO $_{x4}$. The general picture of the excited states is very similar in all three emitters with the T_1 state being generally of ^3LE_A (excited state localised on the acceptor) nature, while the S_1 state is

associated with an intramolecular charge transfer (^1CT) character. One may note S_1 and S_2 are associated with distinctive CT transitions involving different donor moieties. The DEST calculated directly from the S_1 and T_1 energies are: 0.53 eV in $\text{POCz}_2\text{-BTBTOx}_4$, 0.07 eV in $\text{PTz}_2\text{-BTBTOx}_4$, and 0.59 eV in $\text{MPA}_2\text{-BTBTOx}_4$. Given the small DEST in $\text{PTz}_2\text{-BTBTOx}_4$ one may reasonably expect this emitter to display TADF. At first the DEST for $\text{POCz}_2\text{-BTBTOx}_4$ and $\text{MPA}_2\text{-BTBTOx}_4$ appear too large to support potential TADF behaviour. However, a closer look at the reasons for the magnitude of DEST opens an alternative pathway to interpret these results. At the minimal S_1 geometry of $\text{PTz}_2\text{-BTBTOx}_4$ the donor and acceptor are nearly completely decoupled, hence the T_1 represents a ‘pure’ $^3\text{LE}_A$ state with an energy of 1.75 eV. The optimised S_1 geometry of $\text{POCz}_2\text{-BTBTOx}_4$ and $\text{MPA}_2\text{-BTBTOx}_4$ however shows a partial conjugation between the donor and acceptor. In this case the T_1 energy drops ever so slightly to 1.74 eV in $\text{POCz}_2\text{-BTBTOx}_4$ and more significantly to 1.51 eV in $\text{MPA}_2\text{-BTBTOx}_4$. We believe that, however, the influence of the partial donor–acceptor conjugation may be exaggerated in this case with respect to the real system. For example, the donors will be allowed to freely rotate around the C–N bonds due to the small activation energy for this motion. We believe that the contribution of configurations with more decoupled donor and acceptor pairs appearing in real systems may lead to the T_1 energy being closer to that of a fully decoupled system than that determined in this calculation. By using the energy of a ‘pure’ $^3\text{LE}_A$ state with an energy of 1.75 eV from $\text{PTz}_2\text{-BTBTOx}_4$ we estimate DEST of 0.51 eV for $\text{POCz}_2\text{-BTBTOx}_4$ and 0.35 eV for $\text{MPA}_2\text{-BTBTOx}_4$, hence demonstrating that TADF may be possible at least in $\text{MPA}_2\text{-BTBTOx}_4$. Spin–orbit coupling matrix elements (SOCME) between the lowest singlet and triplet states are shown in Table 7. They clearly demonstrate potential pathways for ISC and RISC within these systems. For example, in $\text{PTz}_2\text{-BTBTOx}_4$ the $\langle T_1 | \hat{H}_{\text{so}} | S_1 \rangle$ and $\langle T_1 | \hat{H}_{\text{so}} | S_2 \rangle$ are 0.2–0.5 cm^{-1} , one order of magnitude larger than $\langle T_2 | \hat{H}_{\text{so}} | S_1 \rangle$ and $\langle T_2 | \hat{H}_{\text{so}} | S_2 \rangle$. In this case the role of the T_1 ($^3\text{LE}_A$) is necessary to promote RISC to the ^1CT state. Somewhat similarly, the $\langle T_1 | \hat{H}_{\text{so}} | S_1 \rangle$ and $\langle T_1 | \hat{H}_{\text{so}} | S_2 \rangle$ in $\text{POCz}_2\text{-BTBTOx}_4$ and $\text{MPA}_2\text{-BTBTOx}_4$ are larger than other pairings due to the analogous orbital nature of these two states as in $\text{PTz}_2\text{-BTBTOx}_4$.

Table 7. SOC matrix for the lowest excited states at the S_1 geometry for $\text{POCz}_2\text{-BTBTOx}_4$, $\text{PTz}_2\text{-BTBTOx}_4$ and $\text{MPA}_2\text{-BTBTOx}_4$. Values in the table represent $\langle T_i | \hat{H}_{\text{so}} | S_j \rangle$ or SOCME in cm^{-1} .

POCz₂-BTBTOx₄				PTz₂-BTBTOx₄				MPA₂-BTBTOx₄			
State	S₁	S₂	S₃	State	S₁	S₂	S₃	State	S₁	S₂	S₃
T₁	0.57	0.56	0.16	T₁	0.25	0.49	0.91	T₁	0.54	0.41	0.85
T₂	0.02	0.19	0.16	T₂	0.02	0.01	0.22	T₂	0.09	0.53	0.87
T₃	0.15	0.16	0.12	T₃	0.02	0.02	0.62	T₃	0.48	0.20	0.62

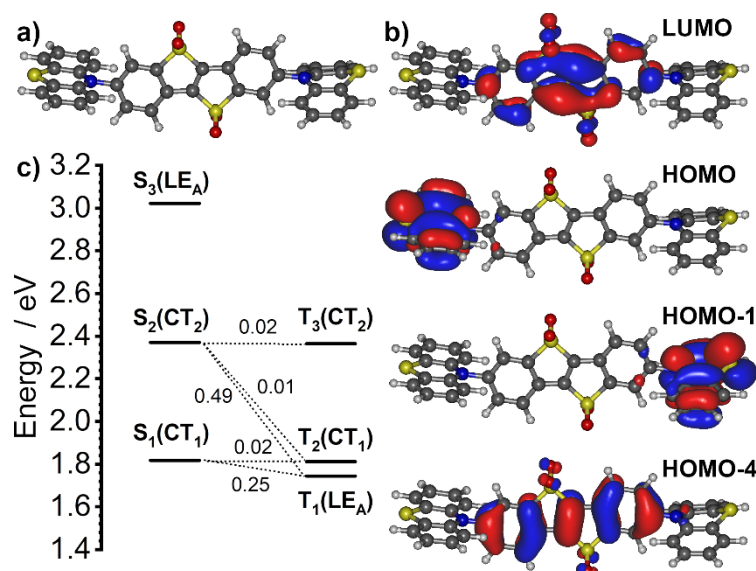


Figure 42. TD-DFT calculations for PTz₂-BTBTOx₄ at S₁ geometry: (a) structure in the S₁ state; (b) isosurfaces of the relevant molecular orbitals; (c) excited state energy diagram with the orbital character of each of the excited states; the values and dotted lines represent SOCME in cm⁻¹ between the indicated states.

4.2.5 Photophysical Properties

In this section, the photophysical characteristics of PTz₂-BTBTOx₄, MPA₂-BTBTOx₄ and POCz₂-BTBTOx₄ were explored, aiming to understand how different donor units influence their optical behaviour and thus their potential as TADF materials in OLEDs. Specifically, the three donor units, phenothiazine (PTz), dimethoxyphenylamine (MPA) and carbazole (Cz) derivative (POCz) exhibit different electron-donating and steric behaviours. A comprehensive study of these compounds was conducted using UV-vis absorption, steady-state and time-resolved fluorescence spectroscopy. The initial investigation involved studying the photophysical properties in diluted solution (10⁻⁵ M) in three solvents with different polarity: cyclohexane (CH), toluene (Tol) and dichloromethane (DCM). Then, we moved to the solid-state (as isolated molecules) by means of two polymer matrices with different polarity, namely zeonex and poly(methyl methacrylate) (PMMA). Finally, the steady-state photophysical properties of the neat films (drop casting) were also explored. A summary of the photophysical results for all three compounds can be found in Table 8 e 9.

Absorption spectra

The UV-vis absorption spectra of the three compounds PTz₂-BTBTOx₄, MPA₂-BTBTOx₄ and POCz₂-BTBTOx₄ were recorded in diluted solutions (10⁻⁵ M) of three solvents with different polarity: cyclohexane (CH), toluene (Tol) and dichloromethane (DCM) (Figure 43). In all systems, the lowest energy band is attributed to Intramolecular Charge Transfer (ICT) processes between the donor (D) and the acceptor (A) units. This finding is consistent with the TD-DFT calculations since it is identified as a CT or CT + LE HOMO–LUMO transition between the donor and acceptor units.

Specifically, we observed that the CT band appears Gaussian in all cases, except for POCz₂-BTBTO_{x4} in CH, where it is well-resolved indicating the presence of a hybrid localized charge transfer (HLCT or CT + LE) state, again in line with calculations. By increasing the solvent polarity, a red-shifted Gaussian emission is observed for all molecules, confirming the CT character of this transition. This shift is attributed to dipolar interactions with the solvent, favouring the stabilization of the CT state. Conversely, the peaks at higher energy remain unaffected by polarity and are associated with locally excited (LE) transitions on the donor or acceptor unit. Specifically, for POCz₂-BTBTO_{x4}, the absorption band at ~290 nm is assigned to the π - π^* localized absorption of Cz, as well as that at 330 nm [171]. For PTz₂-BTBTO_{x4}, the absorption bands at λ_{max} = 315 and 330 nm, along with the shoulder at 290 nm, are assigned to the localized absorption of phenothiazine [172]. In the case of MPA₂-BTBTO_{x4}, at higher energy, two bands are observed at 280 and 375 nm, corresponding to LE transitions of dimethoxyphenylamine. Lastly, in the deep UV region, the transitions between 225 and 260 nm are associated with LE states of the acceptors for all the systems.

Table 8. Photophysical results for POCz₂-BTBTO_{x4}, PTz₂-BTBTO_{x4} and MPA₂-BTBTO_{x4} in PMMA and Zeonex.

	PMMA			Zeonex		
	% Φ_{PL} air/deox.	τ_1/τ_2 (ns) deox.	τ_1/τ_2 (ms) deox.	% Φ_{PL} air/deox.	τ_1/τ_2 (ns) deox.	τ_1/τ_2 (ms) deox.
POCz₂-BTBTO_{x4}	44/59	$\lambda_{\text{Em}} = 500$ nm 8.3(100%)	$\lambda_{\text{Em}} = 500$ nm 0.3(18%), 1.7(82%) $\tau_{\text{av}} = 1.7$	25/76	$\lambda_{\text{Em}} = 500$ nm 4.1(59%), 6.0(41%) $\tau_{\text{av}} = 5.4$	$\lambda_{\text{Em}} = 500$ nm 4.1(59%), 6.0(41%) $\tau_{\text{av}} = 5.4$
PTz₂-BTBTO_{x4}	18/30	$\lambda_{\text{Em}} = 490$ nm 8.6(100%)	$\lambda_{\text{Em}} = 490$ nm 0.5(38%), 3.1(61%) $\tau_{\text{av}} = 2.9$	10/30	$\lambda_{\text{Em}} = 480$ nm 1.9(20%), 4.2(80%) $\tau_{\text{av}} = 4.0$ $\lambda_{\text{Em}} = 550$ nm 2.9(44%), 5.8(56%) $\tau_{\text{av}} = 5.0$	$\lambda_{\text{Em}} = 480$ nm NO DF $\lambda_{\text{Em}} = 550$ nm 87.4(61%), 253.3(39%) $\tau_{\text{av}} = 195$
MPA₂-BTBTO_{x4}	58/85	$\lambda_{\text{Em}} = 560$ nm 6.2(100%)	$\lambda_{\text{Em}} = 560$ nm 0.3(25%), 1.7(75%) $\tau_{\text{av}} = 1.6$	60/93	$\lambda_{\text{Em}} = 530$ nm 4.9(100%)/5.0(100%) $\tau_{\text{av}} = 5.0$	$\lambda_{\text{Em}} = 530$ nm 7.4(71%), 88.5(29%) $\tau_{\text{av}} = 74.7$

Table 9. Photophysical data for POCz₂-BTBTO_{x4}, PTz₂-BTBTO_{x4} and MPA₂-BTBTO_{x4} in neat film.

Compound	Absorption (λ_{max} , nm)	Emission (λ_{max} , nm)	% Φ_{PL}
POCz₂-BTBTO_{x4}	267, 296, 347(s), 439	560	22
PTz₂-BTBTO_{x4}	262, 341, 416, 600	516, 630	1.2
MPA₂-BTBTO_{x4}	293, 372, 467, 632	593	1.3

Solution PL (steady-state and time-resolved)

The photoluminescence (PL) spectra in diluted solutions measured in three solvents with increasing polarity (CH, Tol and DCM), reveal distinct patterns among **POCz₂-BTBTOx₄**, **PTz₂-BTBTOx₄** and **MPA₂-BTBTOx₄** (Figure 44). Notably, **POCz₂-BTBTOx₄** and **PTz₂-BTBTOx₄** exhibit two distinct bands (except in DCM where **PTz₂-BTBTOx₄** displays only one band), while **MPA₂-BTBTOx₄** shows a single band in all the three solvents. For all the samples, the low-lying band is the most intense and displays positive solvatochromic behaviour, typical for donor–acceptor (D–A) systems. In CH, its structured profile suggests a hybrid local and charge transfer (HLCT) character, while in toluene, the band becomes Gaussian and is red shifted due to the increased solvent polarity that stabilizes the CT state. Further increasing the polarity in DCM results in a red

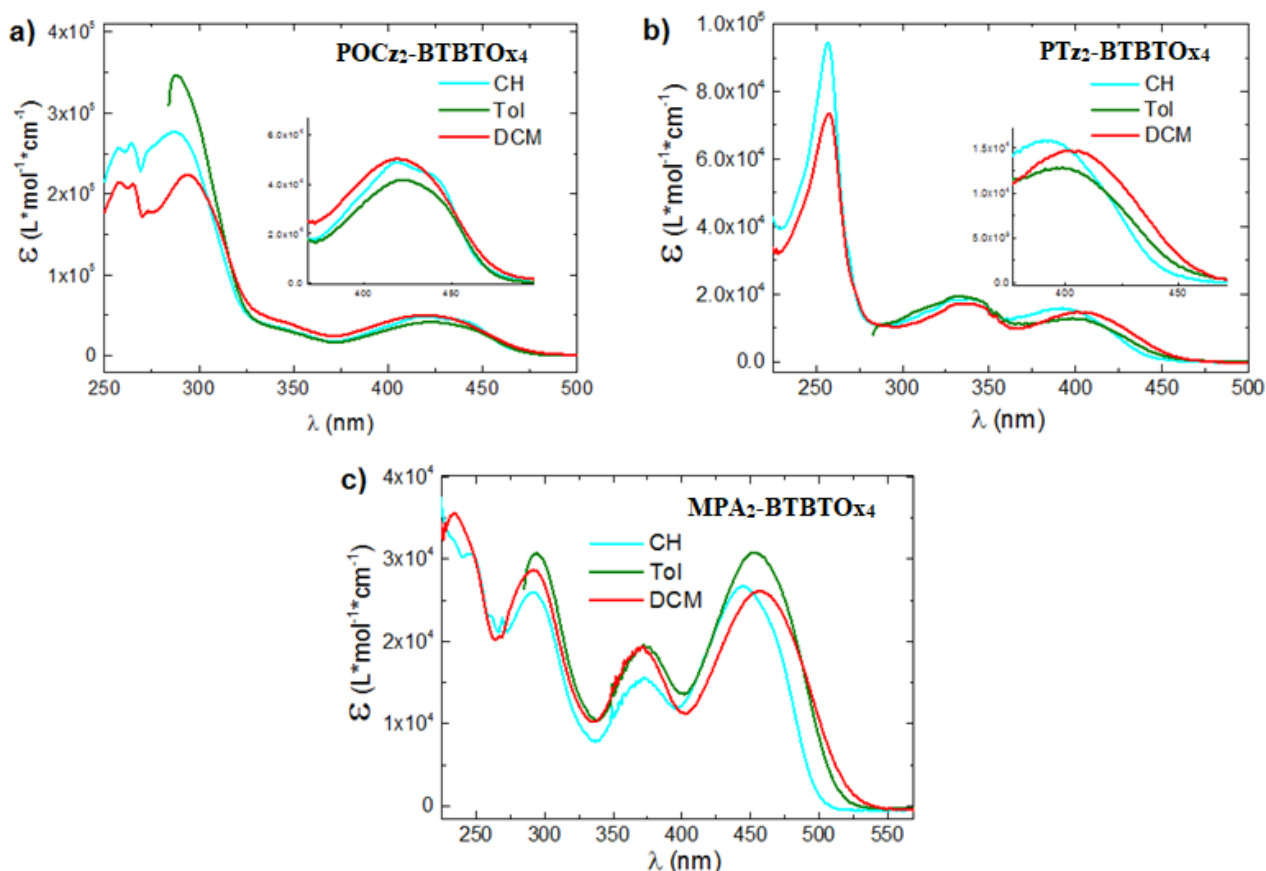


Figure 43. UV-vis absorption spectra in CH (10^{-5} M, cyan), in Tol (10^{-5} M, green) and DCM (10^{-5} M, red) of (a) **POCz₂-BTBTOx₄**, (b) **PTz₂-BTBTOx₄**, and (c) **MPA₂-BTBTOx₄**. In toluene, the UV-vis absorption below 285 nm is not reported since it is obscured by the solvent UV-vis absorption cut-off wavelength.

shift of the CT band for **POCz₂-BTBTOx₄** and **MPA₂-BTBTOx₄**. For **PTz₂-BTBTOx₄** a strong stabilization effect is responsible for the extinction of the CT emission. Concerning the higher-energy band, especially in **POCz₂-BTBTOx₄** (the inset in Figure 44a), it remains unperturbed by solvent polarity, indicating locally excited (LE) character. For deeper insights into the photophysical mechanism, decay profiles (Figure 45) were acquired, and lifetimes were determined (Table 10). We note that, in the cases of **POCz₂-BTBTOx₄** in CH and DCM, and **MPA₂-BTBTOx₄** in DCM, the decay collected for the lower energy band exhibits a bi-exponential decay, with the longer component assigned to the CT state, while the shorter one can be assigned to a HLCT

state. In the other cases, *i.e.* for all systems in Tol, for **PTz₂-BTBTOx₄** in CH and DCM and for **MPA₂-BTBTOx₄** in CH, the decay collected for the lower energy band exhibited a mono-exponential course, originating from the CT state. For **POCz₂-BTBTOx₄** and **PTz₂-BTBTOx₄** we also collected the decay for the LE band (higher energy, Figure 45), nevertheless, since the excitation is at 405 nm we acquired the decay at 430–450 nm and thus the double lifetime observed in some depends on the tail of the CT band (Table 10). The photoluminescence quantum yields (Φ_{PL}) were determined for all three compounds (Table 10) The values reduce upon increasing solvent polarity, which can be assigned to polarity-related stabilization of the excited state. The higher Φ_{PL} in CH is attributed to the presence of a HLCT transition which, in comparison to the CT transition, displays a larger HOMO–LUMO overlap and hence higher oscillator strength ($f(S_1 \rightarrow S_0)$). Notably, Φ_{PL} exceeds 50% for **POCz₂-BTBTOx₄** and **MPA₂-BTBTOx₄**, while for **PTz₂-BTBTOx₄** it reaches only 3%, indicating a reduction in the donor–acceptor conjugation in the last example and thus of the transition oscillator strength. Furthermore, the effect of oxygen quenching on quantum yields and lifetimes was tested for all three compounds. However, after deoxygenation, none of the compounds showed intensity variation with long-lived emission, ruling out the possibility of TADF activity in solution.

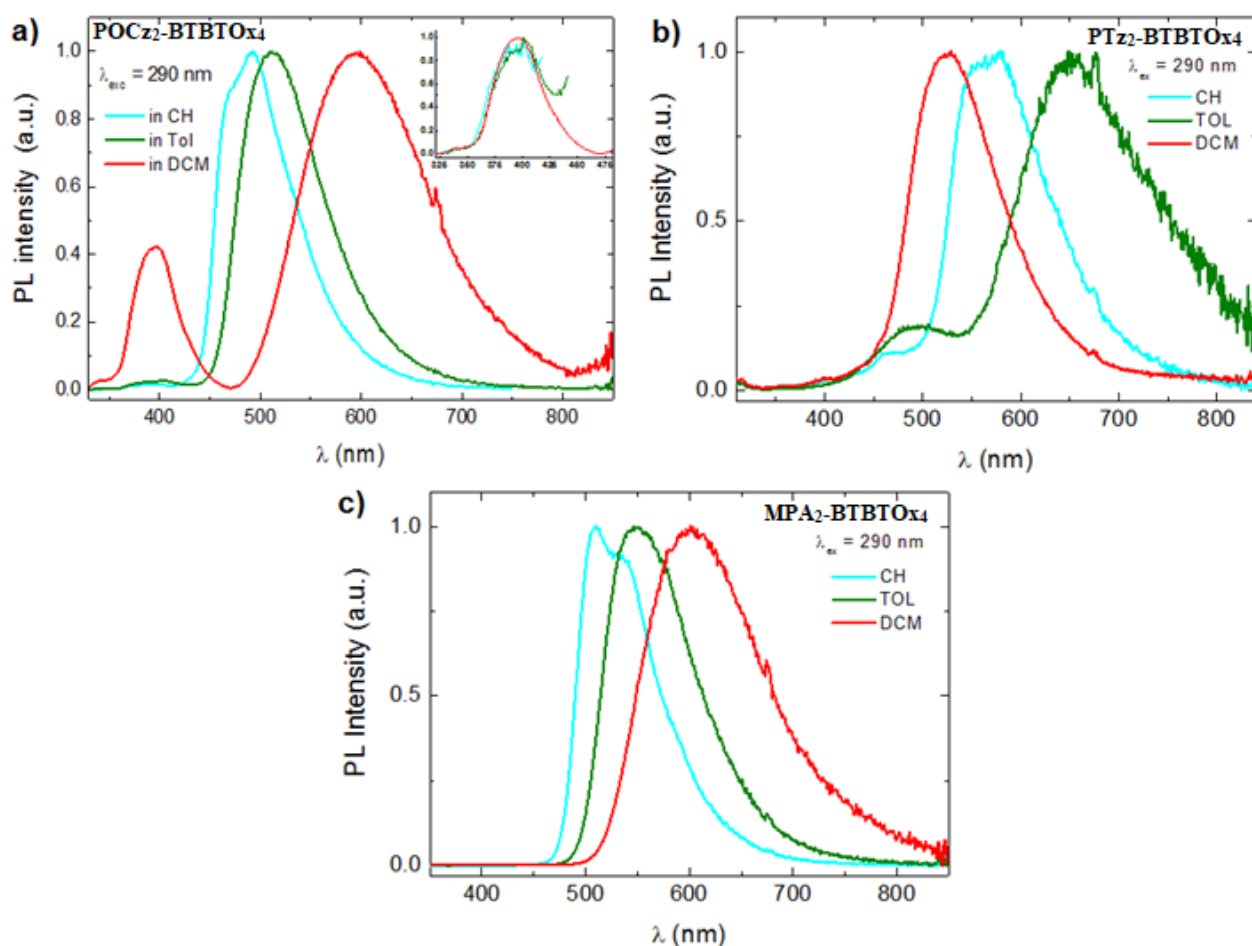


Figure 44. Normalized PL spectra in CH (10^{-5} M, cyan), Tol (10^{-5} M, green) and DCM (10^{-5} M, red) of (a) POCz₂-BTBTOx₄, inset: normalized higher energy band, (b) PTz₂-BTBTOx₄, and (c) MPA₂-BTBTOx₄.

Steady-state and time-resolved PL emission properties in solid polymer thin film matrices

We also explored the photoluminescence features of **POCz₂-BTBTOx₄**, **PTz₂-BTBTOx₄** and **MPA₂-BTBTOx₄** in the solid state by dispersing the samples at a low concentration (0.1% by weight) in two different polarity polymer matrices, namely Zeonex and PMMA. The steady-state emission of all the three compounds reveals distinct behaviours (Figure 46). In Zeonex, the profile appears resolved with HLCT character while, in PMMA, it becomes Gaussian due to its higher polarity stabilizing the CT state. A noteworthy observation is the bathochromic shift of the PL emission of **MPA₂-BTBTOx₄** in both polymers compared to **POCz₂-BTBTOx₄** and **PTz₂-BTBTOx₄**. We can also observe that **PTz₂-BTBTOx₄** in Zeonex exhibits a broadened emission compared to PMMA, with the formation of a new shoulder at 550 nm, suggesting the presence of multiple emissive states. The photophysical properties of all the three compounds in Zeonex were also investigated under deoxygenated conditions. In Figure 47 we can note that while the emission spectrum of **POCz₂-BTBTOx₄** and **MPA₂-BTBTOx₄** remains almost unchanged, **PTz₂-BTBTOx₄** in Zeonex reveals an additional intense band at lower energy. Further experiments, using various excitation wavelengths and doping concentrations (0.1, 1 and 5 %wt) (Figure 47), demonstrate that the lower energy PL band in **PTz₂-BTBTOx₄** is affected by these parameters. Notably, the lower energy PL band gradually diminishes as the excitation shifts to longer wavelengths (λ_{ex} in Figure 48), resulting in fully Gaussian emission at $\lambda_{\text{ex}} = 400$ nm. This behaviour can be observed at all doping concentrations, with the lower energy band being markedly more pronounced at the highest load. Based on these findings, we can identify two distinct emissive species. Specifically, it exhibits emission varying with excitation wavelength: one PL band evident for λ_{exc} (below 400 nm) and another for $\lambda_{\text{exc}} = 300\text{--}350$ nm. According to the DFT calculations, these two species can be potentially attributed to the two different phenothiazine conformers on the same molecule (planar and equatorial), aligning with previous reports on phenothiazine-substituted compounds [169,170]. The increased presence of conformers at higher doping concentrations indicates that intermolecular interactions occurring in the condensed phase are crucial for the formation of lower energy emissive conformers. As shown in (Table 8), **POCz₂-BTBTOx₄** and **PTz₂-BTBTOx₄** in PMMA display double the PLQY values in air compared to the same conditions in Zeonex, while that for **MPA₂-BTBTOx₄** in air is very similar in both polymers.

Table 10. Photophysical data of POCz₂-BTBTOx₄, PTz₂-BTBTOx₄ and MPA₂-BTBTOx₄ in CH, Tol and DCM

	CH		Tol		DCM	
	Φ_{PL} (%)	τ (ns)	Φ_{PL} (%)	τ (ns)	Φ_{PL} (%)	τ (ns)
POCz₂-BTBTOx₄	68.8	$\lambda_{\text{Em}} = 430$ nm 2.8(25%), 3.8(75%) $\lambda_{\text{Em}} = 500$ nm 2.7(23%), 4.9(77%)	51.2	$\lambda_{\text{Em}} = 430$ nm 1(7%), 5.4(93%) $\lambda_{\text{Em}} = 510$ nm 5.5(100%)	3.8	$\lambda_{\text{Em}} = 440$ nm 1.8(32%), 5.4(68%) $\lambda_{\text{Em}} = 600$ nm 1.4(94%), 5.4(6%)
PTz₂-BTBTOx₄	2.7	$\lambda_{\text{Em}} = 450$ nm 3.2(100%) $\lambda_{\text{Em}} = 570$ nm	1.2	$\lambda_{\text{Em}} = 450$ nm 2.5(100%) $\lambda_{\text{Em}} = 600$ nm	0.3	$\lambda_{\text{Em}} = 450$ nm 1.3(60%), 4.2(40%) $\lambda_{\text{Em}} = 530$ nm

		5.1(100%)		4.1(100%)		4.0(100%)
MPA₂-BTBTO_{x4}	59.6	$\lambda_{Em} = 517$ nm 4.1(100%)	55.6	$\lambda_{Em} = 550$ nm 4.5(100%)	11.2	$\lambda_{Em} = 600$ nm 1.7(95%), 3.9(5%)

Furthermore, when comparing the Φ_{PL} of **POCz₂-BTBTO_{x4}** in polymers with that in dilute solutions, it is evident that the Φ_{PL} is higher in CH and Tol than in both polymers, particularly in Zeonex. This potentially suggests an aggregation-caused quenching (ACQ) effect, which is more pronounced in Zeonex, probably due to the lower compatibility of this polymer with **POCz₂-BTBTO_{x4}**. On the other hand, **PTz₂-BTBTO_{x4}** displays a larger Φ_{PL} in both polymer matrices, especially in PMMA, than in solution, indicating that rigido-chromic effects dominate. Finally, for **MPA₂-BTBTO_{x4}** Φ_{PL} remains almost unchanged from solution to both polymer matrices, and this effect may be attributed to the presence of bulky dimethoxyphenylamine donors, which likely prevent both π - π stacking and other non-radiative deactivation processes. We also studied photoluminescence quenching in both polymer matrices for all three emitters.

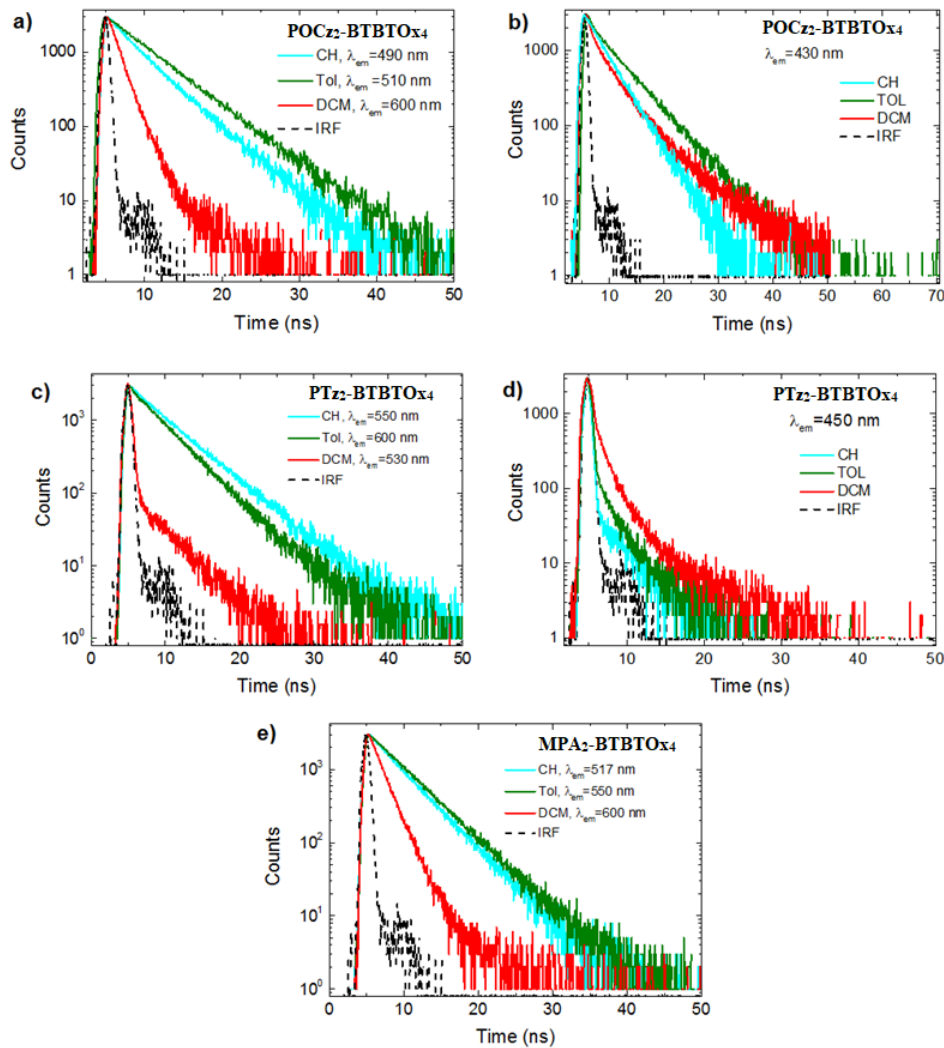


Figure 45. Decay curves in CH (10^{-5} M, cyan), Tol (10^{-5} M, green) and DCM (10^{-5} M, red) of: a) and b) **POCz₂-BTBTO_{x4}**, c) and d) **PTz₂-BTBTO_{x4}** and e) **MPA₂-BTBTO_{x4}**. IRF = Instrumental response function.

Interestingly, after deoxygenation, the PL intensity increases for all three compounds in both polymer matrices (Table 8), thus suggesting that all three materials may present TADF properties. In particular, for **PTz₂-BTBTO_{x4}**, the Φ_{PL} in Zeonex films gradually decreases with increasing doping concentration. Still, the ratio $\Phi_{\text{PL}}^{\text{air}}/\Phi_{\text{PL}}^{\text{deox}}$ (Table 11) is higher for 0.1 %wt film upon deoxygenation, suggesting that around a concentration of 0.1 %wt in Zeonex, the formation of species with delayed fluorescence (DF) properties is favoured. We conducted time-resolved PL studies of all three compounds in deoxygenated thin film in Zeonex, where the Φ_{PL} in deoxygenated conditions is higher, and the resulting decay lifetimes are shown in Table 8. Additionally, we performed time-resolved emission spectroscopy (TRES) mode measurements, allowing the reconstruction of individual spectra at specific time delays (TD), for all three compounds in Zeonex (0.1 %wt). The time-resolved spectra at rt for all three compounds depicted in Figure 49, display distinct behaviours among the three systems. Specifically, for **POCz₂-BTBTO_{x4}** (Figure 49a), the high-energy emission peak is visible only in the early times, attributed to a locally excited state (¹LE) from direct excitation and emission from the D or A moiety. At longer time delays (TD = 30 ns), the initial ¹LE emission disappears, and only the lower energy band attributed to CT emission remains invariant throughout the decay. This indicates luminescence from the singlet state for both prompt and delayed components, suggesting TADF origin of this emission [173, 174] For **MPA₂-BTBTO_{x4}** (Figure 49e), the emission

Table 11. Photoluminescence quantum yields.

PTz₂-BTBTO_{x4} in Zeonex	%$\Phi_{\text{PL}}^{\text{air/deox}}$	$\Phi_{\text{PL}}^{\text{air}}/\Phi_{\text{PL}}^{\text{deox}}$
0.1%wt	9.7/27.6	2.8
1%wt	7.6/13.0	1.7
5%wt	8.1/13.8	1.7

spectra appear more Gaussian-shaped, remain invariant throughout the decay, suggesting TADF emission for this molecule in Zeonex at room temperature. For both **POCz₂-BTBTO_{x4}** and **MPA₂-BTBTO_{x4}**, PL decays were collected, and lifetimes were measured (Table 8), showing two characteristic average lifetimes (τ_{av}): one in the nano-second regime attributed to the prompt fluorescence (PF) and the other in the micro-/milli-second one due to TADF. However, as observed in the decay curves (Figure 49b and f), it is important to note that for both **POCz₂-BTBTO_{x4}** and **MPA₂-BTBTO_{x4}**, the contribution of the TADF appears rather insignificant. This is clearly visible through the relative counts of the longer component in the decay, below 10³, more than two orders of magnitude lower than the PF component. Additionally, a higher laser power is required to observe the DF component, especially in **POCz₂-BTBTO_{x4}**. These observations are consistent with the singlet–triplet energy gap obtained from the DFT calculations, which is particularly high for **POCz₂-BTBTO_{x4}**. Conversely, the analysis of spectra acquired for **PTz₂-BTBTO_{x4}** (Figure 49c) reveals a different behaviour for different time delays. At early times (0–2 ns), the emission arises entirely from the higher energy emissive state (λ_{max} = 480 nm), while the emission associated with the low-energy emissive state (570 nm) appears after 5 ns, becoming dominant at TD = 25 ns. Upon increasing delay time (after 1 μ s), only the state centred at 570 nm

remains invariant, with the spectral shape almost invariant, even with an increased delay time up to a few milliseconds. This behaviour is attributed to the presence of TADF, observed in the low-energy emissive state only [173, 174], which is attributed, according to DFT calculations, to the conformer with phenothiazine in the planar configuration. Additional confirmations come from the decay profiles (Figure 49d) collected at both emission peaks ($\lambda = 480$ nm and 570 nm, respectively), where a strong long-lived DF component (*i.e.* significantly more intense than in the case of the other two emitters) is present only for collection at 570 nm, while for collection at 480 nm, only a short decay typical of prompt fluorescence is detected. This pattern implies that at 0.1 %wt concentration, the higher energy emissive state (with phenothiazine equatorial) is more abundant, overshadowing the prompt fluorescence of the low-energy emissive state. Nonetheless, with longer TD, the low-energy emissive associated to the planar phenothiazine conformer, becomes discernible since it is the sole emitting state exhibiting delayed fluorescence. We have also carried out time-resolved experiments at 77 K (Figure 50 and 51), which allow us to gain more insight into the photophysics of these materials. However, we were unable to obtain reliable results for **MPA₂-BTBTO_{x4}** and **POC_{z2}-BTBTO_{x4}**. This is certainly related to the very weak delayed fluorescence in the two molecules and could be due either to an inefficient ISC or to the presence of non-radiative deactivation channels that are also efficient at 77 K. On the other hand, we were able to observe phosphorescence for **PT_{z2}-BTBTO_{x4}** allowing us to estimate a ΔE_{ST} of 0.1 eV (Figure 43) between the triplet and the singlet resulting from the energetically lower photoluminescence component exhibiting TADF. We have also determined the K_{RISC} to be on the order of 10^4 s⁻¹. For the method previously used by some of the current authors [175] $K_{RISC} = 0.6 \times 10^4$ s⁻¹, while for a more simplified approach [159], $K_{RISC} = 0.6 \times 10^4$ s⁻¹. Due to the overall extremely low TADF intensity in the other two emitters we were unable to determine the K_{RISC} values. In conclusion, the photophysical study is in agreement with TD-DFT calculations. For example, the best compound in terms of TADF properties is **PT_{z2}-BTBTO_{x4}**, while **MPA₂-BTBTO_{x4}** presents less impressive TADF behaviour. At the same time, **POC_{z2}-BTBTO_{x4}** shows the worst TADF properties. This ordering agrees with the ΔE_{ST} values predicted by TD-DFT.

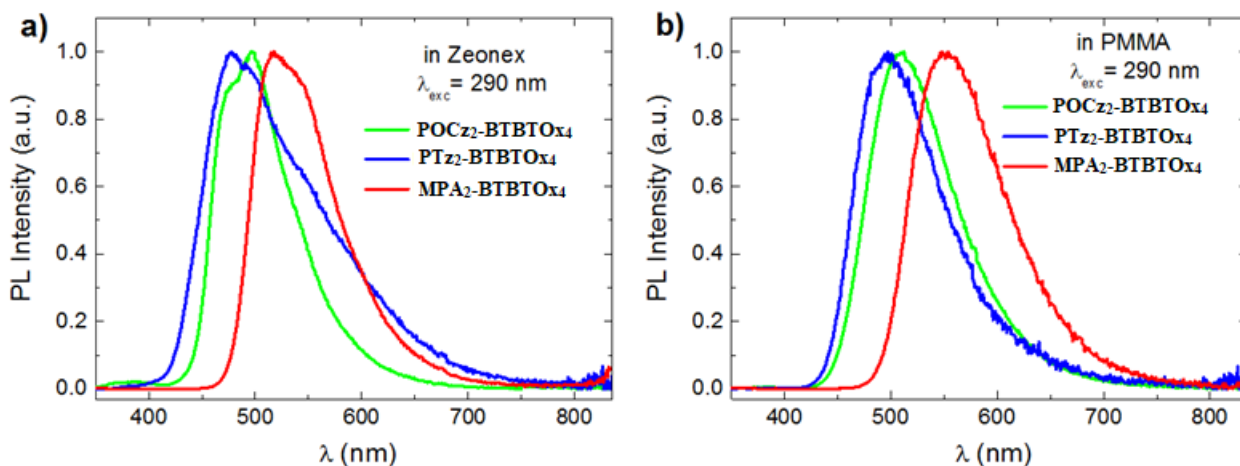


Figure 46. Normalized PL spectra of POC_{z2}-BTBTO_{x4}, PT_{z2}-BTBTO_{x4} and MPA₂-BTBTO_{x4} in: (a) Zeonex (0.1 %wt) and (b) PMMA (0.1 %wt).

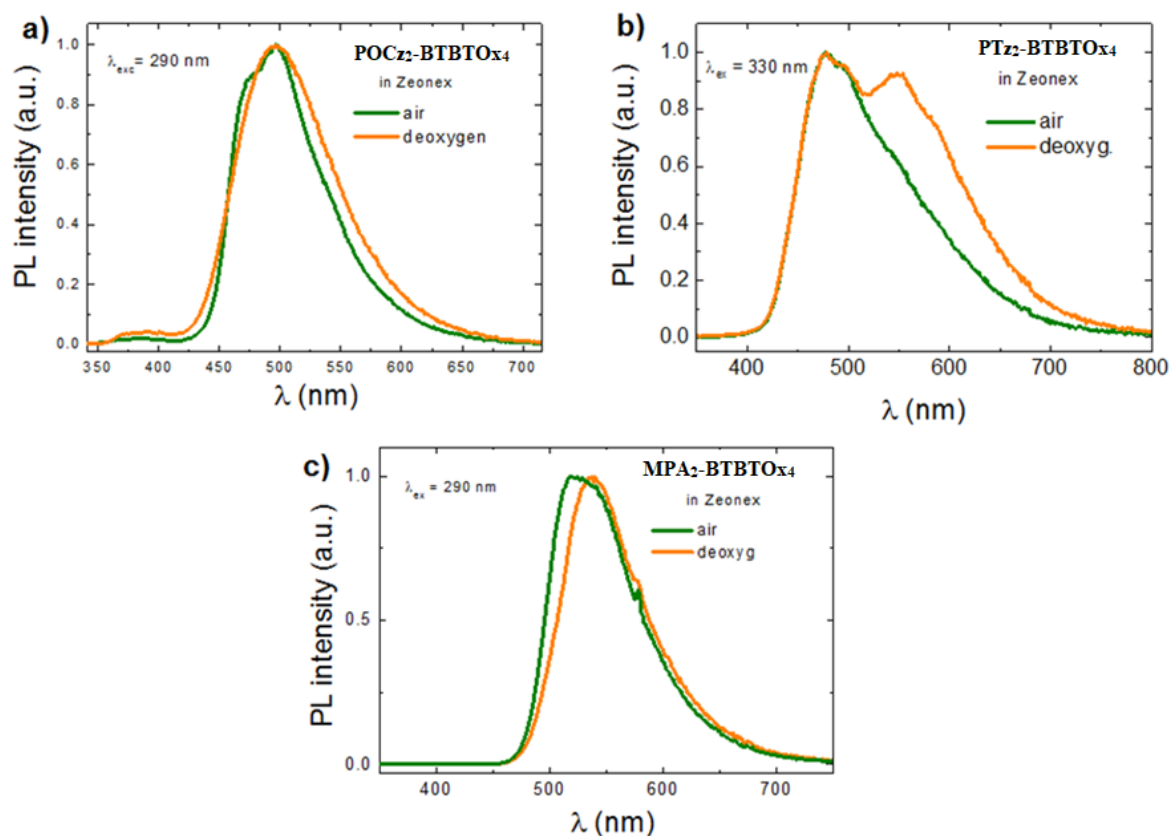


Figure 47. Normalized steady-state PL spectra in Zeonex (0.1 %wt) in aerated and deoxygenated conditions of: a) POCz₂-BTBTO_x₄, b) PTz₂-BTBTO_x₄, and c) MPA₂-BTBTO_x₄.

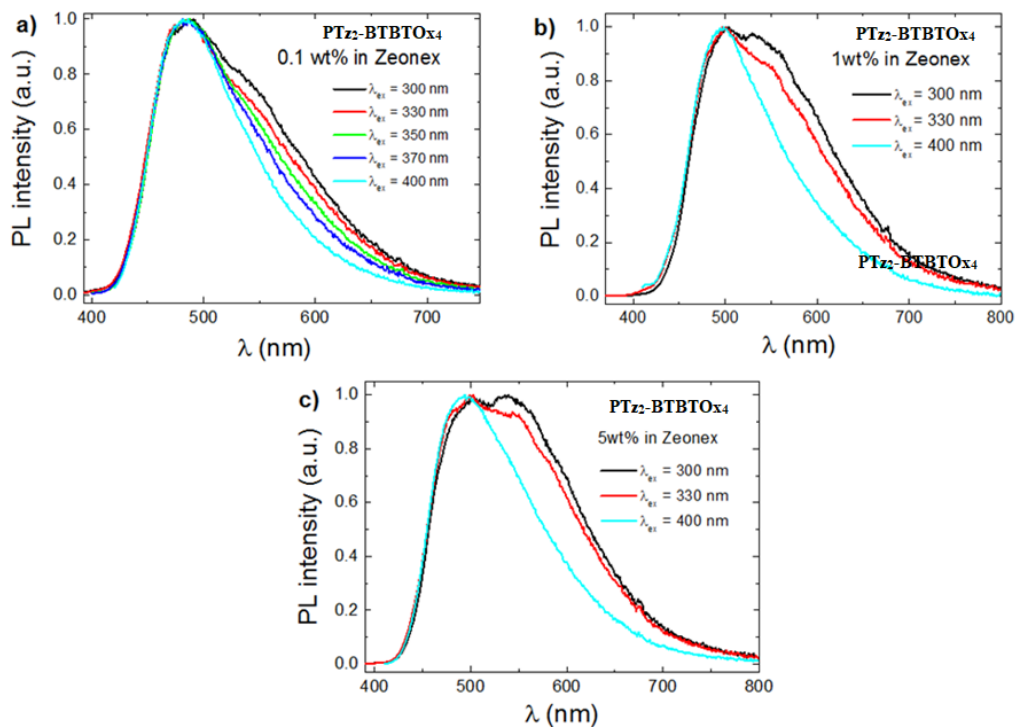


Figure 48. Normalized steady-state PL spectra of PTz₂-BTBTO_x₄ at different excitation wavelengths, in air and: a) at 0.1 wt% in Zeonex, b) 1 wt% in Zeonex, c) 5 %wt in Zeonex.

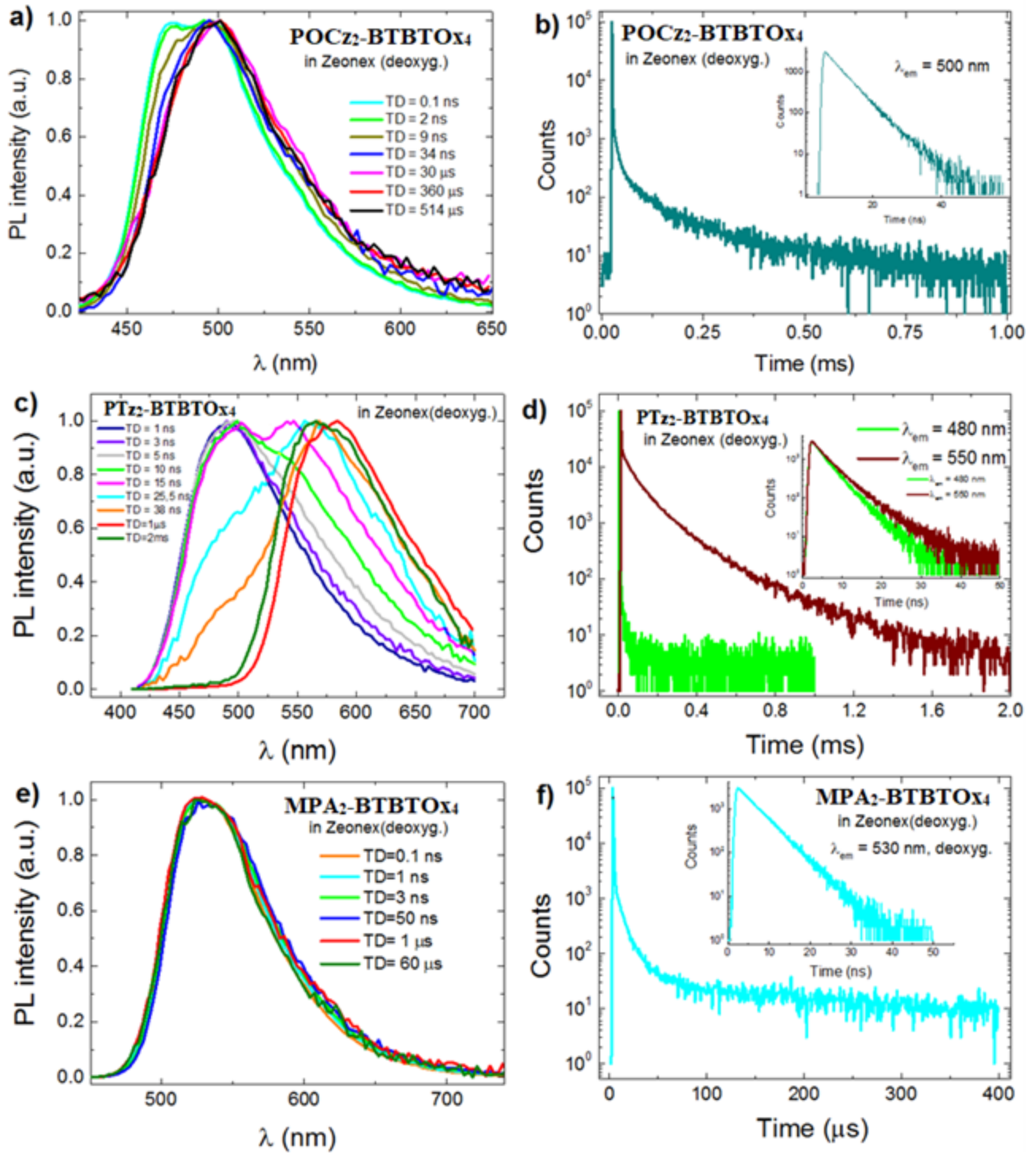


Figure 49. (a) Time-resolved emission spectra in Zeonex (0.1 %wt) of (a) POCz₂-BTBTOx₄, (c) PTz₂-BTBTOx₄, and (e) MPA₂-BTBTOx₄. PL decay in Zeonex (0.1 %wt) in the microsecond scale (insets: decay in the nanosecond scale) of (b) POCz₂-BTBTOx₄, (d) PTz₂-BTBTOx₄, and (f) MPA₂-BTBTOx₄.

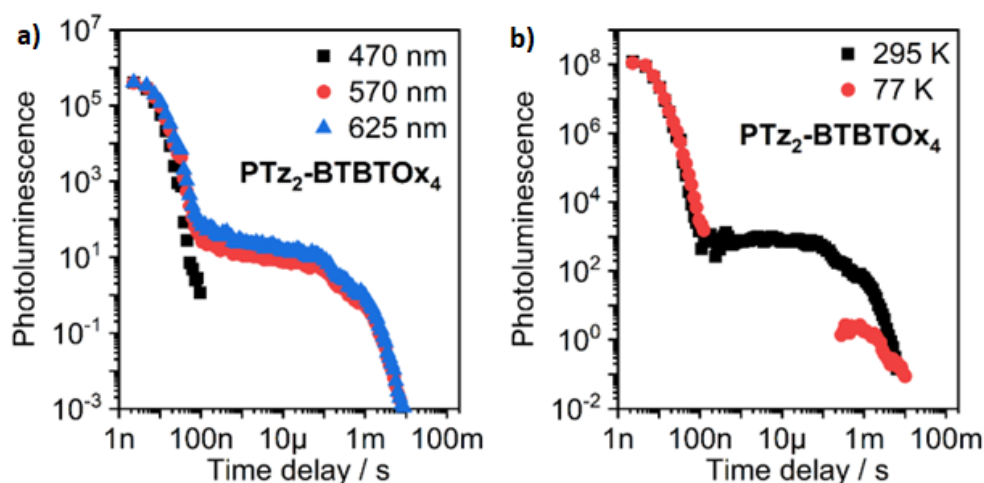


Figure 50. a) Photoluminescence decay of PTz₂-BTBTOx₄ in Zeonex (0.1 %wt) at 295 K acquired at different collection wavelengths (λ_{em} =470, 570 and 625 nm). b) Photoluminescence decay of PTz₂BTBTOx₄ in Zeonex (0.1 %wt) at 295 K obtained by integration over photoluminescence from 380 to 680 nm. All decays were acquired using the iCCD setup described above, λ_{exc} =355 nm.

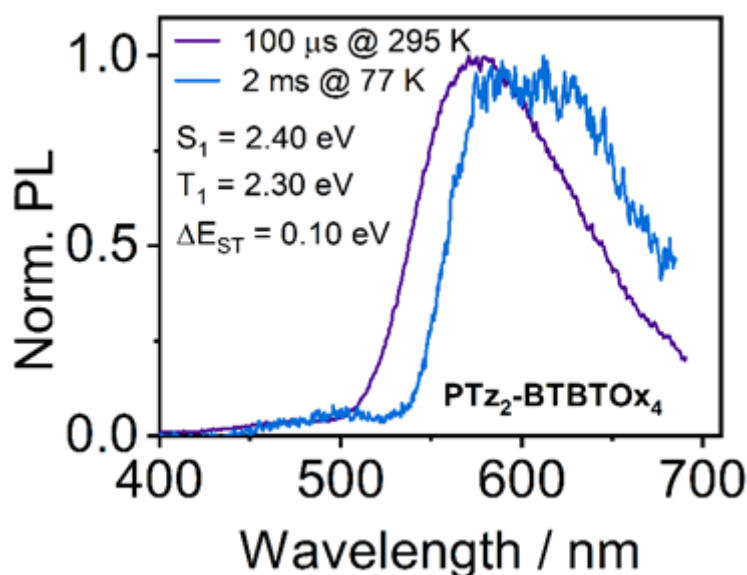


Figure 51. Time-resolved emission spectra of PTz₂-BTBTOx₄ in Zeonex (0.1 %wt) at 295 K and 77 K.

Steady-state photophysical properties in neat films

In this section a short study of the photophysical properties of the three emitting materials in neat films to assess their potential as self-hosted emitters in OLED devices is presented. First, their UV-Vis properties were investigated, as shown in Figure 52, in comparison to the isolated molecules in CH solution. While the higher energy transitions associated with the LE states retain their location found in solvents, all pure films show a clear bathochromic shift in the lower energy band associated with the CT transition. This red shift is consistent with the stabilizing effect induced by the dipoles of neighbouring molecules in the neat film. Notably, an additional weak broad band at lower energy is observed, in both POCz₂-BTBTOx₄ and PTz₂-BTBTOx₄ neat films, possibly indicating the formation of new aggregate-induced electronic states.

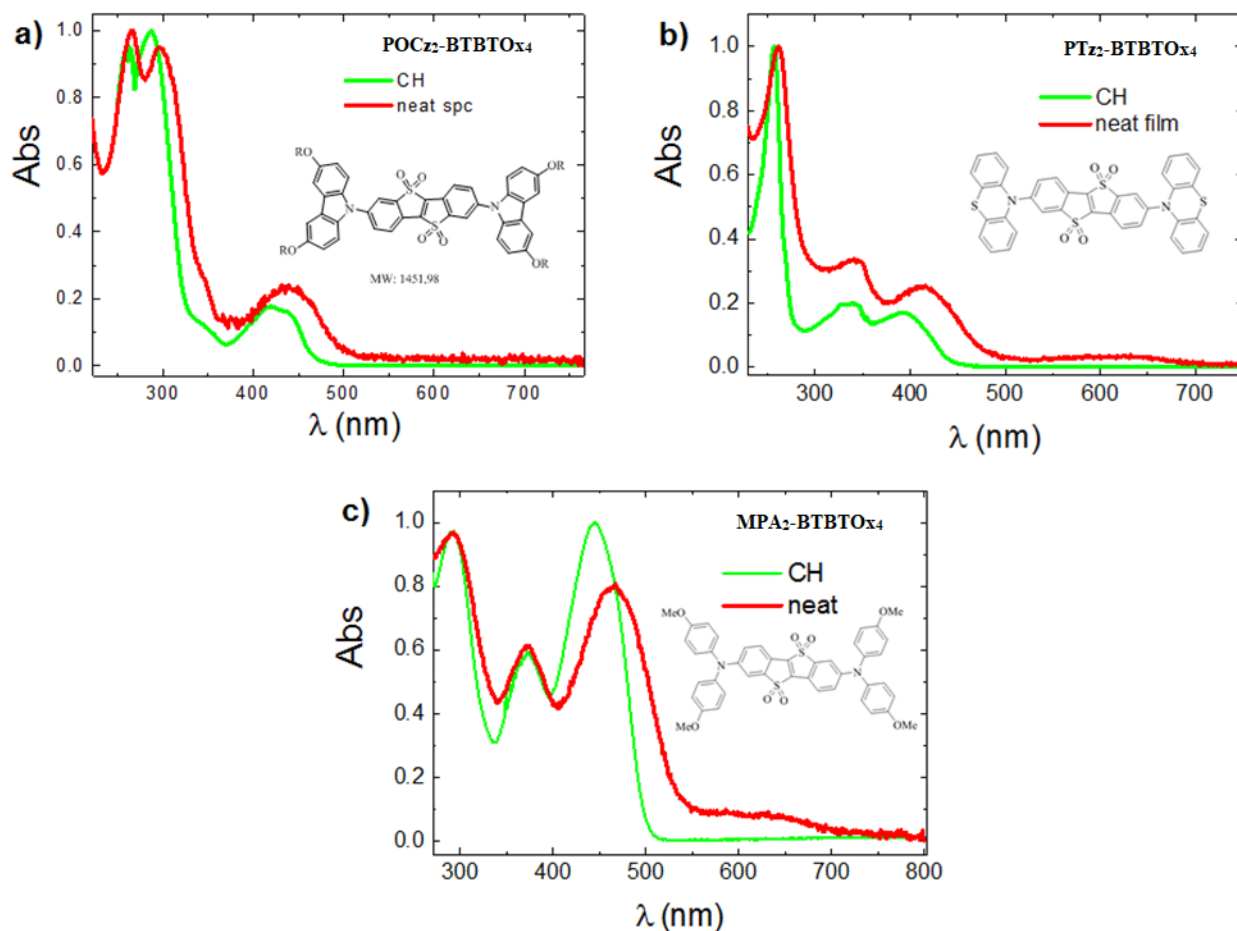


Figure 52. UV-Vis absorption spectra in CH (10-5 M, cyan) vs neat film of: a) POCz₂-BTBTOx₄, b) PTz₂-BTBTOx₄, and c) MPA₂-BTBTOx₄.

The PL spectra of the three emitting materials in neat films (Figure 53) were compared with those of isolated molecules dispersed in polymer matrices (Zeonex and PMMA, Figure 46). POCz₂-BTBTOx₄ and MPA₂-BTBTOx₄ neat films show Gaussian shaped emissions with a bathochromic shift of about 50 nm compared to PMMA. In addition, POCz₂-BTBTOx₄ shows a tail in the red region of the PL (700–800 nm), possibly associated with emission from aggregates. Conversely, the PTz₂-BTBTOx₄ neat film shows two distinct bands, one less intense at higher energy (525 nm) and another much more intense at 625 nm, probably due to different molecular conformers of the phenothiazine unit. The PL of the lower energy conformer is more intense in the neat film due to favoured Förster energy transfer between neighbouring molecules. We also determined the Φ_{PL} of compounds in neat films which is summarized in Table 12. Only POCz₂-BTBTOx₄ maintains a good Φ_{PL} in neat film (22%), compared to that in Zeonex, and half of that in PMMA, indicating minimal self-quenching. On the other hand, self-quenching is pronounced in PTz₂-BTBTOx₄ and MPA₂-BTBTOx₄, with Φ_{PL} dropping to around 1% in neat film. The bulky POCz moieties linked to the BTBTOx₄ in POCz₂-BTBTOx₄ likely prevent self-quenching in the solid state by hindering close packing of molecules, thereby reducing non-radiative pathways *via* strong π - π stacking interactions. Based on these observations, POCz₂-BTBTOx₄ is the only emitting molecule suitable for use in neat film form for self-hosted OLED devices. Furthermore, the neat phase can be used to achieve more red-shifted electroluminescence.

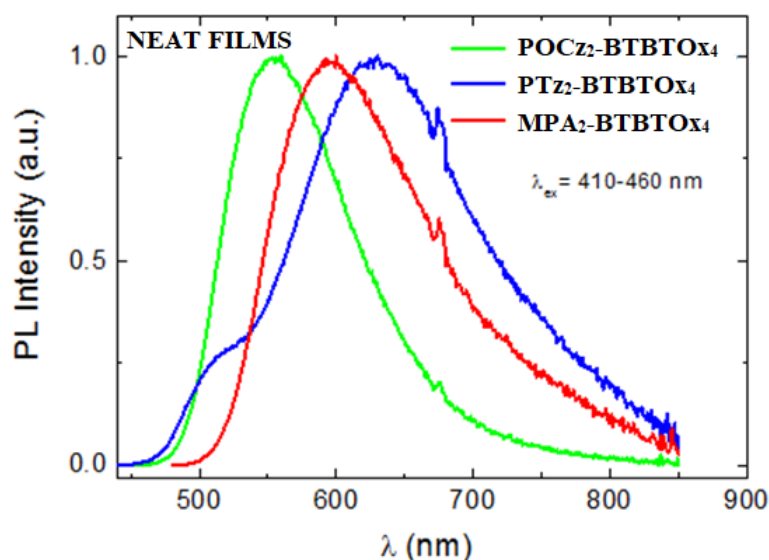


Figure 53. Normalized PL spectra of POCz₂-BTBTO_{x4}, PTz₂-BTBTO_{x4} and MPA₂-BTBTO_{x4} in neat films.

4.2.6 OLED Devices

Proof of concept OLED devices with a simple structure were fabricated using PTz₂-BTBTO_{x4}, MPA₂-BTBTO_{x4} and POCz₂-BTBTO_{x4} in the emitting layer. In particular, these materials have been tested as neat emitting layers, avoiding the use of a host material and thus simplifying the device architecture. The OLEDs consist of indium-tin-oxide (ITO) as the anode, poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate) (PEDOT:PSS, 35 nm) as the hole transport layer (HTL), poly(9-vinylcarbazole) (PVK) as the electron blocking layer (EBL, 15 nm), an emitting layer (EML, 35 nm – PTz₂-BTBTO_{x4} or MPA₂-BTBTO_{x4} or POCz₂-BTBTO_{x4}), 1,3,5-tris(1-phenyl-1*H*-benzimidazol-2-yl)benzene (TPBi) as the electron transport layer (ETL, 50 nm), and LiF (1 nm) and Al (100 nm) as the cathode. The device architecture is shown in Figure 54a. A summary of all OLED characteristics is reported in Table 12.

Table 12. Summary of the main OLED characteristics, including external quantum efficiency (EQE) and exciton utilization efficiency (EUE)

Emitting Layer	Current Density (mA cm ⁻²) at max efficiency	Max luminance (cd m ⁻²)	Current Efficiency (cd A ⁻¹) @ 100 cd m ⁻²	Current Efficiency (cd A ⁻¹) @ 1000 cd m ⁻²	Turn of voltage (@ 10 cd m ⁻²)	Peak Wavelength (nm)	EML Φ_{PL} (%)	EQE (%)	EUE (%)
POCz ₂ -BTBTO _{x4} spin coated	0.48@4.2 V	5016@8 V	3.8	3.35	4 V	553	28.9	1.19	20.6
POCz ₂ -BTBTO _{x4} printed	5.5@5.5 V	2524@10 V	3.46	3.35	4 V	553	25.8	1.01	19.6
PTz ₂ -BTBTO _{x4} spin coated	1.23@4 V	381@10 V	0.17	n.a.	4.8 V	624	2.1	0.14	33.3
MPA ₂ -BTBTO _{x4} spin coated	0.47@3 V	3733@7 V	1.13	0.97	3.1 V	583	8.52	0.45	26.7

A comparison of the performance of the three OLEDs shows that the MPA₂-BTBTOx₄-based device has a higher current density than that using PTz₂-BTBTOx₄ and POCz₂-BTBTOx₄ in the emitting layer (Figure 54b). The maximum luminance values are very similar for the devices based on MPA₂-BTBTOx₄ and POCz₂-BTBTOx₄, while they are considerably lower for the device based on PTz₂-BTBTOx₄. This results in higher efficiency for the POCz₂-BTBTOx₄-based device, with a maximum current efficiency of about 4 cd A⁻¹ compared to significantly lower values for PTz₂-BTBTOx₄ and MPA₂-BTBTOx₄, of 0.17 and 1.1 cd A⁻¹, respectively (Figure 54c). Our results are in line with the photophysical study of PTz₂-BTBTOx₄, MPA₂-BTBTOx₄ and POCz₂-BTBTOx₄ in neat film (Figure 47 and Table 12). POCz₂-BTBTOx₄ exhibits the highest photoluminescence quantum yield in neat film (around 20%), while PTz₂-BTBTOx₄ and MPA₂-BTBTOx₄ undergo significant self-quenching phenomena, with quantum yields in the order of a few percent. The difference in the turn on voltage values of these devices is probably related to a different charge balance, due to the combined effect of the energy levels and the peculiar charge carrier mobilities of the active materials. These results agree with the charge carrier mobility of our emitters, which is higher for MPA₂-BTBTOx₄ and POCz₂-BTBTOx₄ ($1.1 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) and about two orders of magnitude lower for PTz₂-BTBTOx₄ ($5.2 \times 10^{-8} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$). The electroluminescence spectra are also shown in Figure 54d and the peak emission wavelengths confirm the trend observed in the photoluminescence spectra of the neat film (Figure 53). Taking into account our results, the best performing material POCz₂-BTBTOx₄ was also tested with an inkjet-printed emissive layer. The ink formulation was selected according to our recent work [177]. A comparison between the devices obtained by spin coating and inkjet printing the active layer is shown in Figure 54e f. As reported in our previous work, solution processing of EML (spin coating or printing) can cause a slight redissolution of the underlying PVK-based EBL layer, resulting in a blurred/mixed interface between the EBL and the EML. This, therefore, affects the electrical characteristics of the printed device, introducing slight differences between OLEDs with printed and spin coated EML. Indeed, we note that the current density is lower for the printed EML (Figure 54e), and similarly, the luminance is also lower than that with the spin coated EML. This is probably due to a slight difference in the total thickness of the PVK-EML bilayer, as a consequence of the different deposition technique. As a result, the efficiency of the device with the spin coated active layer is slightly higher than one with the printed film, and the maximum efficiency of the latter is shifted to higher voltages. In any case, the performances of the two devices are comparable, demonstrating the quality of the printing process for the deposition of active layers in non-doped OLED devices. Table 12 also reports the external quantum efficiency (EQE) and exciton utilization efficiency (EUE, η_i) values for each device (calculated as described in Sec. 2.2.13). EQE and EUE values are in line with the photophysical study of PTz₂-BTBTOx₄, MPA₂-BTBTOx₄ and POCz₂-BTBTOx₄. As expected, the photoluminescence quantum yields of EMLs are higher than those measured for neat films, with a particularly strong self-quenching in the case of PTz₂-BTBTOx₄. Although from the EQE point of view PTz₂-BTBTOx₄ and MPA₂-BTBTOx₄ show the lowest performances (0.14% and 0.45%, respectively) compared to POCz₂-BTBTOx₄ (1.19%), the related EUE values exceed the spin-statistic limitation of 25% for fluorescent materials. This suggests the presence of a triplet-harvesting mechanism in line with TADF behavior in these two materials, in agreement with our

photophysical study. The electroluminescence spectra are shown in Figure 54d, and the peak emission wavelengths are in line with the photoluminescence spectra of the neat film (Figure 53). As already highlighted, the wet deposition process of the EML causes a partial redissolution of the PVK. This is confirmed by the blue shift of the EL peaks with respect to the PL peaks of the neat films, for all materials, due to the presence of PVK, which dilutes the active materials inside the EMLs. All the EL spectra show a weak band at around 400 nm, attributed to PVK or TPBi emission. In our opinion, considering that EMLs are virtually non-doped the presence of such a peak, highlights a slight imbalance in the charge injection, which causes excitonic recombination near one of the interfaces between the EML and the HTL (or ETL).

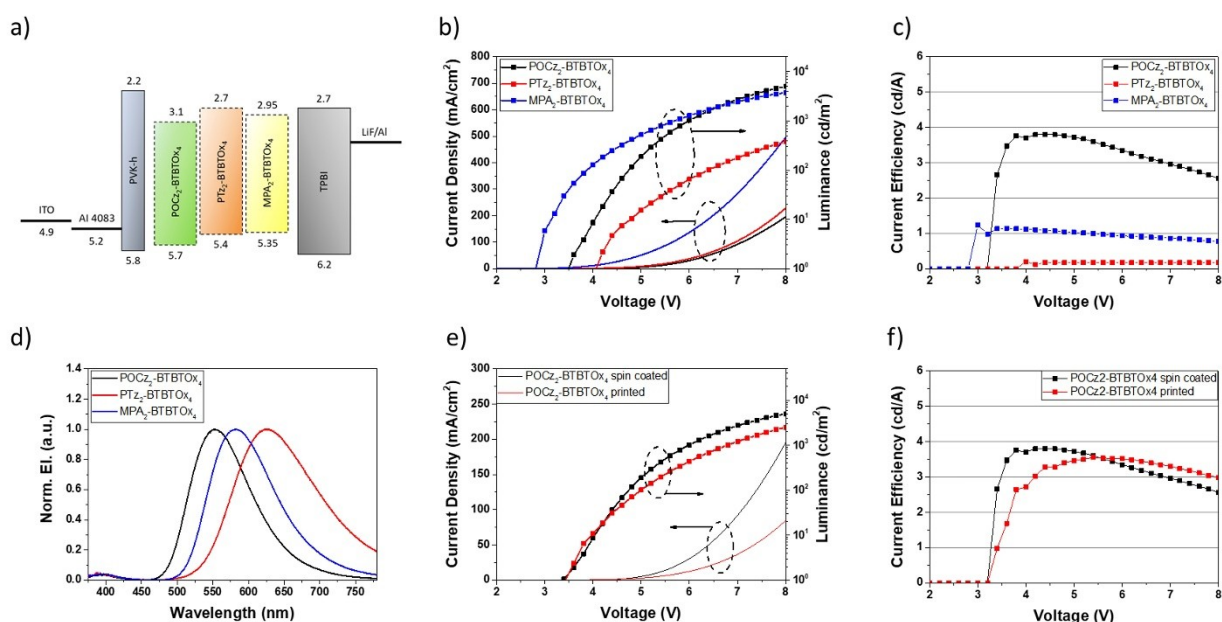


Figure 54. Device architecture and characterization: (a) energy level diagram for the fabricated OLEDs using POCz₂-BTBT0_x or PTz₂-BTBT0_x or MPA₂-BTBT0_x as the EML; (b) device current density and luminance for the three different emitting layers; (c) the current efficiency of OLEDs; (d) electroluminescence spectra; (e) current density and luminance comparison between the OLEDs with spin coated and printed POCz₂-BTBT0_x; (f) comparison of current efficiency for spin coated and printed POCz₂-BTBT0_x-based OLEDs.

4.3 D-A-D Compounds with BTBT Acceptor Core for Organic Electronics

Organic semiconductors (OSCs) have emerged as a compelling alternative to inorganic materials for a wide range of applications, including energy harvesting [178-181], lighting [182,183], and sensing technologies [184,185]. In many of these devices, OSCs are incorporated into multilayer architectures, typically positioned between two electrodes. To promote efficient charge carrier transport to and from the active layer, selective charge transport layers—namely hole-transporting layers (HTLs) and electron-transporting layers (ETLs)—are strategically introduced. These layers play a pivotal role in determining the overall performance of the device.

Over the past decades, a variety of small organic molecules have been explored as charge-transporting materials in optoelectronic devices. While most of these compounds exhibit either hole or electron transport characteristics [186,187], ambipolar materials—capable of transporting both types of charge carriers—are less

frequently reported [188]. Among the most promising candidates are thiophene-based fused-ring systems, which have been extensively studied for their applications in organic field-effect transistors (OFETs) [189]. Their appeal lies in their high chemical stability and the ease with which their properties can be fine-tuned through functionalization. Typically, thiophene-based fused-ring materials function as hole-transporting materials, [190,191]. However, electron-transporting behavior can be induced by incorporating electron-withdrawing groups such as fluorine or cyano substituents [125]. An alternative strategy involves oxidation of the sulfur atom in the thiophene ring to form sulfone groups (thiophene-*S,S*-dioxide), which significantly enhances electron transport. This improvement is attributed to the strong electron-withdrawing nature of the sulfone moiety, which facilitates the movement of negatively charged carriers [192,193].

In this study, the differences in electrochemistry, electronic molecular structures, and charge carrier mobilities of the six compounds were systematically studied. Three new D-A-D molecules containing thiophene-based fused-ring systems, [1]benzothieno[2,3-*b*]benzothiophene (BTBT) were compared with corresponding tetraoxide derivative [1]benzothieno[2,3-*b*]benzothiophene-tetraoxide (BTBTO₄)-based molecules. Our investigation focused on elucidating the structure–property relationships of these materials. Specifically, we demonstrated that varying the electron-donating end groups and the π -bridge core provides an effective strategy for tuning the electronic properties of the resulting conjugated systems.

The structural and electronic characteristics of the compounds were examined using UV–vis spectroscopy, cyclic voltammetry, theoretical calculations, and photo-MIS-CELIV measurements. To assess charge transport behavior, we employed the photo-MIS-CELIV technique, which combines the advantages of MIS-CELIV and photo-CELIV. This method enables the separation of hole and electron mobilities, as in standard MIS-CELIV [155,157,194], while eliminating the need for ohmic contacts by generating free carriers through photoexcitation, as in photo-CELIV [156,194-196]. The results were analyzed with particular emphasis on the influence of the end groups and π -bridges on charge transport mechanisms.

4.3.1 Photophysical Characterization

Here, we report the UV–vis absorption spectra of POCz₂BTBT vs. POCz₂BTBTO₄, MPA₂BTBT vs. MPA₂-BTBTO₄, and PTz₂BTBT vs. PTz₂BTBTO₄ (Figure 55), all recorded in dichloromethane (DCM). A comparison between BTBTO₄- and BTBT-based compounds reveals marked differences in the absorption spectra. In the systems employing POCz and MPA as donor units (i.e. POCz₂BTBT vs. POCz₂BTBTO₄, MPA₂BTBT vs. MPA₂-BTBTO₄), the introduction of the *S,S*-dioxide moiety leads to the emergence of a new, intense Gaussian-like band at lower energies, which is absent or only weakly evident in the non-oxidized counterparts. This low-energy band suggests a significant increase in the intramolecular charge-transfer (ICT) character, in agreement with the known strong electron-withdrawing effect of the *S,S*-dioxide functionality [197,198]. For the systems employing PTz as the donor, a somewhat different behaviour is observed. The non-

oxidized derivatives display well-defined vibronic fine structures at higher energies, typical of rigid conjugated systems. However, at lower energy, a broad Gaussian band appears as a shoulder in these spectra. Upon oxidation to the S,S-dioxide form, this band becomes considerably broader, more intense, and strongly red-shifted. This behaviour again indicates enhanced ICT contributions and a narrowing of the optical bandgap upon oxidation. The bathochromic shift observed for BTBT Ox_4 -based compounds compared to BTBT-based ones is consistent with the significantly increased electron-accepting character of the oxidized oligothiophene core [199]. Moreover, this shift aligns with the narrowing of the optical bandgap, as determined from the onset of the absorption spectra (the estimated optical energy gap values are reported Table 13). In contrast, the more intense higher-energy bands observed across all compounds can be attributed to $\pi-\pi^*$ transitions localized on either the donor or acceptor fragments, in line with literature reports on conjugated D–A systems [200].

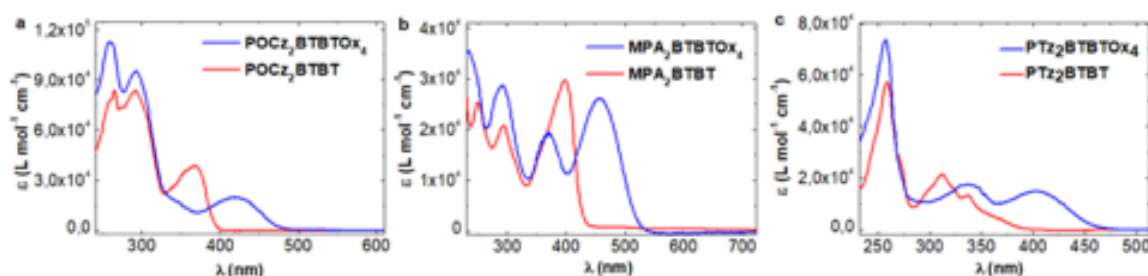


Figure 55. UV-Vis absorption spectra of compounds (a) POCz₂BTBT and POCz₂BTBT Ox_4 , (b) MPA₂BTBT and MPA₂BTBT Ox_4 , (c) PTz₂BTBT and PTz₂BTBT Ox_4 in DCM (10⁻⁵ M).

4.3.2 Electrochemical Properties

Cyclic voltammetry (CV) of BTBT derivatives (MPA₂-BTBT, PTz₂-BTBT, and POCz₂-BTBT) was performed to estimate their electrochemical properties. Measurements were performed at room temperature, in CH₂Cl₂ solution using tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M), and analyte concentration $c = 10^{-3}$ M. The electrochemical behaviour of MPA₂-BTBT Ox_4 , PTz₂-BTBT Ox_4 , and POCz₂-BTBT Ox_4 was investigated in our previous work (Sec. 4.2.1) [66], their CV curves and the electrochemical data are reported in Figure 56 and in the Table 13, together with the CV curves and electrochemical data of the BTBT derivatives. The CV curves were recorded in a potential window between + 0.0 and + 1.4 V vs Ag/AgCl. All compounds exhibited reversible oxidation processes while no reduction signals could be recorded in these conditions. The oxidation potentials of MPA₂-BTBT, PTz₂-BTBT, and POCz₂-BTBT were found to be 0.55 V, 0.79 V and 0.93V respectively. From the potential of the oxidation onset, upon calibration with ferrocene, the highest occupied molecular orbital (HOMO) energy levels of MPA₂-BTBT, PTz₂-BTBT, and POCz₂-BTBT were estimated to be - 5.17 eV, - 5.41 eV and - 5.62 eV; and the lowest unoccupied molecular orbital (LUMO) energy levels were estimated to be - 2.25 eV, - 2.19 eV and - 2.48 eV, according to the equation:

$$E_{LUMO} = E_g^{opt} + E_{HOMO} \quad \text{eq. (11)}$$

The optical energy gap (E_g^{opt}) values were estimated from absorption edge of experimental UV–Vis spectra (Figure 55). For MPA₂-BTBT and MPA₂-BTBTOx₄ two well-separated oxidation signals can be observed, which we attribute to sequential oxidation processes of the arylamino moieties leading to the generation of the radical cation and dication species, respectively. For both compounds the potential splitting between the two oxidation processes (ΔE) is 240 mV and the comproportionation constant ($K_{CO} = 10^{\Delta E/59 \text{ mV}}$) is calculated to be 1.17×10^4 indicating an excellent thermodynamic stability of the monocation species for both the compounds [137,201].

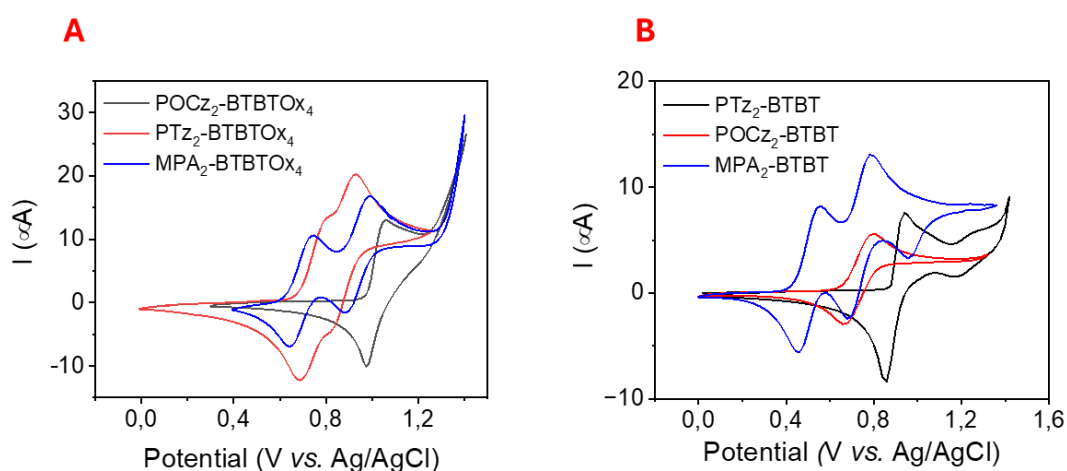


Figure 56. Cyclic voltammetry A) of MPA₂-BTBTOx₄, PTz₂-BTBTOx₄ and POCz₂-BTBTOx₄ and B) of MPA₂-BTBT, PTz₂-BTBT and POCz₂-BTBT at $c = 1 \times 10^{-3}$ mol/L in CH₂Cl₂ /TBAPF 6 (0.1 M) vs. AgCl/Ag, scan rate (50 mV/s).

Also, PTz₂-BTBT and POCz₂-BTBT show a shift toward lower oxidation potentials compared to PTz₂-BTBTOx₄ and POCz₂-BTBTOx₄, respectively. For POCz₂-BTBT and POCz₂-BTBTOx₄ the K_{CO} values were estimated to be 73.18 and 10.81, ($\Delta E_{\text{POCz}_2\text{-BTBT}} = 110$ mV and $\Delta E_{\text{POCz}_2\text{-BTBTOx}_4} = 61$ mV) respectively. While, for PTz₂-BTBT and PTz₂-BTBTOx₄, in these conditions it was possible to obtain the value of K_{CO} only for the latter, which is equal to 108 ($\Delta E_{\text{PTz}_2\text{-BTBTOx}_4} = 120$ mV).

Table 13. Electrochemical Properties and Corresponding Energy Levels^a

Compound	$E_{ox} (1) (V)$	$E_{ox} (2) (V)$	$^b E_{HOMO} (eV)$	$^c E_{LUMO} (eV)$	$^d E_g^{opt} (eV)$
POCz ₂ -BTBTOx ₄	1.00	1.06	- 5.70	- 3.04	2.67
PTz ₂ -BTBTOx ₄	0.81	0.93	- 5.42	- 2.70	2.72
MPA ₂ -BTBTOx ₄	0.73	0.97	- 5.35	- 2.97	2.39

MPA₂-BTBT	0.55	0.78	- 5.17	-2.25	2.92
PTz₂-BTBT	0.79	-	- 5.41	- 2.19	3.22
POCz₂-BTBT	0.93	1.04	- 5.62	-2.48	3.14

a) $c = 10^{-3}$ in CH₂Cl₂/TBAPF₆ (0.1 M) vs. Fe⁺/Fe at 50 mV/s.

b) $E_{HOMO} = -(E_{ox1}^{onset} + 5.16)(eV)$.

c) $E_{LUMO} = E_{HOMO} + E_g^{opt}(eV)$.

d) E_g^{opt} was estimated from absorption onset

4.3.3 Theoretical Studies

We use density functional theory (DFT) in order to understand the electronic properties of the studied molecules and the nature of their molecular orbitals and how it varies between the molecules featuring the BTBTOx₄ and BTBT cores. We also study their ground state geometries to highlight the differences in the dihedral angle between the core and the peripheral units in the two groups of molecules. Frontier molecular orbital iso-surfaces of all discussed molecules are presented in Figure 57, while Table 14 summarizes the relevant dihedral angles. Energy and iso-surfaces of the selected relevant molecular orbitals beyond the frontier MOs are presented in Experimental Part, Sec. 5.21.

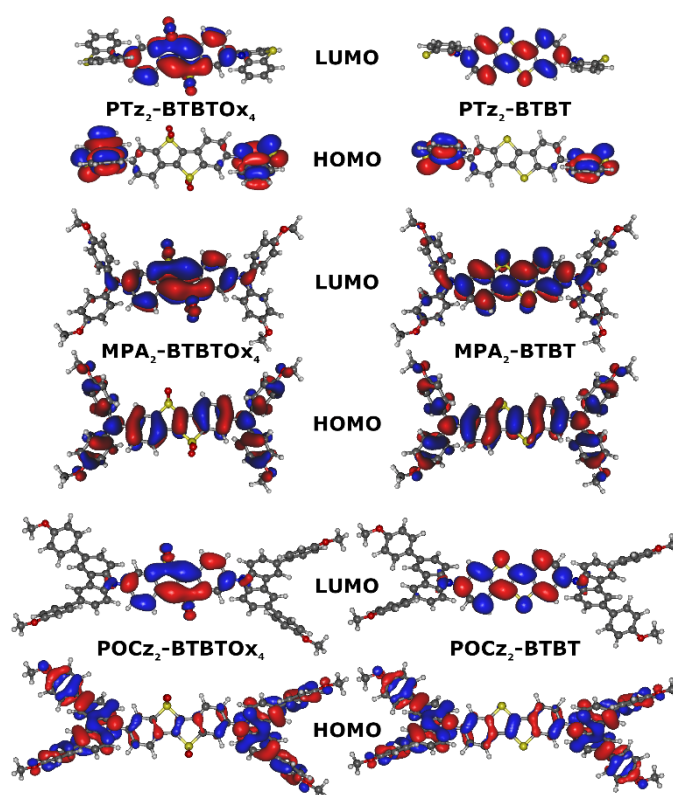


Figure 57. Frontier molecular orbital iso-surfaces at the S₀ geometry. Iso-value 0.02.

Table 14. Calculated D-A dihedral angles at the S_0 geometry.

Molecule	D-A dihedral angle (mean plane), ° ^a
PTZ₂-BTBTOx₄	85.7 / 85.8
PTZ₂-BTBT	90.0 / 90.0
MPA₂-BTBTOx₄	26.4 / 26.9
MPA₂-BTBT	33.8 / 34.3
POCZ₂-BTBTOx₄	48.5 / 48.9
POCZ₂-BTBT	54.1 / 54.3

a) The values refer to each donor individually.

The two groups of molecules generally display similar behaviors with the BTBTOx₄ and BTBT cores being planar and acting as electron acceptors in respect to the peripheral units, donors (D). The geometries of the BTBTOx₄ and BTBT analogues are alike, with the respective donors adopting similar conformations around the central core. The D-A dihedral angle between the mean planes is systematically smaller for BTBTOx₄-based compounds, as a consequence of the higher electron-withdrawing character of BTBTOx₄ compared to BTBT, which competes with the steric hindrance favoring planarization of the conjugated system. The HOMO→LUMO transition in each case involves a net charge transfer from D to A with the effect being the most prominent for PTZ₂-BTBTOx₄ and PTZ₂-BTBT. The aforementioned molecules display a small frontier molecular orbital overlap with the HOMO being fully localized on the donors and the LUMO on the acceptor. The other four molecules display a visible contribution from the acceptor to the HOMO, while the LUMO is again localized on the central acceptor core. In this way the molecules POCZ₂-BTBTOx₄, MPA₂-BTBTOx₄, POCZ₂-BTBT, MPA₂-BTBT display a higher oscillator strength $f_{osc}(S_0 \rightarrow S_1)$ and a weaker CT character of the S₁ state than PTZ₂-BTBTOx₄ and PTZ₂-BTBT, respectively, due to a larger orbital overlap in the former group caused by the acceptor contributing to the HOMO.

Selected molecular orbital energies are summarized in Figure 58. As they indicate the energy levels to which an electron can be accepted to or withdrawn from then they will affect the charge transporting properties of the materials. This however only if they are associated with behaviour of individual molecules. While one may not always expect a perfect agreement of MO energies with experimental oxidation and reduction potentials, the calculation provides a view into the trend between the BTBTOx₄ and BTBT analogues. Somewhat expectedly the LUMO of BTBTOx₄-based molecules is significantly lower in energy than BTBT-based analogues. This occurs because of the higher electron-withdrawing character of BTBTOx₄ with respect to BTBT. Change of the acceptor core also affects the HOMO energy. A stronger acceptor lowers the HOMO energy perhaps through a mixture of π and σ interactions, with the former being negligible in PTZ₂-BTBTOx₄ and PTZ₂-BTBT due to the orthogonal configuration of the D and A units. The trends visible in the MO energies are in agreement with experimental oxidation potentials.

Analysis of the selected molecular orbitals of all discussed molecules provides some additional insights into their electronic energy levels. Considering the donors and acceptors as formally independent species for this particular analysis, we have identified the orbitals associated with the isolated local moieties and named as 'local HOMO' and 'local LUMO'. The 'local HOMO' for the BTBTO_{x4} is ~ 8.5 eV, while the 'local LUMO' is ~ 2.2 - 2.4 eV. The 'local' orbital energies for the BTBT core are ~ 7.3 - 7.4 eV and ~ 1 eV, respectively. The 'local LUMO' orbitals of donors are generally > 0 eV, hence unlikely to participate in electron transport, while their 'local HOMO' levels are generally the HOMO/HOMO-1 of the D-A molecules, therefore likely taking part in hole transport. With HOMOs generally in the range of -6 to -7 eV the 'local HOMO' for the BTBT is relatively close, hence its role in hole transport cannot be ruled out. This analysis suggests that the only moiety to promote electron transport properties could be the BTBTO_{x4}, but it is highly improbable to participate in hole transport due to its deep 'local HOMO'. The LUMO of the BTBT moiety is too high, giving a high electron injection barrier. Considering solely the molecular properties of the material, it is expected that the group of molecules containing the BTBTO_{x4} core has a potential to display ambipolar charge transport behavior, considering the presence of donors with their relatively shallow HOMOs. On the contrary, the systems with the BTBT core are less likely to display electron transport properties due to the higher LUMO energy of the acceptor, but as they feature the same donors their hole transport properties are retained.

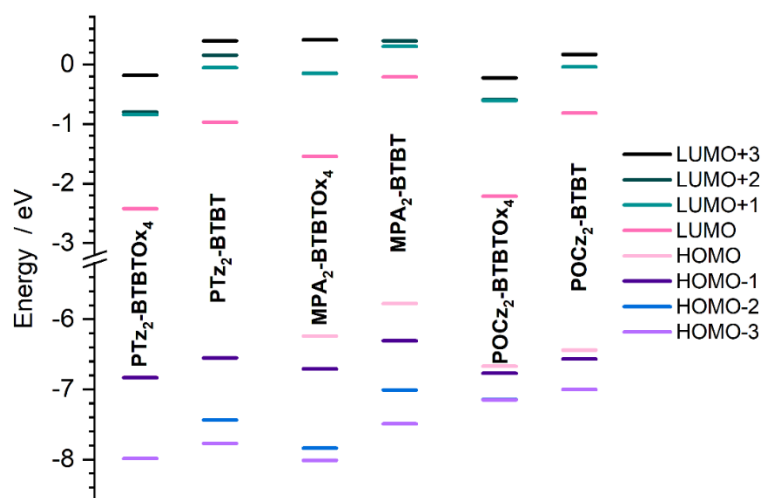


Figure 58. Energy of selected molecular orbitals at the S_0 geometry.

4.3.4 Photo-MIS-CELIV Transients

The charge transport properties of the synthesized compounds were investigated through dark and photo transient measurements using the MIS-CELIV technique. This method enables the evaluation of carrier mobility in the direction perpendicular to the film surface, which is particularly relevant for many optoelectronic applications [202-204]. Figure 59 presents representative photo-MIS-CELIV transients (red curves) for the BTBTO_{x4}-based compounds (**PTz₂-BTBTO₄**, **MPA₂-BTBTO₄** and **POCz₂-BTBTO_{x4}**), with the corresponding mobilities summarized in Table 15. All three compounds exhibit intrinsic ambipolar

behavior, consistent with DFT calculations. In these systems, the BTBTO₄ core primarily facilitates electron transport by contributing significantly to the LUMO, while the peripheral donor units are mainly responsible for hole transport. Despite their shared ambipolar nature, the three BTBTO₄-based compounds display markedly different charge transport efficiencies. **MPA₂-BTBTO₄** and **POCz₂-BTBTO₄** exhibit hole and electron mobilities nearly two orders of magnitude higher than **PTz₂-BTBTO₄**. This suggests that arylamino and carbazole substituents significantly enhance charge mobility [165,205]. The reduced performance of **PTz₂-BTBTO₄** is attributed to the non-planar geometry of the dibenzothiophene-*S,S*-dioxide–phenothiazine linkage, which hinders molecular packing and suppresses π – π interactions [66,206]. This interpretation is supported by dihedral angle calculations, which show a nearly orthogonal arrangement ($\sim 90^\circ$) between the BTBTO₄ core and the phenothiazine units (Table 14). To complement these findings, Figure 60 displays the photo-MIS-CELIV transients for the BTBT-based compounds (**PTz₂-BTBT**, **MPA₂-BTBT**, and **POCz₂-BTBT**), with calculated mobility values also reported in Table 15. These compounds generally exhibit higher mobilities than their BTBTO₄ counterparts. The presence of *S,S*-dioxide groups in BTBTO₄ increases steric hindrance, leading to larger intermolecular distances and reduced charge transport efficiency [207].

Table 15. Hole and electron mobility values measured at a ramp speed $A = 7 \times 10^4 \text{ Vs}^{-1}$.

Compounds	Hole mobility [cm ² V ⁻¹ s ⁻¹]	Electron mobility [cm ² V ⁻¹ s ⁻¹]
PTz₂-BTBTO₄	4.9×10^{-8}	1.1×10^{-7}
MPA₂-BTBTO₄	1.7×10^{-6}	5.4×10^{-6}
POCz₂-BTBTO₄	5.2×10^{-6}	5.1×10^{-6}
PTz₂-BTBT	7.0×10^{-6}	-
MPA₂-BTBT	2.6×10^{-5}	6.6×10^{-5}
POCz₂-BTBT	4.8×10^{-5}	-

Notably, **PTz₂-BTBT** and **POCz₂-BTBT** display unipolar transport behavior, in agreement with DFT predictions. In contrast, **MPA₂-BTBT** exhibits ambipolar transport, similar to the BTBTO₄-based compounds. This difference is attributed to structural and electronic factors, particularly the planarity of the donor–acceptor interface. Dihedral angle analysis reveals that **MPA₂-BTBT** adopts a more planar geometry, which enhances π – π stacking and facilitates both hole and electron transport through improved orbital overlap and charge delocalization [208,209]. Conversely, the less planar structures of **PTz₂-BTBT** and **POCz₂-BTBT** likely hinder such interactions, resulting in unipolar behavior.

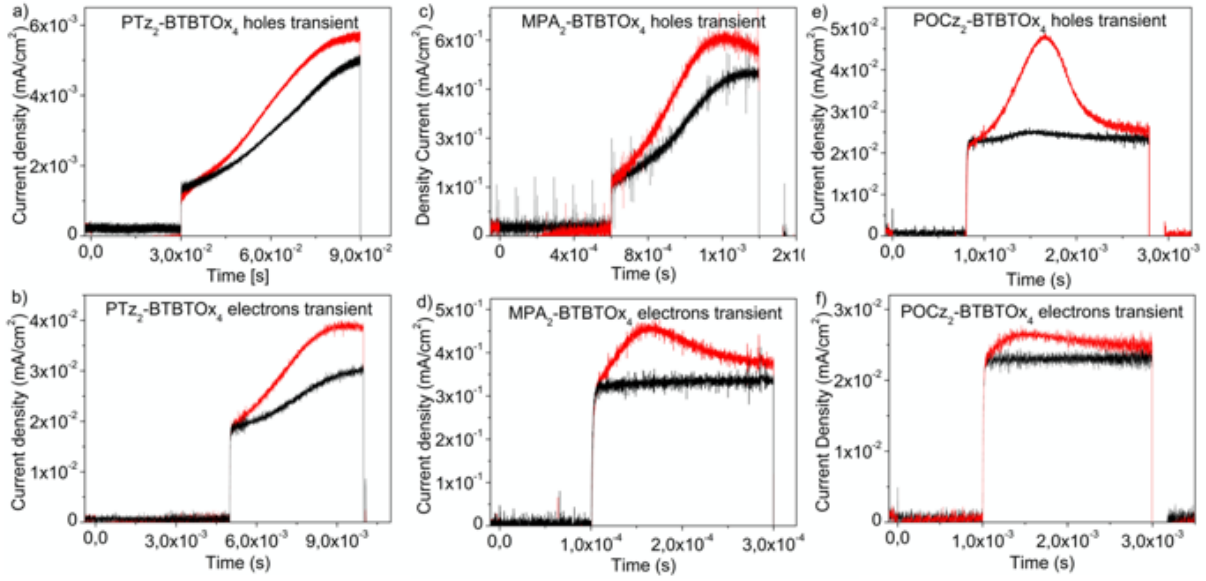


Figure 59. MIS-CELIV transients for BTBTO₄-based compounds: PTz₂-BTBTO₄ (a, b), MPA₂-BTBTO₄ (c, d), and POCz₂-BTBTO₄ (e, f), showing separate measurements for hole (upper column) and electron (bottom column) transport. Red and black curves represent different experimental conditions: photo and dark transients, respectively.

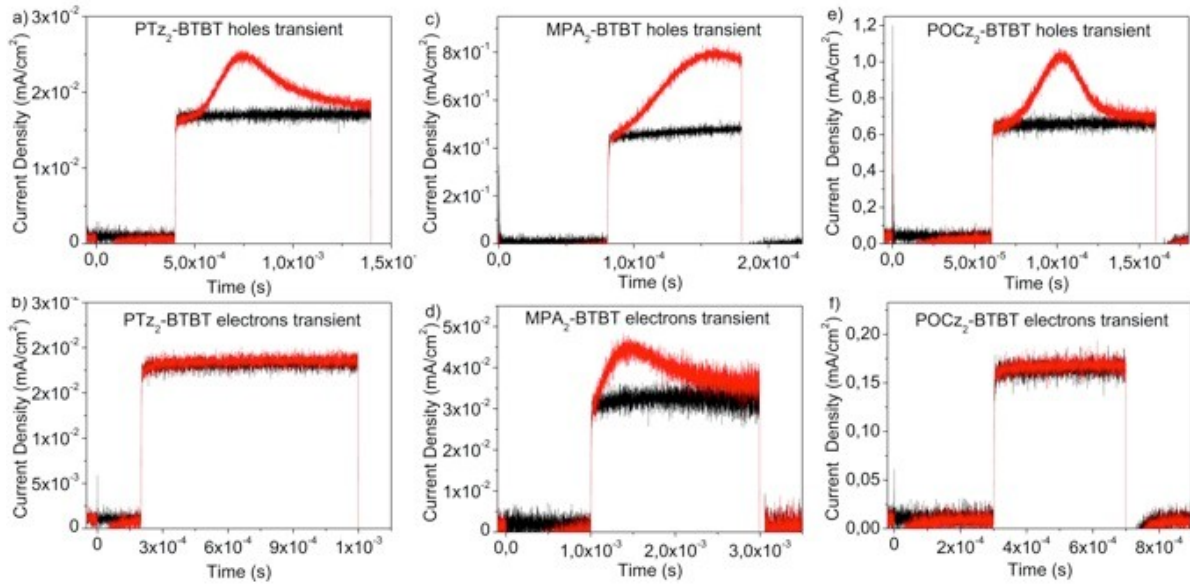


Figure 60. MIS-CELIV transients for BTBT-based compounds: PTz₂-BTBT (a, b), MPA₂-BTBT (c, d), and POCz₂-BTBT (e, f), showing separate measurements for hole (upper column) and electron (bottom column) transport. Red and black curves represent different experimental conditions: photo and dark transients, respectively.

4.3.5 Mobility Field Dependence

In CELIV experiments, the applied electric field is not constant during charge carrier extraction; instead, it increases linearly over time. However, the main extraction occurs at time $t = t_{\max}$, when the electric field reaches its maximum. Therefore, the mobility calculated using Equation 9 approximately corresponds to the value at the electric field [210]:

$$E(t_{max}) = \frac{A \times t_{max}}{d} \quad \text{eq. (12)}$$

In particular, the electric-field dependence of mobility was investigated by varying the duration of the voltage ramp while keeping its maximum value constant [211]. The experimentally estimated mobility was then plotted as a function of the squared electric field, as shown in Figure 61. For the BTBTOx₄-based compounds, we observe a slight increase in mobility at lower fields ($E^{1/2} < 100 \text{ (Vcm}^{-1})^{1/2}$). This may be attributed to the fact that Equation 12 does not account for the presence of equilibrium carriers prior to the application of the voltage ramp. In such cases, the film is assumed to contain no or negligible background carriers. As a result, using Equation 8 may lead to an overestimation of mobility at low fields [212]. This interpretation is consistent with our dark-MIS-CELIV measurements, which reveal the presence of equilibrium carriers in these compounds (see next section).

At higher electric fields (Figure 61), BTBTOx₄- and BTBT-based compounds exhibit distinct behaviors: the former shows a weak dependence of mobility on the electric field within the investigated range, while the latter displays a typical Poole–Frenkel-type field dependence [156,213].

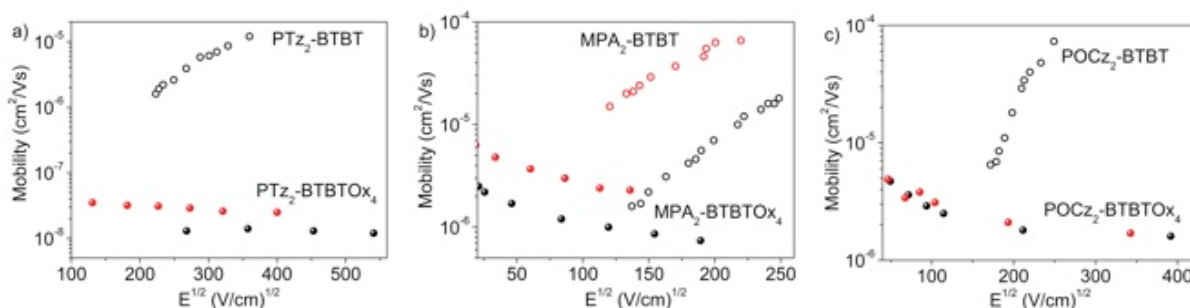


Figure 61. Holes (black dots) and electrons (red dots) mobility values against the square root of the electric field calculated according to Equation 1, for compounds a) PTz₂-BTBTOx₄ and PTz₂-BTBT, b) MPA₂-BTBTOx₄ and MPA₂-BTBT, c) POCz₂-BTBTOx₄ and POCz₂-BTBT.

4.3.6 Dark-MIS-CELIV Transients

CELIV offers the possibility to measure dark (equilibrium) carriers [196,214]. This feature is particularly useful for investigating the presence of free carriers resulting from either intentional or unintentional doping of the material [210,215]. Typically, unintentional doping—caused by oxidation or structural defects—is associated with material degradation, whereas intentional doping is employed to enhance conductivity by introducing a small amount of an additional dopant molecule [216,217].

We observe a strong dark hole transient for the compounds **PTz₂-BTBTOx₄** and **MPA₂-BTBTOx₄** (Figure 59, black curves), whose amplitude is comparable to that of the photo-induced transients, indicating the presence of free holes (p-doping). The weaker p-doping observed in **POCz₂-BTBTOx₄** may be attributed to the lower electron-donating ability of the carbazole derivative unit compared to phenothiazine and bis(4-methoxyphenyl)amine. This interpretation is consistent with our cyclic voltammetry (CV) measurements. Conversely, all BTBT-based compounds exhibit no detectable dark hole transients (Figure 60, black curves).

Figure 60 clearly demonstrates that the p-doping observed in BTBTO_{x4}-based compounds is related to the oxidation of the bridge unit [218,219].

Uniquely among the studied compounds, **PTz₂-BTBTO_{x4}** exhibits both dark hole and dark electron transport transients, as revealed by dark-MIS-CELIV measurements. This dual behavior can be rationalized by its distinctive electronic structure. DFT calculations show that **PTz₂-BTBTO_{x4}** features a large dihedral angle between the donor and the BTBTO_{x4} acceptor core, which reduces π -conjugation and induces strong intramolecular polarization. As illustrated in Figure 57, the HOMO is fully localized on the donor units, while the LUMO is entirely confined to the acceptor, indicating a pronounced charge separation. This spatial decoupling, combined with the deep LUMO energy of the BTBTO_{x4} core (~ -2.2 to -2.4 eV), facilitates the stabilization of equilibrium electrons even in the absence of illumination, enabling observable n-type transport. In contrast, the other BTBTO_{x4}-based compounds show only dark hole transport, likely due to greater HOMO–LUMO overlap or shallower LUMO levels, which limit the stabilization of electrons under dark conditions.

4.4 D-A-D Compounds with BTBT/ BTBTO_{x4} Acceptor Core for Electrochromic Devices

In previous studies, **PTz₂-BTBTO_{x4}**, **MPA₂-BTBTO_{x4}**, **POCz₂-BTBTO_{x4}**, **PTz₂-BTBT**, **MPA₂-BTBT** and **POCz₂-BTBT** were comprehensively characterized from photophysical, structural, electronic, and electrochemical perspectives. Among the six molecules in the series, two derivatives were selected, sharing the same donor group but differing in the nature of the central acceptor unit — oxidized in one case and non-oxidized in the other. These two compounds, **MPA₂-BTBTO_{x4}** and **MPA₂-BTBT**, were identified as the most promising candidates for this type of application, based on the outcomes of the previous characterization studies. The present work aims to further investigate their electrochemical behavior and to evaluate their potential for integration into electrochromic devices.

4.4.1 Electrochemical Characterization

The color-changing behavior of **MPA₂-BTBTO_{x4}** and **MPA₂-BTBT** upon oxidation, as well as the electronic transition character of the resulting radical species, were investigated by recording the absorption spectra of the radicals generated through oxidation titration (Figure 62). Radical species were generated following gradual chemical oxidation in CH₂Cl₂ solution (ca. 2×10^{-5} M) and the electronic transitions of **MPA₂-BTBTO_{x4}•** and **MPA₂-BTBT•** were investigated monitoring the changes in the UV–vis–NIR absorption. In detail, spectra were recorded after stepwise additions of a solution of SbCl₅ in CH₂Cl₂ (1×10^{-3} M) starting from the neutral species of the **MPA₂** derivatives. Upon the first oxidation step, both compounds exhibit a broad absorption band in the NIR region, centred at 1384 nm for **MPA₂-BTBTO_{x4}•** and at 1678 nm for **MPA₂-BTBT•**. This band is associated with an optically induced hole transfer, intervalence charge transfer (IV-CT), from the oxidized arylamine moiety to the second neutral arylamine unit. The IV-CT band, for both compounds, appears very intense and well separated from the other absorption bands, indicating good

electronic communication between the redox centres. Furthermore, additional pairs of electronic transitions are observed for **MPA₂-BTBTOx₄•** and **MPA₂-BTBT•** centred at 632/744 nm and 508/558 nm, respectively.

By continuing the oxidation process through the gradual addition of small amounts of SbCl₅, the dicationic species (**MPA₂-BTBTOx₄²⁺** and **MPA₂-BTBT²⁺**) are generated. In this stage, the IV-CT band progressively decreases until it disappears completely, while a new set of absorption bands emerges and increases in intensity within the 670–1070 nm range. These optically induced transitions are attributed to charge-transfer processes occurring from the molecular bridge toward the N-radical cation sites.

Overall, this experiment proved fundamental in revealing the chromic responsiveness of **MPA₂-BTBTOx₄** and **MPA₂-BTBT** to oxidative processes, demonstrating their potential as redox-active materials with tunable optical properties. Combined with the information obtained from cyclic voltammetry, which confirmed that these compounds undergo facile and highly reversible oxidation processes, it can be concluded that **MPA₂-BTBTOx₄** and **MPA₂-BTBT** are excellent candidates for application as electrochromic materials.

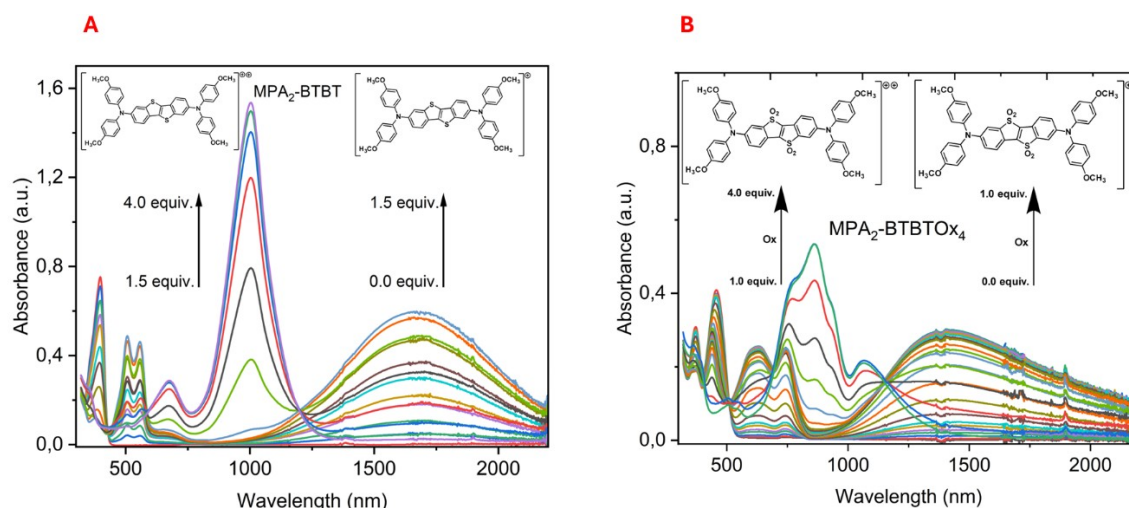


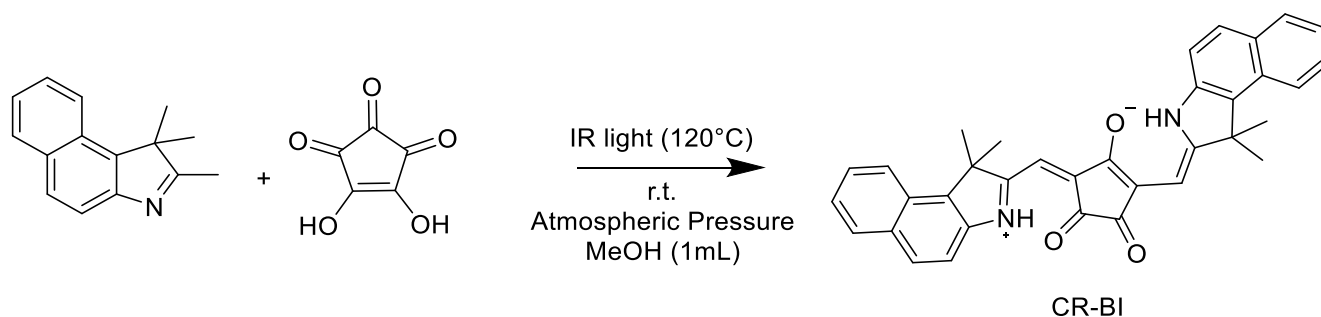
Figure 62. Fig. Absorption spectra of (A) MPA₂-BTBT and (B) MPA₂-BTBTOx₄ in CH₂Cl₂ while adding dropwise a solution of SbCl₅ in CH₂Cl₂ (1 mM).

CHAPTER V

Experimental Part

5.1 Synthesis of CR-BI

(1,1-Dimethyl-1,3-dihydro-2H-benzo[e]indol-2-ylidene)methyl)-5-((1,1-dimethyl-1H-benzo[e]indol-3-io-2-yl)methylene)-3,4-dioxocyclopent-1-en-1-olate (CR-BI)



Croconic acid (340 mg, 2.4 mmol) and 1,1,2-trimethyl-1Hbenzo[e]indole (1 g, 4.48 mmol) reacted in a Pyrex glass dish under IR lamp irradiation. MeOH (1 mL) was added to homogenize the reaction mixture. The lamp was heated to 120 °C, and then the reaction was monitored by TLC using a mixture of n-hexane/ethyl acetate (1:1) as the mobile phase. Finally, the mixture was cooled to room temperature, and the crude product was washed with MeOH and then with n-hexane, obtaining 820 mg of compound (66% yield) as a brown metallic solid.

¹H-NMR (500 MHz, CDCl₃): δ=15.99–14.75 (4 s for overall 2H), 8.06–7.83 (m, 6H), 7.62–7.41 (m, 6H), 6.25–6.09 (3 s for overall 2H), 1.82–1.78 ppm (3 s for overall 12H) [80].

5.2 DSC Analysis of PLA@CR-BI Composite Films

The temperature and enthalpy values, characteristic of thermal transitions, for neat L-PLA and L-PLA@CR-BI composite films are reported in Table 16.

Table 16. DSC parameters of samples from the second heating scan.

Sample	T _g (°C)	T _{cc} (°C)	T _{onset/cc} (°C)	ΔH _{cc} (J/g)	ΔH _{pm-c} (J/g)	T _m (°C)	ΔH _m (J/g)	C (%)
L-PLA	60.4	95.5	90.1	3.5	5.1	175.7	50.7	45
L-PLA@CR-BI*0.1	59.6	96.3	89.3	6.6	5.0	175.9	55.3	47

L-PLA@CR-BI*0.5	59.3	97.9	90.1	10.2	5.1	175.3	49.5	37
L-PLA@CR-BI*1	58.6	104.5	90.5	25.9	4.8	174.3	49.0	20

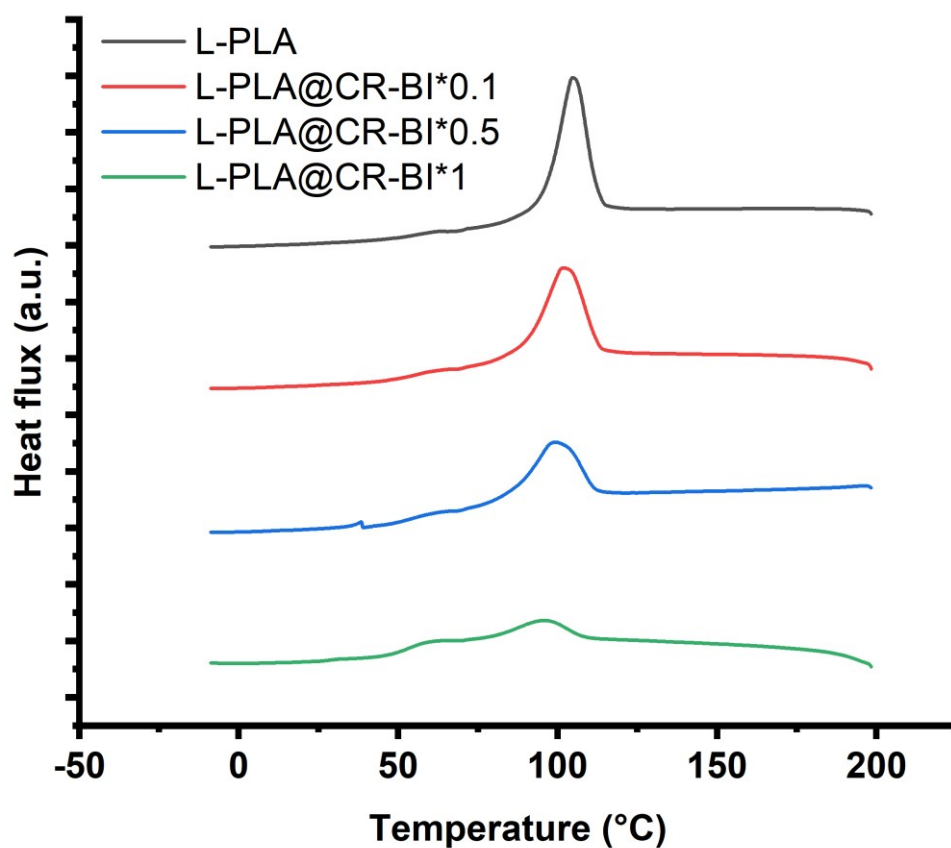
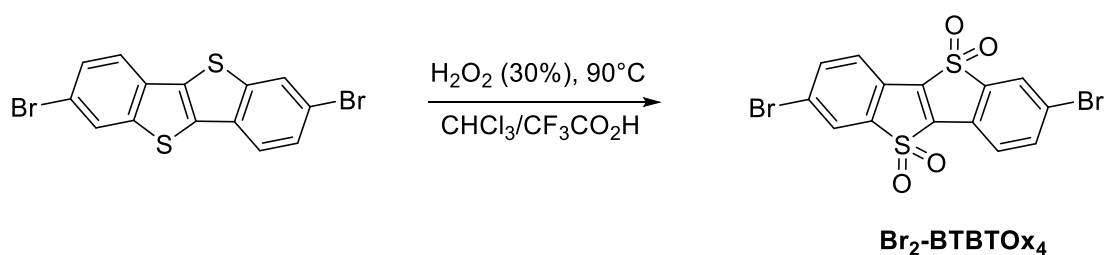


Figure 63. Cooling DSC curves of L-PLA (black), L-PLA@CR-BI*0.1 (red), L-PLA@CR-BI*0.5 (blue) and L-PLA@CR-BI*1 (green) samples.

5.3 Synthesis of Br₂-BTBTOf₄

2,7-dibromo-[1]benzothieno[3,2-b]benzothiophene-5,5,10,10-tetraoxide (Br₂-BTBTOf₄)

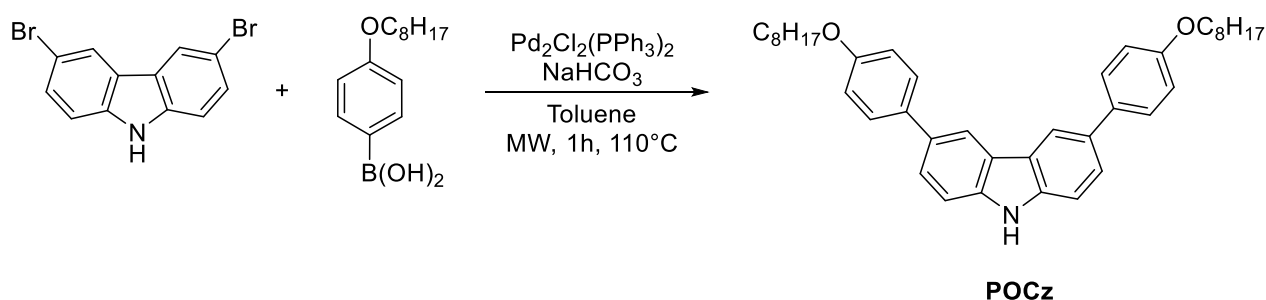


In a 250 mL three-necked round bottom flask 2,7-dibromo-[1]benzothieno[3,2-b]benzothiophene (3.5 g, 8.79 mmol) was dispersed in a mixture of CHCl_3 (30 mL) and $\text{CF}_3\text{CO}_2\text{H}$ (30 mL). To the resulting suspension H_2O_2 30% (35 mL) was slowly added and then the mixture was stirred at 90°C overnight. The reaction mixture was cooled at room temperature, diluted with MeOH (40 mL) and the solid was filtered and washed with H_2O , MeOH and acetone. The solid was dried under vacuum and the pure product $\text{Br}_2\text{-BTBTO}_4$ was obtained as a yellow solid (78% yield). $\text{Mp} > 230^\circ\text{C}$. The low solubility of compound doesn't allow recording NMR spectra.

FT-IR (KBr): ν 1449 (m), 1389 (m), 1302 (s), 1151 (s), 1069 (m), 813 (m), 647 (m), 588 (m), 563 (m) cm^{-1} . MALDI-TOF (dithranol, negative mode) for $\text{C}_{14}\text{H}_6\text{Br}_2\text{O}_4\text{S}_2$: 461.8059 (100), 459.8080. Found: 461.67, 459.66. Anal. Calcd for $\text{C}_{14}\text{H}_6\text{Br}_2\text{O}_4\text{S}_2$: C, 36.39; H, 1.31; Br, 34.58; O, 13.85; S, 13.88. Found: C, 36.22; H, 1.30; S, 13.93.

5.4 Synthesis of POCz

3,6-Bis(4-(octyloxy)phenyl)-9H-carbazole (POCz)

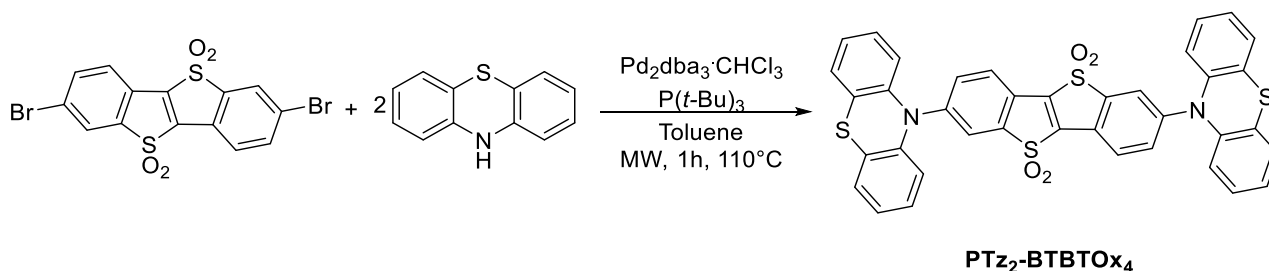


A mixture of toluene (20 mL) and ethanol (12 mL) was purged by bubbling nitrogen for 30 min. Then, 3,6-dibromo-9H-carbazole (1) (0.400 g, 1.23 mmol), 4-(octyloxy(phenyl)boronic acid (0.72 g, 2.88 mmol), NaHCO_3 sat. sol. (12 mL) and $\text{PdCl}_2(\text{PPh}_3)_3$ were added and the resulting mixture was stirred under microwave irradiation at 110°C for 1h. The reaction mixture was cooled at rt and extracted with ethyl acetate. The organic phase was dried over anhydrous sodium sulfate, filtered on neutral Al_2O_3 and the solvent evaporated under a reduced pressure. The crude product was sonicated in hexane for 30 min than the solid was filtered and washed with hexane to yield the pure product POCz as a white solid (80% yield). Mp $125\text{-}126^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 8.27 (bs, 2H), 8.07 (bs, 1H), 7.64 (d, $J = 8.4$ Hz, 2H), 7.63 (d, $J = 8.6$ Hz, 4H), 7.47 (d, $J = 8.4$ Hz, 2H), 7.01 (d, $J = 8.6$ Hz, 4H), 4.02 (t, $J = 6.6$ Hz, 4H), 1.83 (quint, $J = 6.6$ Hz, 4H), 1.49 (quint, $J = 7.2$ Hz, 4H), 1.42-1.23 (bs, 16H), 0.90 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR (100 MHz, CD_2Cl_2) δ 158.94, 139.78, 134.86, 133.26, 128.61, 125.74, 124.50, 118.71, 115.42, 111.55, 68.80, 32.45, 30.00, 29.97, 29.88, 26.68, 23.28, 14.46 ppm. FT-IR (KBr): ν 3042 (s), 2925 (s), 2854 (s), 1608 (s), 1516 (s), 1484 (s), 1469 (s), 1301 (m), 1273 (s), 1239 (s), 1180 (m), 1117 (m), 1035 (m), 804 (s), 802 (s) cm^{-1} . Anal. Calcd for $\text{C}_{40}\text{H}_{49}\text{NO}_2$: C, 83.43; H, 8.58; N, 2.43; O, 5.56. Found: C, 83.57; H, 8.51; N, 2.60.

5.5 Synthesis of PTz₂-BTBTO_{x4}

2,7-Di(10H-phenothiazin-10-yl)-[1]benzothieno[3,2-b]benzothiophene5,5,10,10-tetraoxide (PTz₂-BTBTO_{x4})

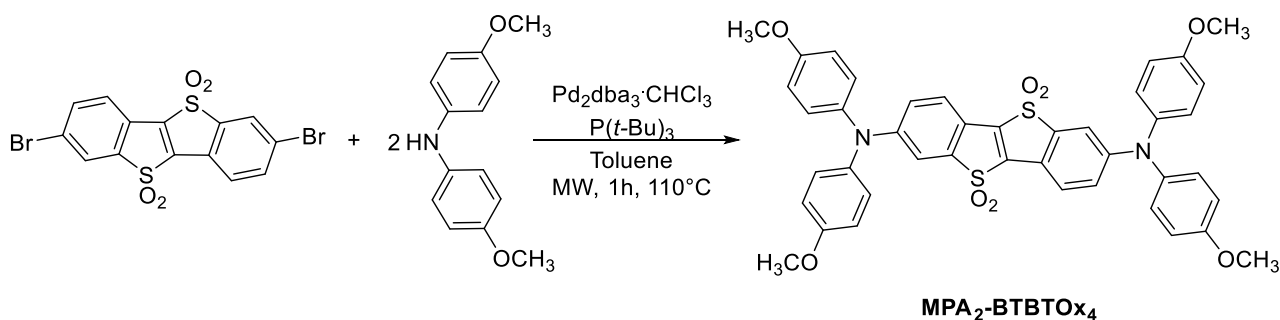


In a 100 mL three-necked round bottom flask, under a nitrogen atmosphere, phenothiazine (0.32 g, 1.6 mmol), Br₂-BTBTO₄ (0.3 g, 0.7 mmol), Pd₂dba₃*CHCl₃ (15 mg, 29 μmol Pd), P(t-Bu)₃ (12 mg, 59 μmol), t-BuONa (0.15 g, 1.56 mmol) and anhydrous toluene (20 mL) were added. The resulting mixture was stirred under microwave irradiation at 110°C for 1h. The reaction mixture was cooled at r.t., quenched with saturated aq. NH₄Cl and extracted with ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄ and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/ethyl acetate (8/2, v/v) as the eluent, to yield the pure product PTz₂-BTBTO₄ as a yellow solid (68% yield). Mp 183-184.

¹H NMR (400 MHz, CDCl₃): δ 8.17 (d, J = 8.5 Hz, 1H), 7.86 (d, J = 1.8 Hz, 1H), 7.53 (dd, J = 8.5, 1.8 Hz, 1H), 7.49 (d, J = 2.2 Hz, 1H), 7.46 (dd, J = 7.8, 1.0 Hz, 2H), 7.38-7.29 (m, 5H), 7.24 (dd, J = 8.8, 1.8 Hz, 1H), 7.21 (dt, J = 8.5, 2.2 Hz, 2H), 7.08 (dd, J = 7.3, 1.8 Hz, 2H), 6.89 (dq, J = 7.8, 1.8 Hz, 4H), 6.31 (dd, J = 7.8, 1.7 Hz, 2H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 147.96, 145.20, 144.21, 144.08, 143.80, 140.97, 139.36, 132.80, 132.02, 129.72, 128.93, 128.80, 127.63, 127.04, 126.98, 126.31, 125.49, 124.47, 123.36, 123.33, 123.14, 121.71, 121.01, 120.86, 117.11, 110.10 ppm. FT-IR (KBr): ν 1727 (m), 1577 (m), 1461 (s), 1307 (s), 1255 (s), 1145 (s), 1038 (m), 925 (w), 816 (m), 745 (s), 618 (w), 586 (w), 560 (w) cm⁻¹. Anal. Calcd for C₃₈H₂₂N₂O₄S₄: C, 65.31; H, 3.17; N, 4.01; O, 9.16; S, 18.35. Found: C, 65.38; H, 3.27; N, 4.09; S, 18.29.

5.6 Synthesis of MPA₂-BTBTO_{x4}

2,7-Bis(bis(4-methoxyphenyl)amino)-[1]benzothieno-[3,2d]benzothiophene-5,5,10,10-tetraoxide (MPA₂-BTBTO_{x4})

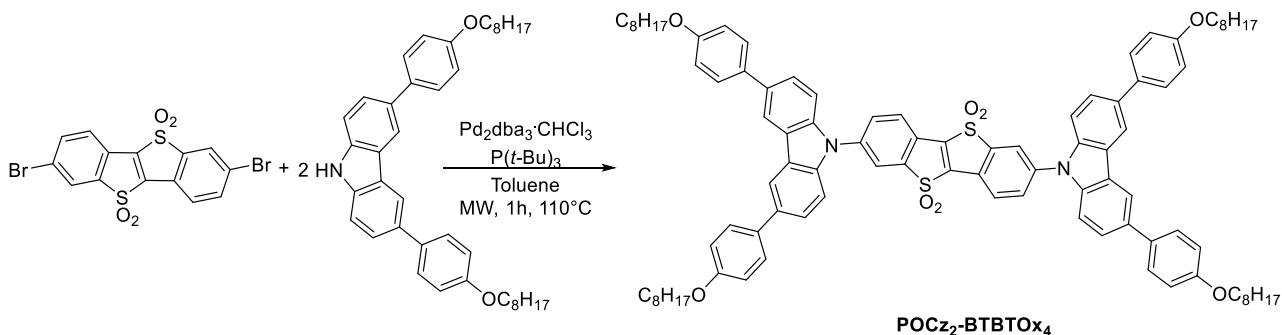


In a 100 mL three-necked round bottom flask, under a nitrogen atmosphere, bis(4methoxyphenyl)amine (0.37 g, 1.6 mmol), Br₂-BTBTO₄ (0.3 g, 0.7 mmol), Pd₂dba₃*CHCl₃ (15 mg, 29 μmol Pd), P(t-Bu)₃ (12 mg, 59 μmol), tBuONa (0.15 g, 1.56 mmol) and anhydrous toluene (20 mL) were added. The resulting mixture was stirred under microwave irradiation at 110°C for 1h. The reaction mixture was cooled at rt, quenched with saturated aq. NH₄Cl and extracted with ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄ and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/ethyl acetate (7/3, v/v) as the eluent, to yield the pure product MPA₂-BTBTO₄ as an orange solid (72% yield). Mp > 230 °C.

¹H NMR (400 MHz, CDCl₃): δ 7.69 (d, J = 8.8 Hz, 1H), 7.24 (d, J = 2.2 Hz, 1H), 7.20 (d, J = 2.2 Hz, 1H), 7.13-7.03 (m, 10H), 6.93-6.82 (m, 9H), 3.82 (s, 6H), 3.81 (s, 6H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 157.16, 156.27, 150.63, 147.28, 143.75, 143.67, 141.46, 140.42, 138.92, 131.29, 127.58, 126.75, 124.09, 122.17, 121.59, 121.22, 120.78, 118.75, 115.23, 114.88, 113.79, 111.58, 55.52, 55.49 ppm. FT-IR (KBr): ν 1600 (m), 1508 (s), 1464 (m), 1331 (m), 1309 (m), 1245 (s), 1147 (m), 1033 (m), 829 (m), 596 (m) cm⁻¹. Anal. Calcd for C₄₂H₃₄N₂O₈S₂: C, 66.48; H, 4.52; N, 3.69; O, 16.87; S, 8.45. Found: C, 66.48; H, 4.55; N, 3.63; S, 8.51.

5.7 Synthesis of POC_{z2}-BTBTO_{x4}

2,7-Bis(3,6-bis(4-octyloxy)phenyl-9H-carbazol-9-yl)[1]benzothieno[3,2d]benzothiophene-5,5,10,10-tetraoxide (POC_{z2}-BTBTO_{x4}).

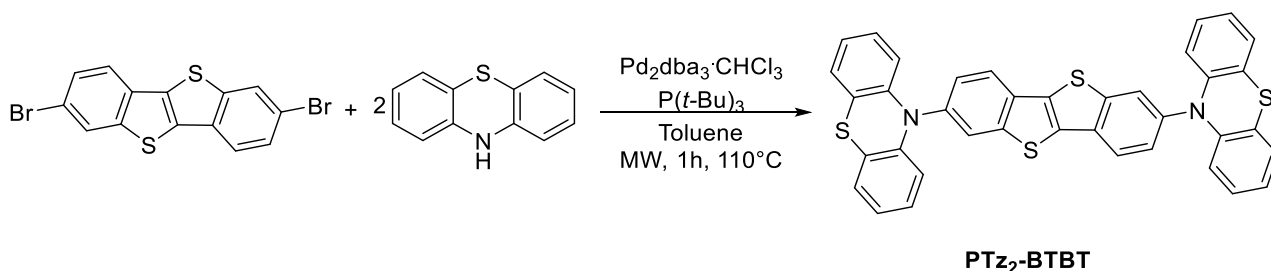


In a 100 mL three-necked round bottom flask, under a nitrogen atmosphere, 3,6-bis(4octyloxy)phenyl)-9H-carbazole (0.3 g, 0.52 mmol), Br₂-BTBTO₄ (0.102 g, 0.24 mmol), Pd₂dba₃·CHCl₃ (5 mg, 10 μmol Pd), P(*t*-Bu)₃ (4 mg, 20 μmol), *t*BuONa (0.055 g, 0.58 mmol) and anhydrous toluene (20 mL) were added. The resulting mixture was stirred under microwave irradiation at 110°C for 1h. The reaction mixture was cooled at rt, quenched with saturated aq. NH₄Cl and extracted with ethyl acetate. The organic layer was dried over anhydrous Na₂SO₄ and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/dichloromethane (6/4, v/v) as the eluent, to yield the pure product POCz₂-BTBTO₄ as a light orange solid. (76% yield). Mp 140-141 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.34-8.25 (m, 5H), 8.13-8.06 (bs, 2H), 7.87-7.77 (bs, 2H), 7.76-7.69 (bs, 1H), 7.68-7.57 (m, 12H), 7.53 (dd, *J* = 1.9, 8.4 Hz, 2H), 7.47 (dd, *J* = 1.9, 8.4 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 8H), 4.02 (t, *J* = 6.6 Hz, 8H), 1.83 (quint, *J* = 7.1 Hz, 8H), 1.50 (quint, *J* = 7.1 Hz, 8H), 1.43-1.21 (bs, 32H), 0.91 (t, *J* = 6.9 Hz, 12H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 158.46, 158.37, 143.63, 140.20, 139.95, 139.22, 136.40, 134.46, 133.98, 133.95, 133.90, 133.74, 130.85, 129.70, 129.10, 128.18, 128.16, 125.89, 125.65, 125.45, 124.71, 119.75, 118.51, 118.41, 114.88, 114.86, 109.75, 68.14, 31.84, 29.42, 29.36, 29.27, 26.10, 22.67, 14.11 ppm. FT-IR (KBr): ν 2923 (s), 2853 (s), 1605 (s), 1514 (m), 1478 (s), 1456 (s), 1314 (s), 1267 (s), 1023 (s), 1174 (s), 1149 (s), 1036 (m), 804 (s) cm⁻¹. Anal. Calcd for C₉₄H₁₀₂N₂O₈S₂: C, 77.76; H, 7.08; N, 1.93; O, 8.82; S, 4.42. Found: C, 77.72; H, 7.13; N, 2.00; S, 4.46.

5.8 Synthesis of PTz₂-BTBT

2,7-Di(10*H*-phenothiazin-10-yl)-[1]benzothieno[3,2-*b*]benzothiophene (PTz₂-BTBT)

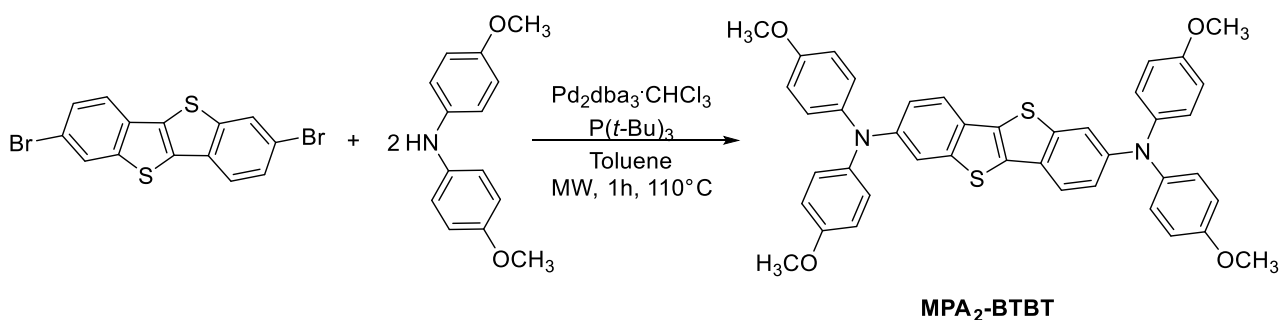


In a 100 mL three-necked round bottom flask, under a nitrogen atmosphere, phenothiazine (0.27 g, 1.35 mmol), Br₂-BTBT (0.25 g, 0.6 mmol), Pd₂dba₃·CHCl₃ (12 mg, 23 μmol Pd), P(*t*-Bu)₃ (9 mg, 46 μmol), *t*-BuONa (0.13 g, 1.32 mmol) and anhydrous toluene (20 mL) were added. The resulting mixture was stirred under microwave irradiation at 110°C for 1h. The reaction mixture was cooled at r.t., diluted with methanol and the precipitate was washed with water and methanol. The crude residue was treated with ethyl acetate and ultrasonicated for 1h, then filtered to yield a light-yellow powder (77% yield). The very low solubility of PTz₂-BTBT in all organic solvents doesn't allow to recovery NRM spectra. Mp > 230 °C.

FT-IR (KBr): ν 1581 (s), 1461 (s), 1437 (s), 1336 (m), 1306 (s), 1238 (s), 1125 (m), 1042 (m), 922 (m), 817 (m), 740 (s), 705 (m), 629 (m) cm^{-1} . Anal. Calcd for $\text{C}_{38}\text{H}_{22}\text{N}_2\text{S}_4$: C, 71.89; H, 3.49; N, 4.41; S, 20.20. Found: C, 71.81; H, 3.60; N, 4.52; S, 20.13.

5.9 Synthesis of $\text{MPA}_2\text{-BTBT}$

2,7-Bis(bis(4-methoxyphenyl)amino)-[1]benzothieno-[3,2-d]benzothiophene ($\text{MPA}_2\text{-BTBT}$)

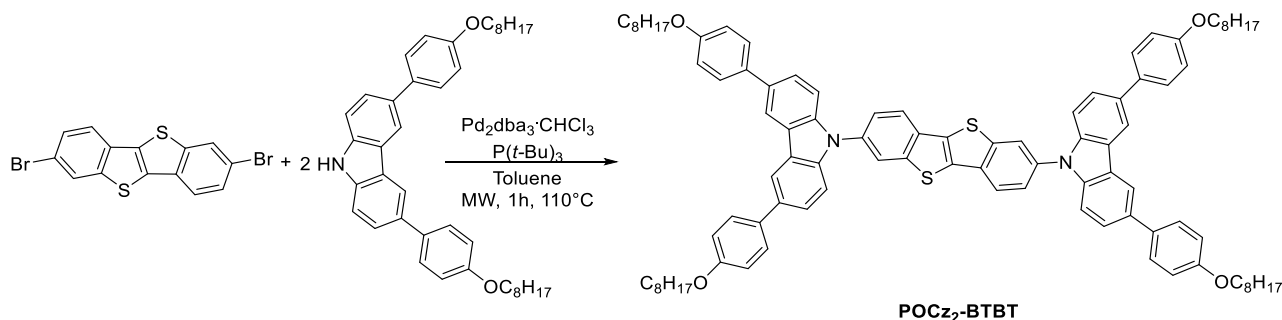


In a 100 mL three-necked round bottom flask, under a nitrogen atmosphere, bis(4-methoxyphenyl)amine (0.26 g, 1.1 mmol), **Br₂-BTBT** (0.2 g, 0.5 mmol), $\text{Pd}_2\text{dba}_3 \cdot \text{CHCl}_3$ (10 mg, 10 μmol Pd), $\text{P}(t\text{-Bu})_3$ (4 mg, 20 μmol), $t\text{-BuONa}$ (0.12 g, 1.25 mmol) and anhydrous toluene (20 mL) were added. The resulting mixture was stirred under microwave irradiation at 110°C for 1h. The reaction mixture was cooled at rt, quenched with saturated aq. NH_4Cl and extracted with dichloromethane. The organic layer was dried over anhydrous Na_2SO_4 and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/dichloromethane (4/6, v/v) as the eluent, to yield the pure product **$\text{MPA}_2\text{-BTBT}$** as a light-yellow solid (73% yield). Mp 139-140 °C.

^1H NMR (400 MHz, CDCl_3): δ 7.69 (d, J = 8.8 Hz, 1H), 7.24 (d, J = 2.2 Hz, 1H), 7.20 (d, J = 2.2 Hz, 1H), 7.13-7.03 (m, 10H), 6.93-6.82 (m, 9H), 3.82 (s, 6H), 3.81 (s, 6H) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ 157.16, 156.27, 150.63, 147.28, 143.75, 143.67, 141.46, 140.42, 138.92, 131.29, 127.58, 126.75, 124.09, 122.17, 121.59, 121.22, 120.78, 118.75, 115.23, 114.88, 113.79, 111.58, 55.52, 55.49 ppm. FT-IR (KBr): ν 1600 (m), 1508 (s), 1464 (m), 1331 (m), 1309 (m), 1245 (s), 1147 (m), 1033 (m), 829 (m), 596 (m) cm^{-1} . Anal. Calcd for $\text{C}_{42}\text{H}_{34}\text{N}_2\text{O}_4\text{S}_2$: C, 72.60; H, 4.93; N, 4.03; O, 9.21; S, 9.23. Found: C, 72.81; H, 4.88; N, 4.16; S, 9.02.

5.10 Synthesis of POCz₂-BTBT

2,7-Bis(3,6-bis(4-octyloxy)phenyl-9H-carbazol-9-yl)[1]benzothieno[3,2-d] benzothiophene (POCz₂-BTBT)



In a 100 mL three-necked round bottom flask, under a nitrogen atmosphere, 3,6-bis(4-octyloxy)phenyl-9H-carbazole (0.24 g, 0.4 mmol), **Br₂-BTBT** (77 Mg, 0.2 mmol), Pd₂dba₃·CHCl₃ (8 mg, 15 μmol Pd), P(*t*-Bu)₃ (6 mg, 30 μmol), *t*-BuONa (0.042 g, 0.4 mmol) and anhydrous toluene (20 mL) were added. The resulting mixture was stirred under microwave irradiation at 110°C for 1h. The reaction mixture was cooled at rt, quenched with saturated aq. NH₄Cl and extracted with dichloromethane. The organic layer was dried over anhydrous Na₂SO₄ and the solvent removed under a reduced pressure. The crude residue was purified by column chromatography using hexane/dichloromethane (6/4, v/v) as the eluent, to yield the pure product **POCz₂-BTBT** as an ivory solid. (76% yield). Mp 129-130 °C.

¹H NMR (400 MHz, CDCl₃): δ 8.34-8.25 (m, 5H), 8.13-8.06 (bs, 2H), 7.87-7.77 (bs, 2H), 7.76-7.69 (bs, 1H), 7.68-7.57 (m, 12H), 7.53 (dd, *J* = 1.9, 8.4 Hz, 2H), 7.47 (dd, *J* = 1.9, 8.4 Hz, 2H), 7.02 (d, *J* = 8.0 Hz, 8H), 4.02 (t, *J* = 6.6 Hz, 8H), 1.83 (quint, *J* = 7.1 Hz, 8H), 1.50 (quint, *J* = 7.1 Hz, 8H), 1.43-1.21 (bs, 32H), 0.91 (t, *J* = 6.9 Hz, 12H) ppm. ¹³C NMR (125 MHz, CDCl₃): δ 158.46, 158.37, 143.63, 140.20, 139.95, 139.22, 136.40, 134.46, 133.98, 133.95, 133.90, 133.74, 130.85, 129.70, 129.10, 128.18, 128.16, 125.89, 125.65, 125.45, 124.71, 119.75, 118.51, 118.41, 114.88, 114.86, 109.75, 68.14, 31.84, 29.42, 29.36, 29.27, 26.10, 22.67, 14.11 ppm. FT-IR (KBr): ν 2948 (m), 2901 (m), 2830 (m), 1599 (s), 1548 (m), 1505 (s), 1458 (s), 1316 (s), 1240 (s), 1174 (s), 1105 (m), 1036 (s), 825 (s), 737 (m) cm⁻¹. Anal. Calcd for C₉₄H₁₀₂N₂O₄S₂: C, 81.34; H, 7.41; N, 2.02; O, 4.61; S, 4.62. Found: C, 81.48; H, 7.38; N, 2.14; S, 4.56.

5.11 NMR Spectra of L-PLA

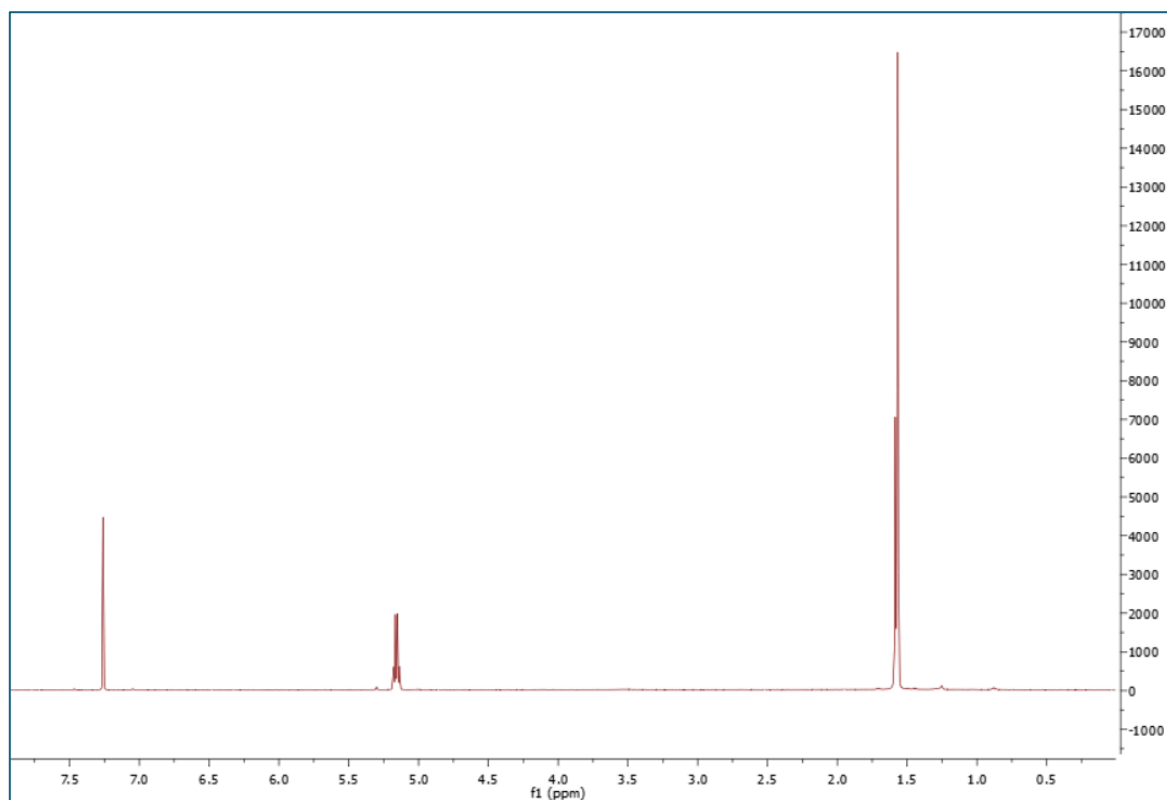


Figure 64. ^1H NMR spectrum L-PLA in CDCl_3 .

5.12 NMR Spectra of POCz

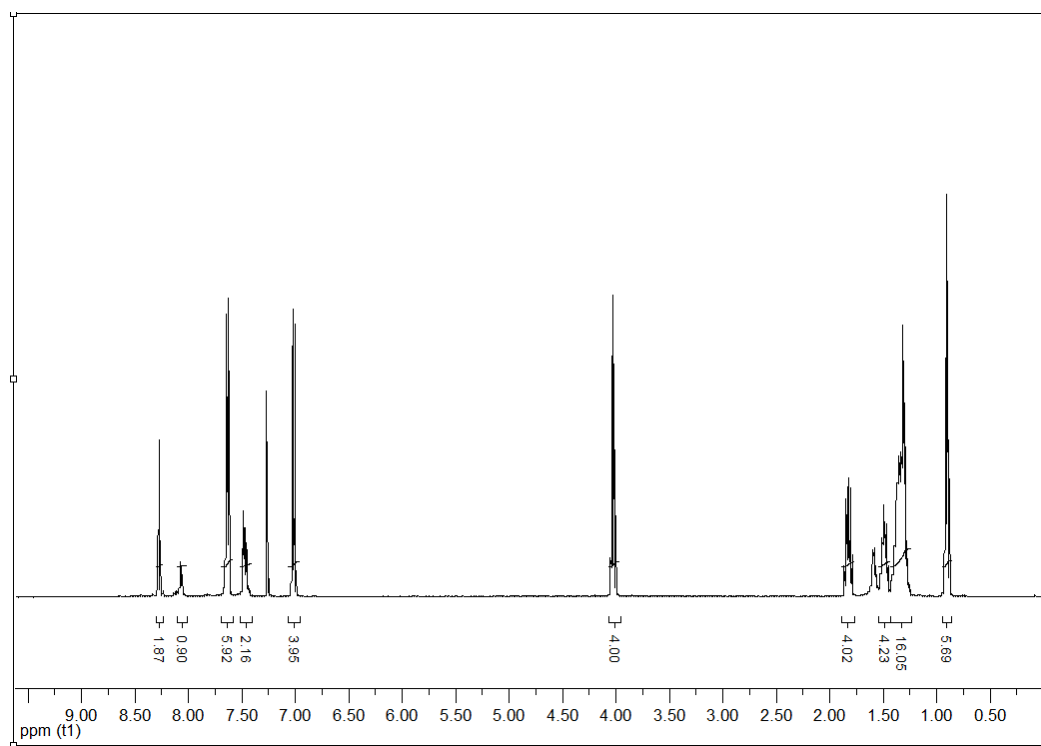


Figure 65. ^1H NMR spectrum of 3,6-Bis(4-(octyloxy)phenyl)-9H-carbazole (POCz) in CDCl_3 .

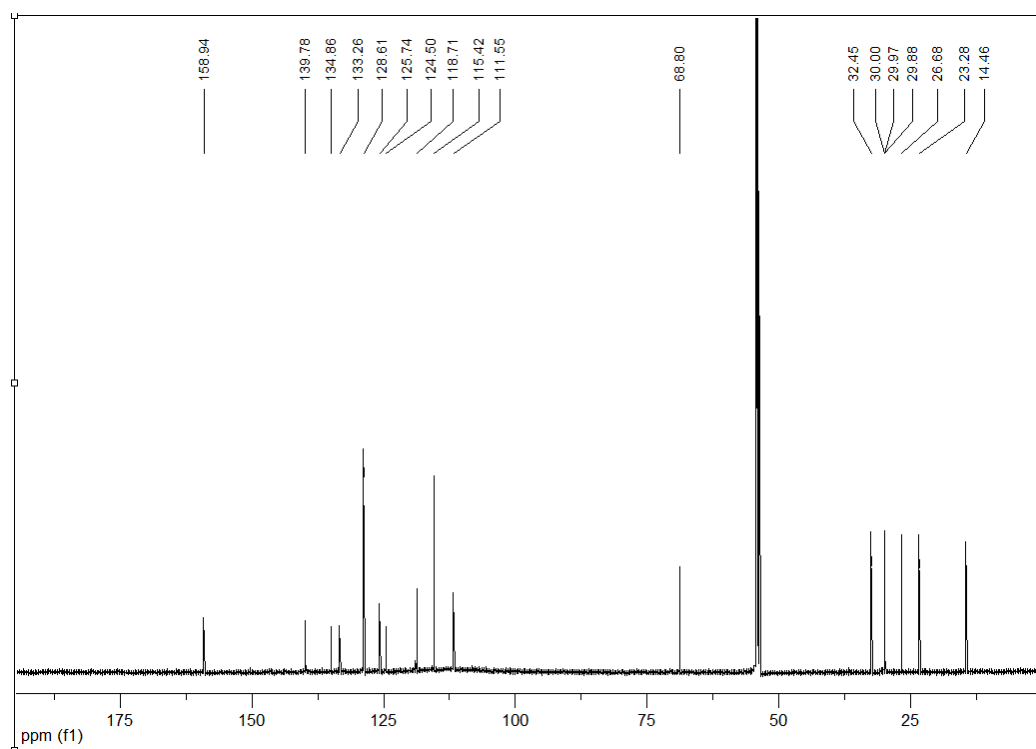


Figure 66. ^{13}C NMR spectrum of 3,6-Bis(4-(octyloxy)phenyl)-9H-carbazole (POCz) in CDCl_3 .

5.13 NMR Spectra of $\text{PTz}_2\text{-BTBTOx}$

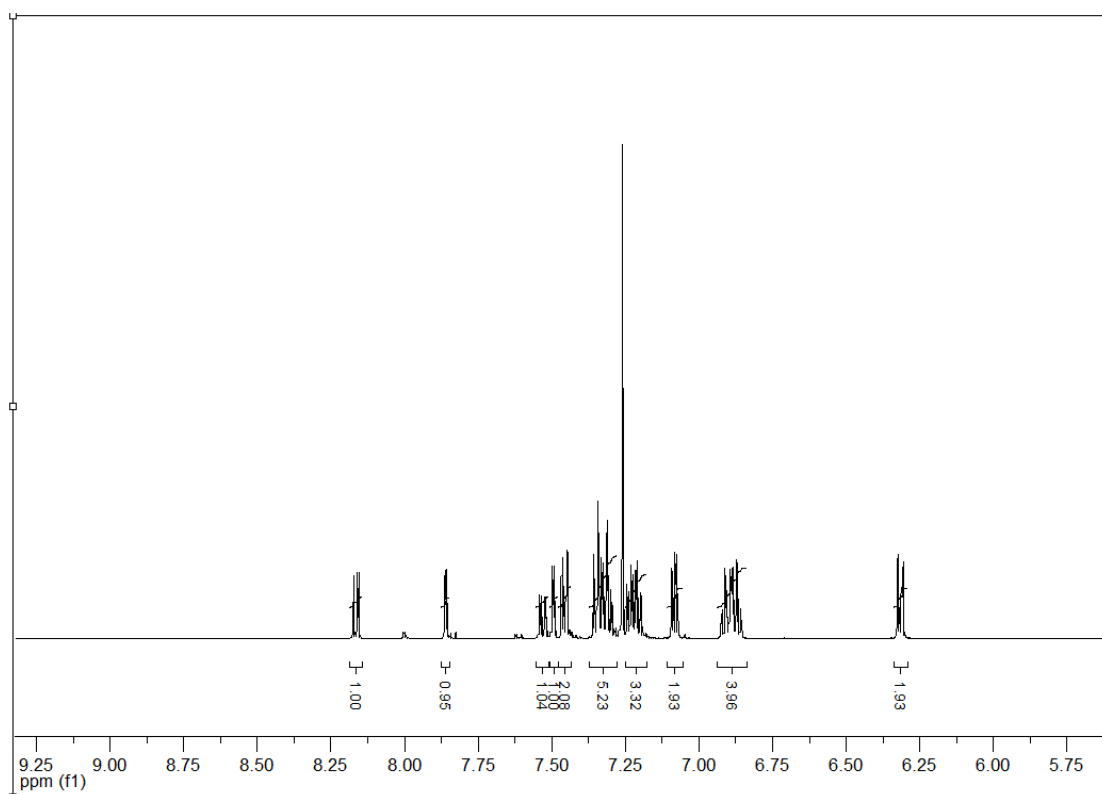


Figure 67. ^1H NMR spectrum of 2,7-Di(10H-phenothiazin-10-yl)-[1]benzothieno[3,2b]benzothiophene-5,5,10,10-tetraoxide ($\text{PTz}_2\text{-BTBTOx}_4$) in CDCl_3 .

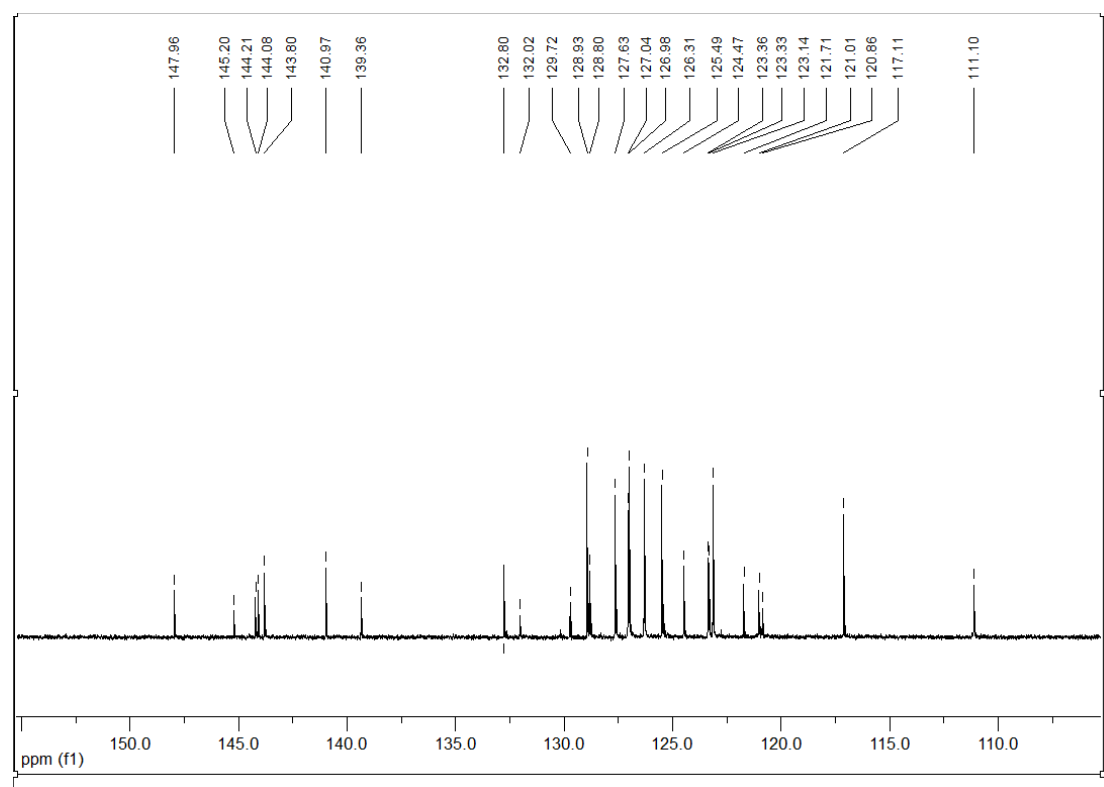


Figure 68. ^{13}C NMR spectrum of 2,7-di(10H-phenothiazin-10-yl)-[1]benzothieno[3,2b]benzothiophene-5,5,10,10-tetraoxide ($\text{PTz}_2\text{-BTBTOx}_4$) in CDCl_3 .

5.14 NMR Spectra of $\text{MPA}_2\text{-BTBTOx}_4$

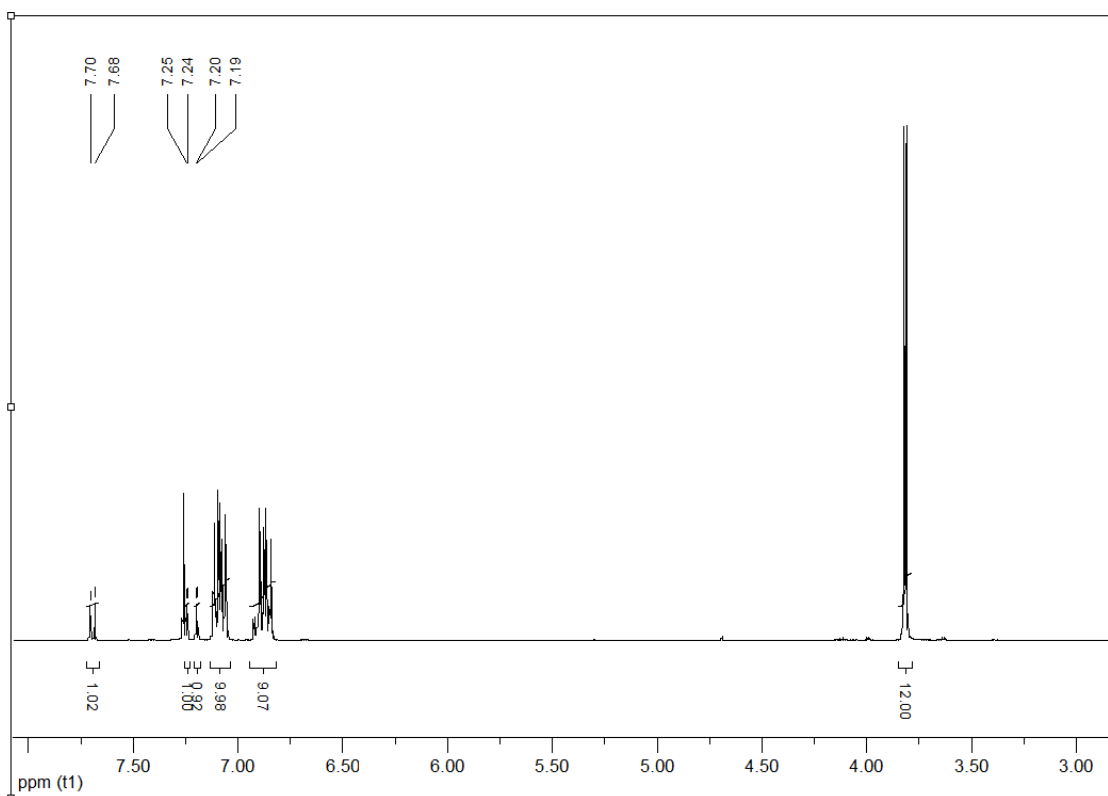


Figure 69. ^1H NMR spectrum of 2,7-Bis(bis(4-methoxyphenyl)amino)-[1]benzothieno-[3,2d]benzothiophene-5,5,10,10-tetraoxide ($\text{MPA}_1\text{-BTBTOx}_4$) in CDCl_3 .

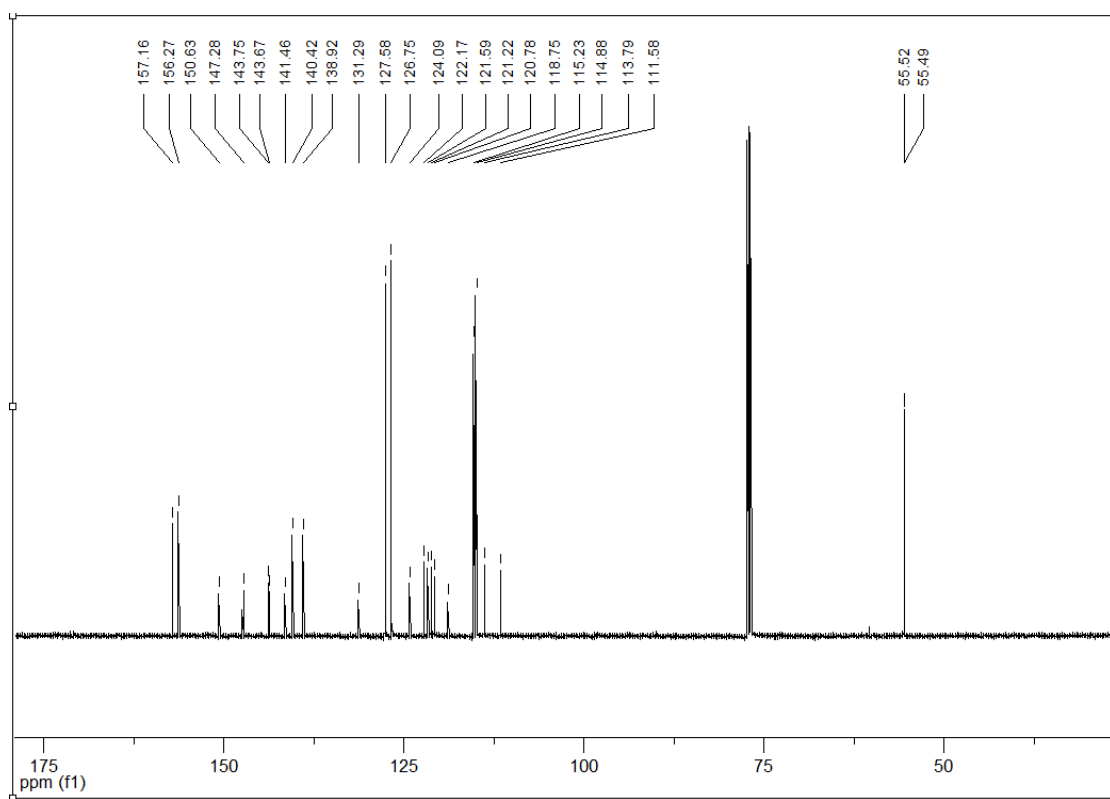


Figure 70. ¹³C NMR spectrum of 2,7-Bis(bis(4-methoxyphenyl)amino)-[1]benzothieno-[3,2-d]benzothiophene-5,5,10,10-tetraoxide (MPA₂-BTBTO_{x4}) in CDCl₃.

5.15 NMR Spectra of POC_{z2}-BTBTO_{x4}

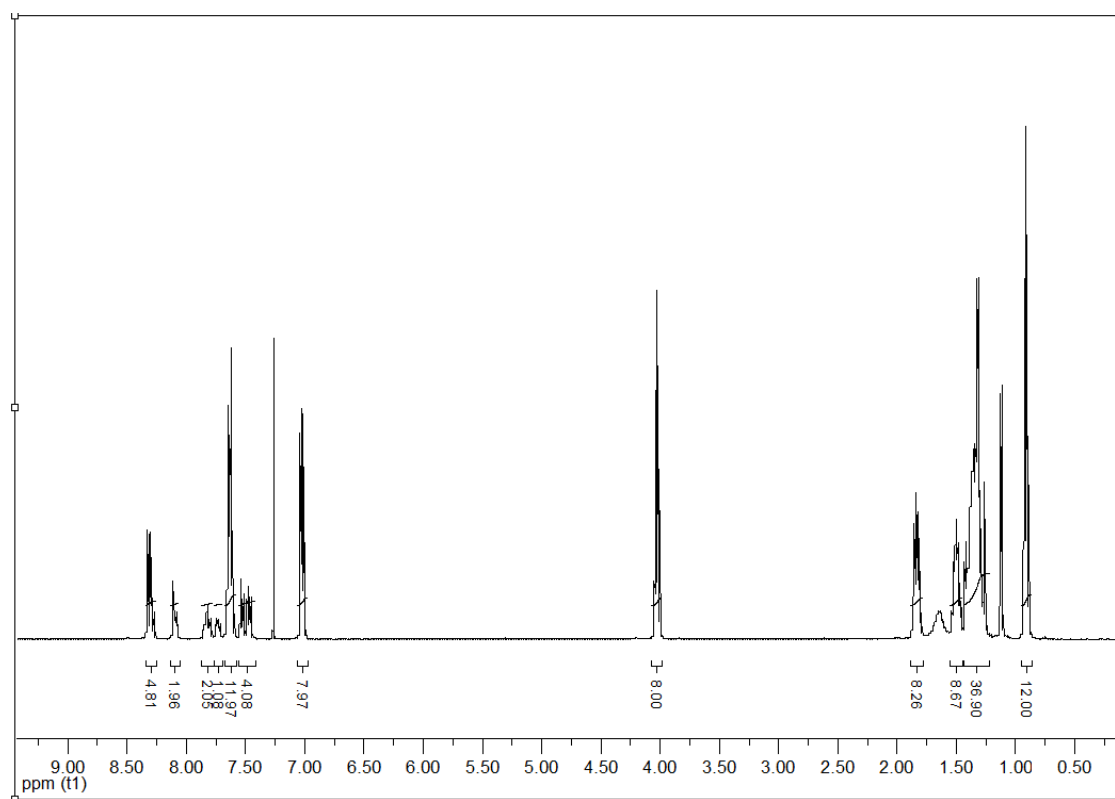


Figure 71. ¹H NMR spectrum of 2,7-Bis(3,6-bis(4-octyloxy)phenyl-9H-carbazol-9-yl)[1]benzothieno[3,2-d]benzothiophene-5,5,10,10-tetraoxide (POC_{z2}-BTBTO_{x4}) in CDCl₃.

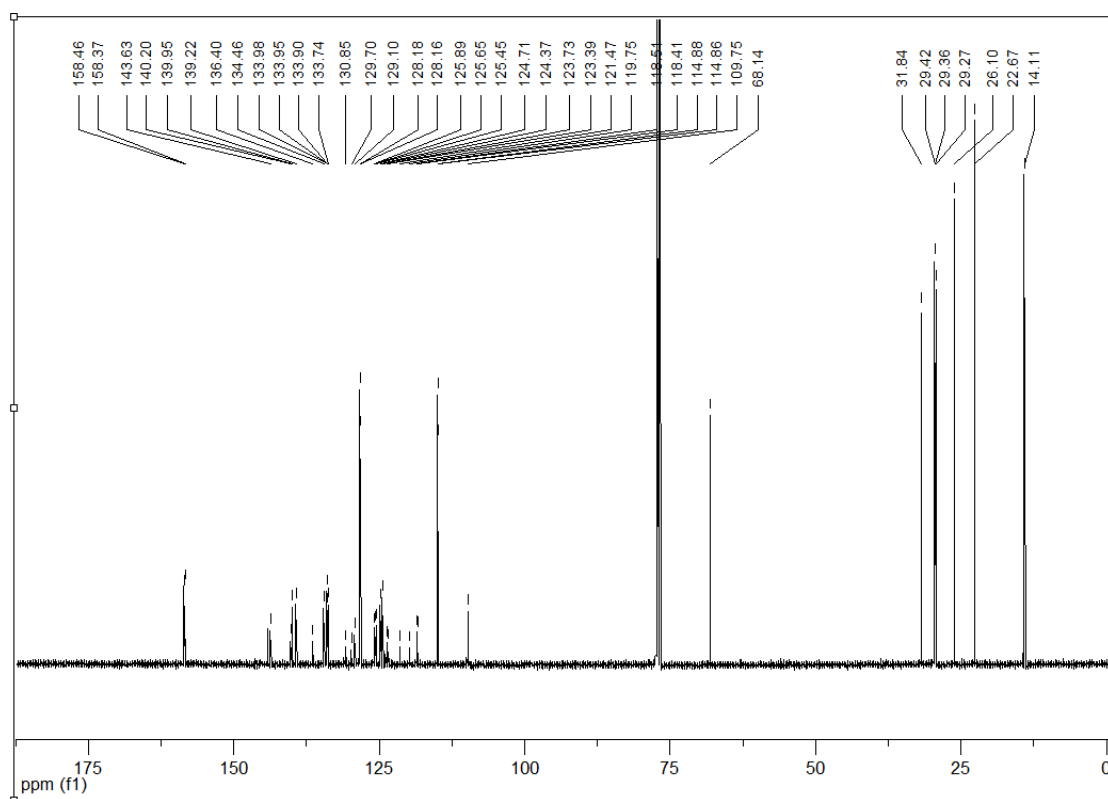


Figure 72. ^{13}C NMR spectrum of 2,7-Bis(3,6-bis(4-octyloxy)phenyl-9H-carbazol-9yl)[1]benzothieno[3,2-d]benzothiophene-5,5,10,10-tetraoxide (POCz₂-BTBTOn) in CDCl_3 .

5.16 NMR Spectra of MPA₂-BTBT

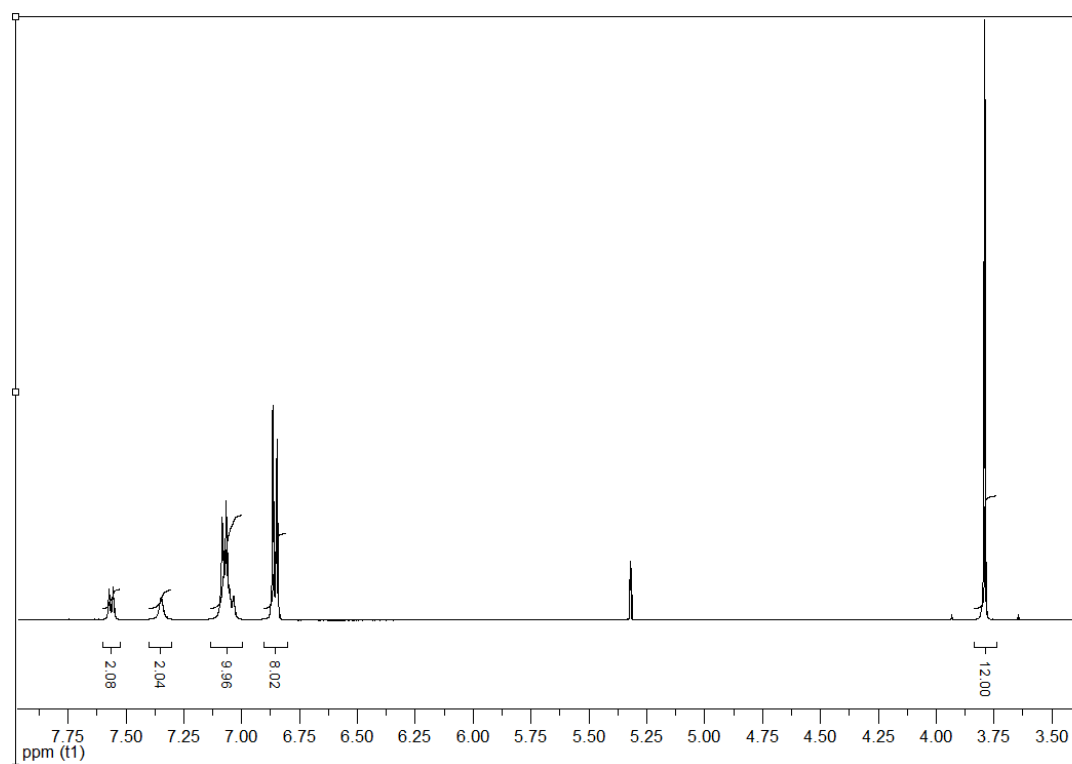


Figure 73. ^1H NMR spectrum of 2,7-Bis(bis(4-methoxyphenyl)amino)-[1]benzothieno-[3,2-d]benzothiophene (MPA₂-BTBT) in CDCl_3 .

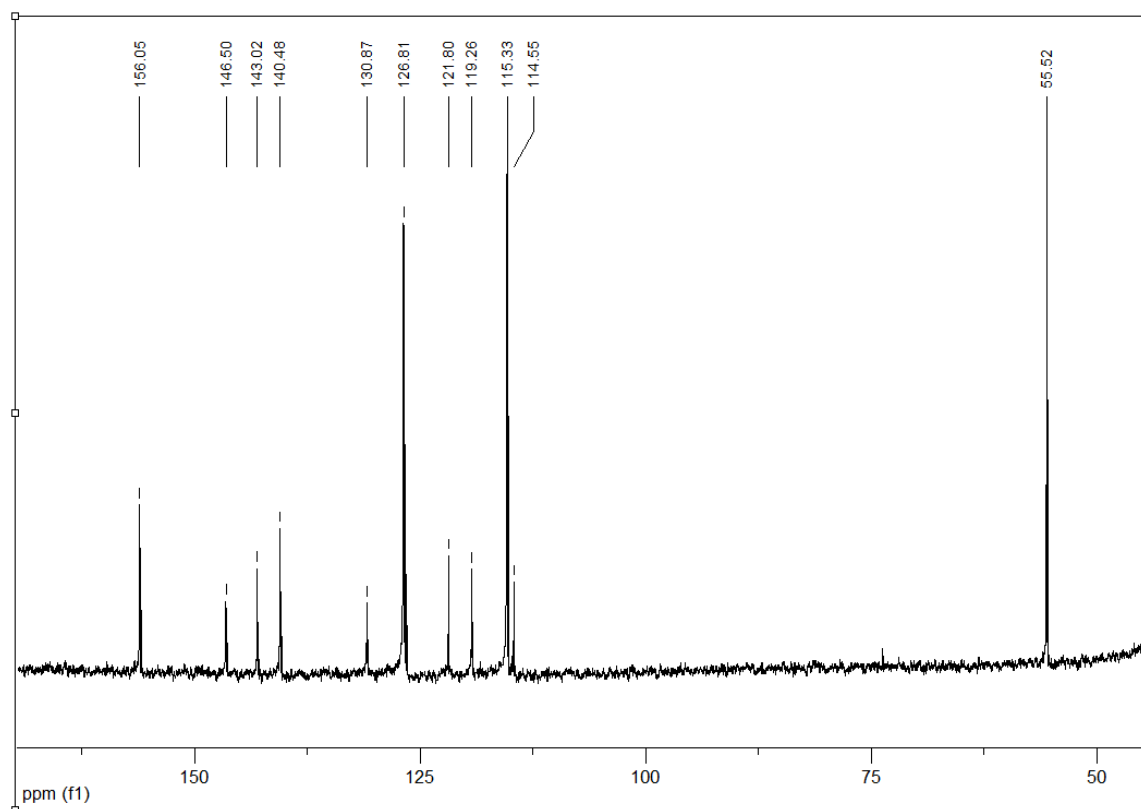


Figure 74. ^{13}C NMR spectrum of 2,7-Bis(bis(4-methoxyphenyl)amino)-[1]benzothieno[3,2-d]benzothiophene-5,5,10,10-tetraoxide (MPA₂-BTBT) in CDCl_3 .

5.17 NMR Spectra of POC_{z2}-BTBT

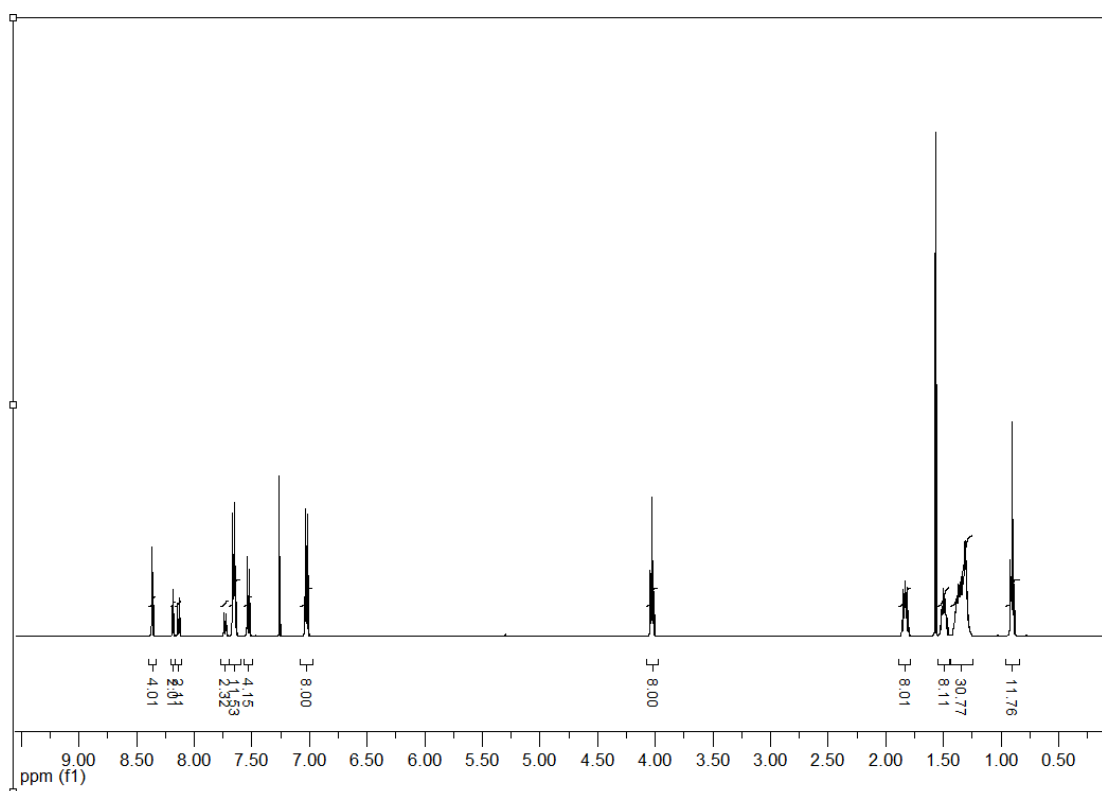


Figure 75. ^1H NMR spectrum of 2,7-Bis(3,6-bis(4-octyloxy)phenyl-9H-carbazol-9-yl)[1]benzothieno[3,2-d]benzothiophene (POC_{z2}-BTBT) in CDCl_3 .

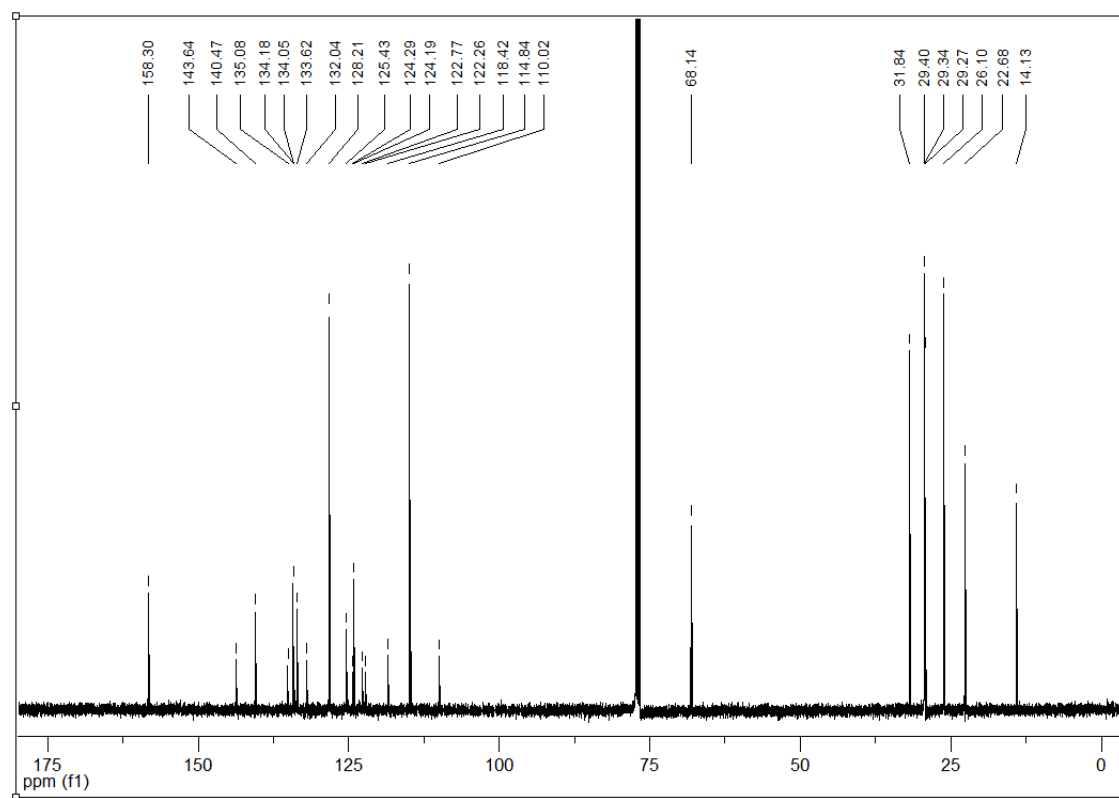


Figure 76. ^{13}C NMR spectrum of 2,7-Bis(3,6-bis(4-octyloxy)phenyl-9H-carbazol-9-yl)[1]benzothieno[3,2-d]benzotriphene-5,5,10,10-tetraoxide (POCz₂-BTBT) in CDCl₃.

5.18 Cyclic Voltammetry of MPA₂-BTBTO_{x4}, PTz₂-BTBTO_{x4} and POCz₂-BTBTO_{x4}

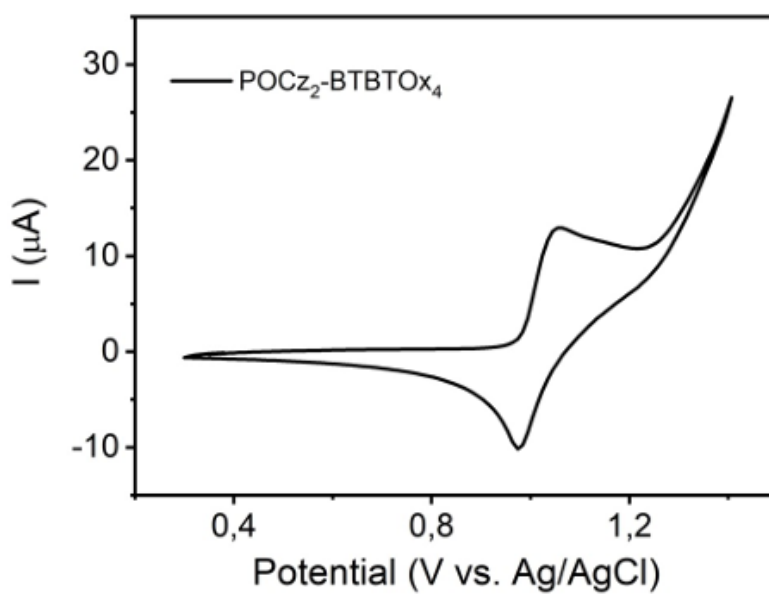


Figure 77. CV curve of POCz₂-BTBTO_{x4}.

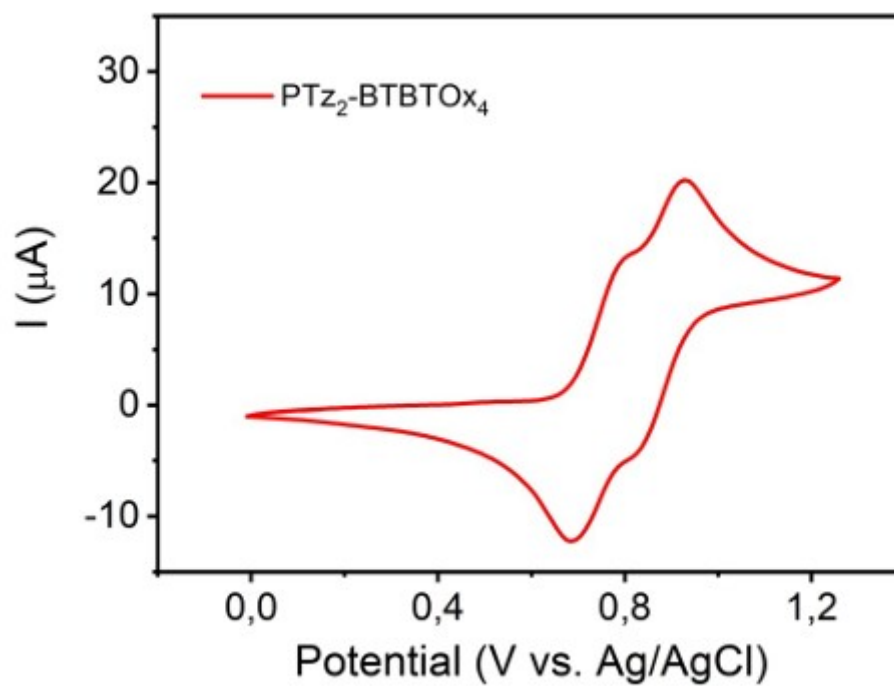


Figure 78. CV curve of PTz₂-BTBTOx₄.

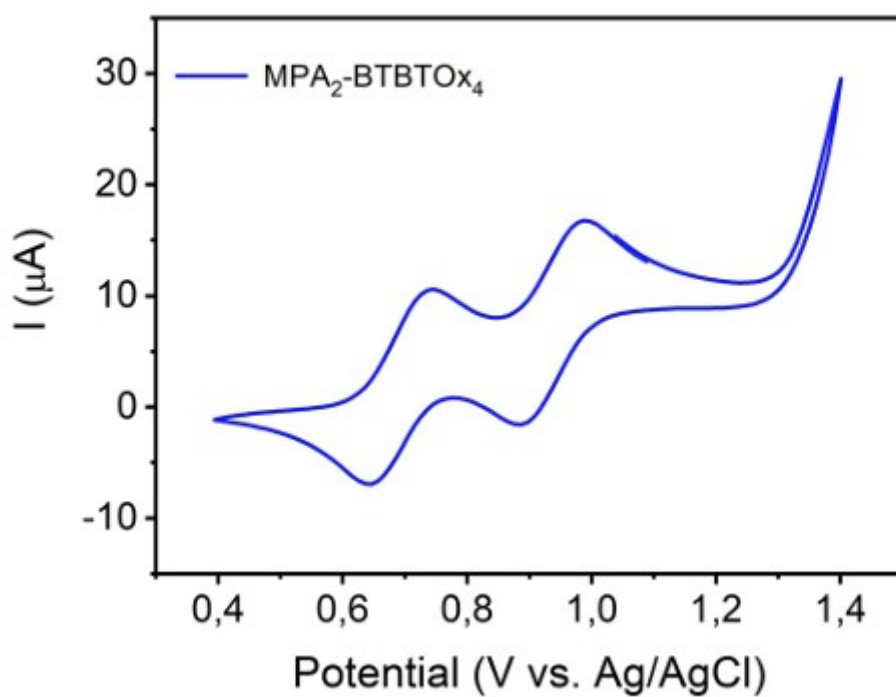


Figure 79. CV curve of MPA₂-BTBTOx₄.

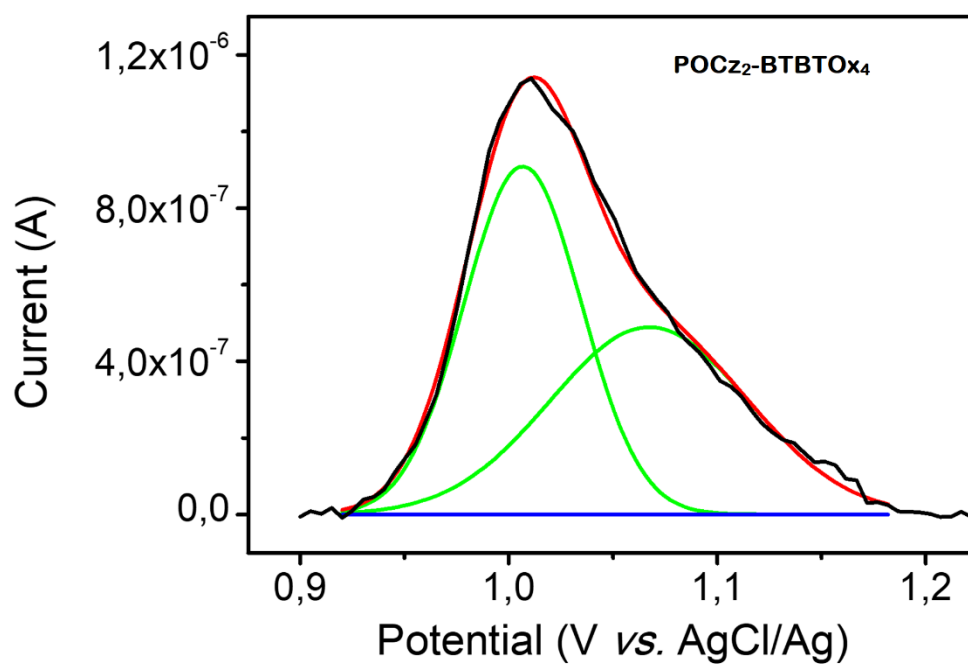


Figure 80. DPV of POCz₂-BTBTO_{x4}. Solvent CH₂Cl₂, supporting electrolyte 0.1 M TBAPF₆. DPV conditions: modulation amplitude, 0.5 eV; modulation time, 0.05 s; interval time (Δt), 0.5 s, step potential (E_{step}), 0.005 V; scan rate, $v = E_{\text{step}}/\Delta t$, 0.01 V s⁻¹.

5.19 Crystallographic Data of PTz₂-BTBTO_{x4}, MPA₂-BTBTO_{x4}, POCz₂-BTBTO_{x4}

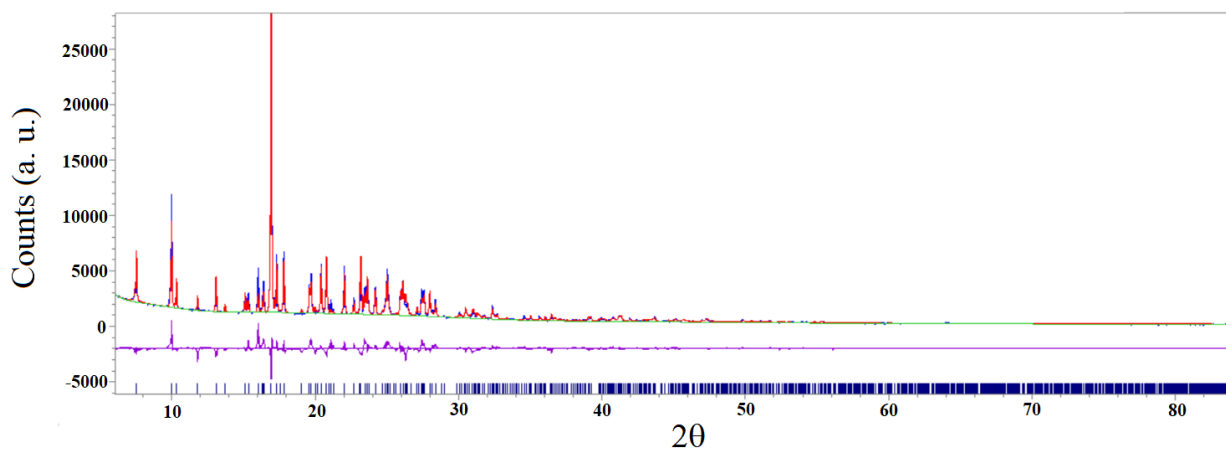


Figure 81. XRPD pattern of MPA₂-BTBTO_{x4}.

Table 17. MPA₂-BTBTO_x: Crystal data, data collection and structure refinement details.

<i>Crystal data</i>	
Chemical formula	C ₂₁ H ₁₇ NO ₄ S
M_r	379.43
Crystal system, space group	Monoclinic, $P2_1/c$
Temperature (K)	293
a, b, c (Å)	11.9830 (18), 13.525 (2), 11.2863 (17)
β (°)	101.538 (3)
V (Å ³)	1792.2 (5)
Z	4
Radiation type	Cu $K\alpha_1$
<i>Data collection</i>	
Diffractometer	Rigaku RINT2500 Powder X Ray Diffractometer
Specimen mounting	Lindemann glass capillary
Data collection mode	Transmission
2 θ values (°)	$2\theta_{\min} = 6.00$ $2\theta_{\max} = 84.24$ $2\theta_{\text{step}} = 0.02$
<i>Structure solution by SA</i>	
No. internal DOF	6
No. external DOF	7
No. used reflections (Res, Å)	233 (2.0)
Cost function:	R_{wp}
No. SA runs	20
<i>Rietveld Refinement</i>	
R factors	$R_p = 0.065$, $R_{\text{wp}} = 0.096$, $R_{\text{exp}} = 0.033$, $R_{\text{Bragg}} = 0.168$
No. data points	3913
No. experimental reflections	1244
No. of parameters	117
H-atom treatment	H-atom parameters constrained
<i>Computer programs</i>	
<i>EXPO</i> [2]	Indexing, Space group determination, Structure solution (Direct Methods and Simulated Annealing), Rietveld refinement
ChemSketch [10]	Model building
Mercury [19]	Molecular graphics
CrystalExplorer [18]	Hirshfeld surface generation
CheckCIF [20]	CIF validation
publCIF [21]	Preparation of material for publication

5.20 DFT Calculations on MPA₂-BTBTO_{x4}, PTZ₂-BTBTO_{x4} and POCZ₂-BTBTO_{x4}

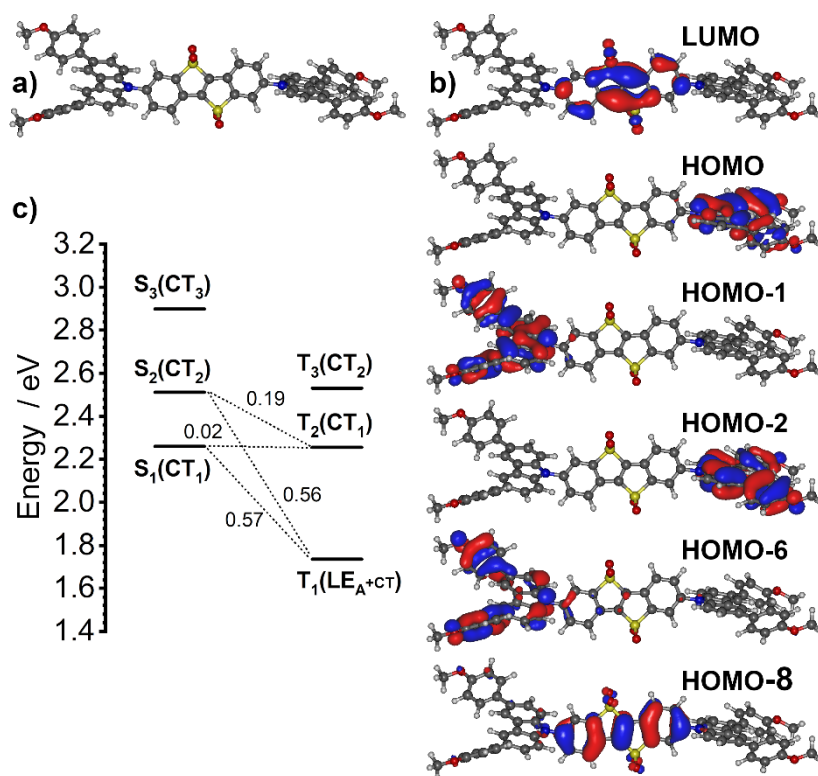


Figure 82. TD-DFT results for POCZ₂-BTBTO_{x4} at S1 geometry: a) Structure in the S1 state; b) isosurfaces of the relevant molecular orbitals; c) excited state energy diagram with the orbital character of each of the excited states; the values and dotted lines represent SOCME in cm⁻¹ between the indicated states.

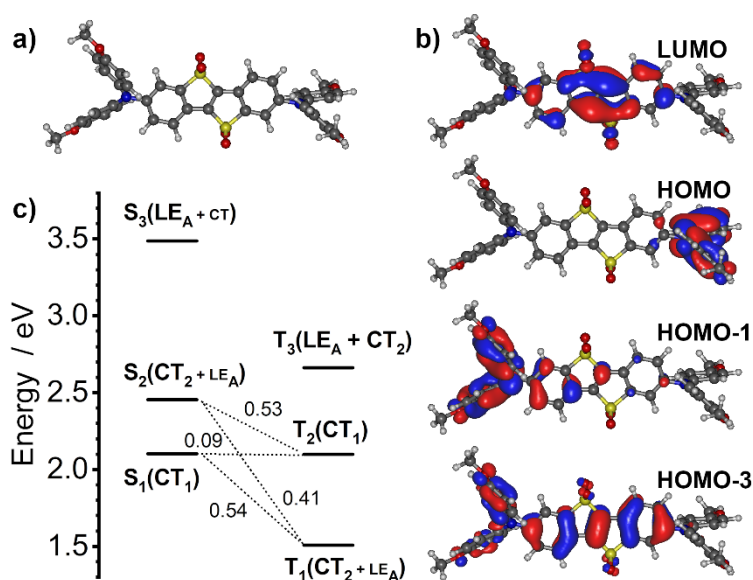


Figure 83. TD-DFT calculations for MPA₂-BTBTO_{x4} at S1 geometry: a) Structure in the S1 state; b) isosurfaces of the relevant molecular orbitals; c) excited state energy diagram with the orbital character of each of the excited states; the values and dotted lines represent SOCME in cm⁻¹ between the indicated states.

Table 18. Orbital pairing of the lowest excited states at the S1 geometry for POCz₂-BTBTO_{x4}, PTz₂-BTBTO_{x4} and MPA₂-BTBTO_{x4}.

POCz₂-BTBTO_{x4}			
State	Energy, eV	Assignment	Orbital pairing
S ₁	2.260	CT ₁	HOMO→LUMO (93%)
S ₂	2.511	CT ₂	HOMO-1→LUMO (87%)
S ₃	2.898	CT ₃	HOMO-2→LUMO (92%)
T ₁	1.735	LE _A + CT	HOMO-8→LUMO (76%), HOMO-6→LUMO (10%)
T ₂	2.255	CT ₁	HOMO→LUMO (93%)
T ₃	2.530	CT ₂	HOMO-1→LUMO (85%)
PTz₂-BTBTO_{x4}			
State	Energy, eV	Assignment	Orbital pairing
S ₁	1.817	CT ₁	HOMO→LUMO (94%)
S ₂	2.371	CT ₂	HOMO-1→LUMO (92%)
S ₃	3.021	LE _A	HOMO-4→LUMO (93%)
T ₁	1.745	CT ₁	HOMO-4→LUMO (90%)
T ₂	1.811	CT ₂	HOMO→LUMO (94%)
T ₃	2.365	LE _A	HOMO-1→LUMO (92%)
MPA₂-BTBTO_{x4}			
State	Energy, eV	Assignment	Orbital pairing
S ₁	2.102	CT ₁	HOMO→LUMO (92%)
S ₂	2.456	CT ₂ + LE _A	HOMO-1→LUMO (82%), HOMO-3→LUMO (10%)
S ₃	3.487	LE _A + CT	HOMO-3→LUMO (68%)
T ₁	1.509	CT ₂ + LE _A	HOMO-1→LUMO (51%), HOMO-3→LUMO (36%)
T ₂	2.100	CT ₁	HOMO→LUMO (87%)
T ₃	2.663	LE _A + CT ₂	HOMO-3→LUMO (36%), HOMO-1→LUMO (25%)

5.21 DFT Calculations on PTz₂-BTBT, MPA₂-BTBT, POCz₂-BTBT and MPA₂-BTBT_{Ox}₄, PTz₂-BTBT_{Ox}₄ and POCz₂-BTBT_{Ox}₄

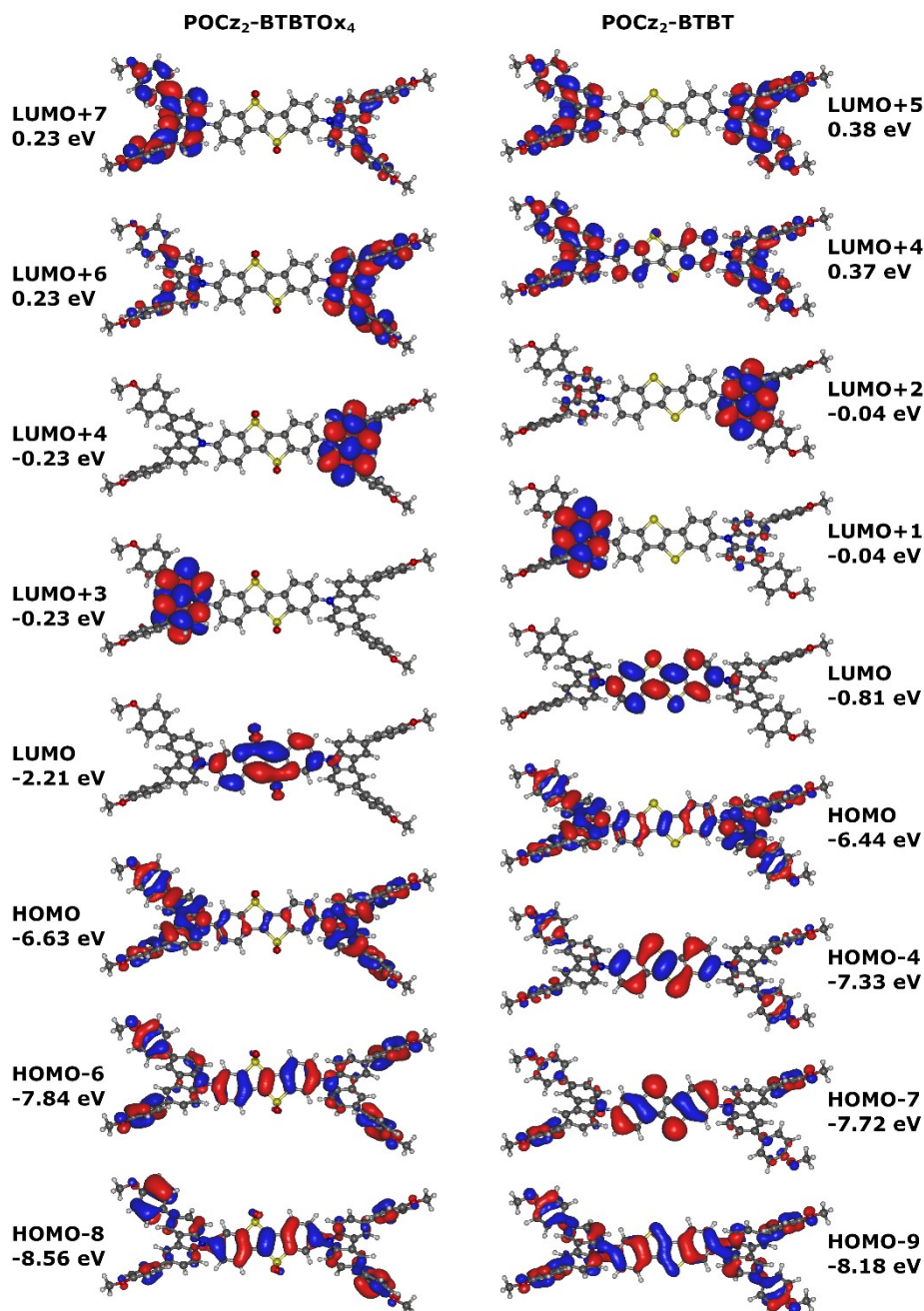


Figure 84. Selected molecular orbital iso-surfaces for POCz₂-BTBT_{Ox}₄ and POCz₂-BTBT at the S₀ geometry. Iso-value 0.02.

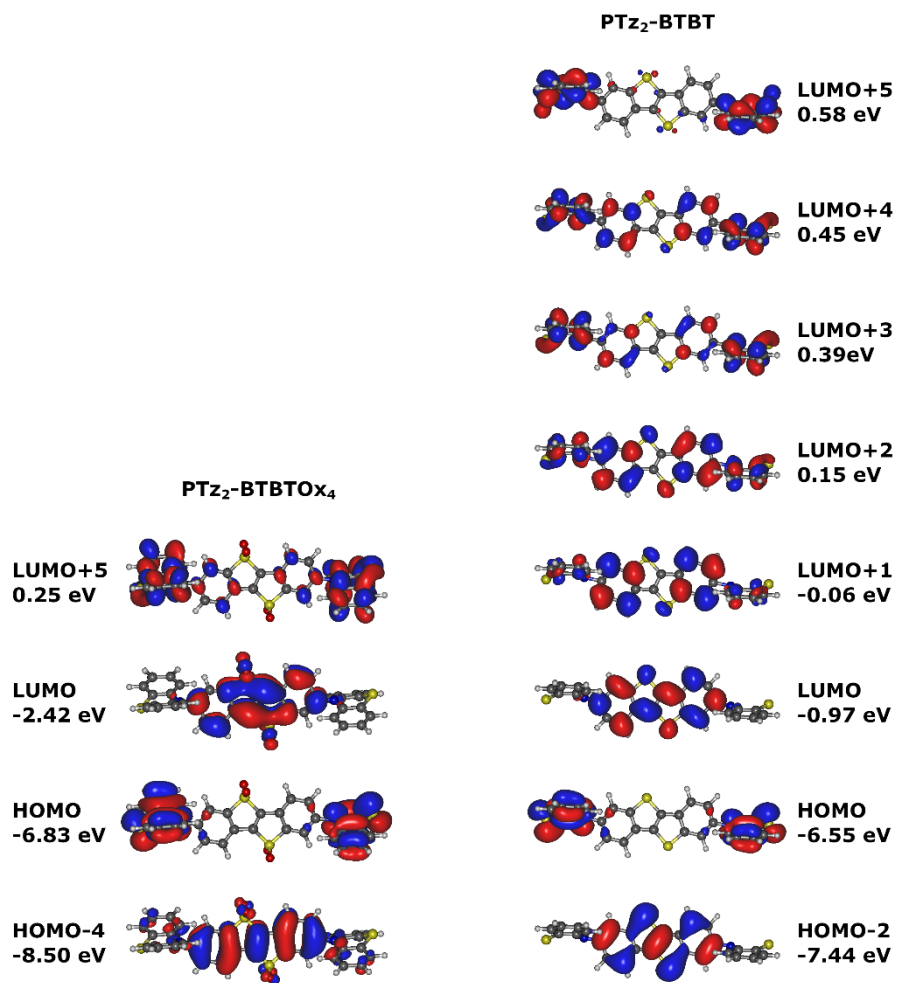


Figure 85. Selected molecular orbital iso-surfaces for PTz₂-BTBTOx₄ and PTz₂-BTBT at the S₀ geometry. Iso-value 0.02.

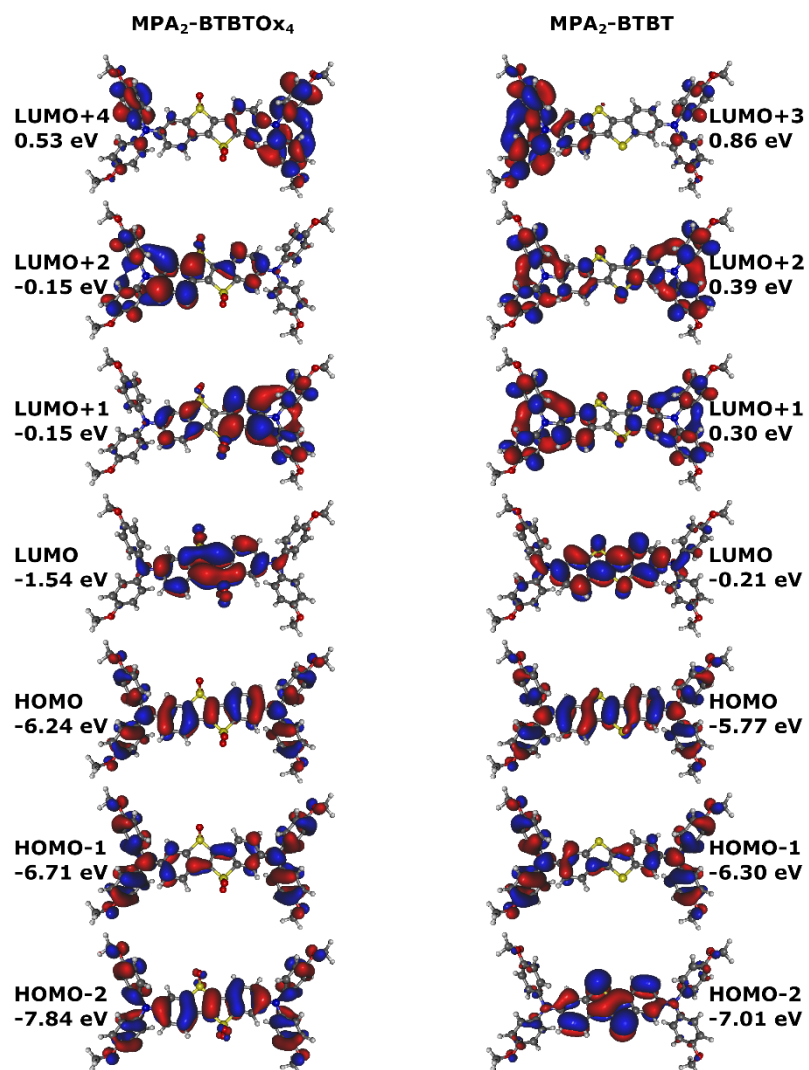


Figure 86. Selected molecular orbital iso-surfaces for MPA₂-BTBTOx₄ and MPA₂-BTBT at the S₀ geometry. Iso-value 0.02.

5.22 Photophysical Data of MPA₂-BTBTO_{x4}, PTz₂-BTBTO_{x4} and POCz₂-BTBTO_{x4}

Table 19. Maximum absorption and emission wavelengths for MPA₂-BTBTO_{x4}, PTz₂-BTBTO_{x4} and POCz₂-BTBTO_{x4} in CH, Tol, DCM and Zeonex. (In bold the most intense absorption and emission peaks).

Absorption (λ_{max} , nm)				Emission (λ_{max} , nm)				
	CH	Tol	DCM	CH	Tol	DCM	0.1%wt Zeonex	0.1%wt PMMA
POCz₂-BTBTO_{x4}	286, 347(s) 411	289, 345(s), 421	295, 348(s), 422	393, 469(s), 492	395, 512	397, 595	386,476, 497	500
PTz₂-BTBTO_{x4}	256,336, 392	337,398	258,339, 407	463(s), 548(s), 577	491, 655	449(s), 528	478,495, 547	490
MPA₂-BTBTO_{x4}	233(s), 247,290, 372,448	294, 373, 454	292,372, 457	509, 534(s)	550, 619(s)	600, 712(s)	515,546	550

s = denotes a shoulder instead of a maximum.

Table 20. Photoluminescence quantum yields.

PTz₂-BTBTO_{x4} In Zeonex	%Φ_{PL} air/deox	$\Phi_{\text{PL}}^{\text{air}} / \Phi_{\text{PL}}^{\text{deox}}$
0.1%wt	9.7/27.6	2.8
1%wt	7.6/13.0	1.7
5%wt	8.1/13.8	1.7

air = in aerated conditions; deox = deoxygenated conditions.

CHAPTER VI

Conclusion

In this doctoral work, two classes of new organic functional materials were designed, synthesized, and characterized with the aim of developing functional systems for energy-related applications: BTBT/BTBTO₄-based molecules and Croconaines.

Firstly, three novel luminescent donor–acceptor–donor (D–A–D) molecules based on the [1]benzothieno[3,2-b]benzothiophene-tetraoxide (BTBTO₄) core were successfully synthesized via the microwave-assisted Buchwald–Hartwig reaction. The new compounds PTZ₂-BTBTO₄, MPA₂-BTBTO₄, and POCZ₂-BTBTO₄ were investigated through a combination of structural, electrical and photophysical techniques, including cyclic voltammetry, X-ray diffraction, UV–vis absorption, and steady-state and time-resolved photoluminescence spectroscopy. All three emitters showed high electrochemical stability and thermally activated delayed fluorescence (TADF) property. Among them, POCZ₂-BTBTO₄ exhibited the lowest self-quenching and the best photoluminescence quantum yield in neat films, making it a promising candidate for self-hosted OLED applications. The results demonstrated the potential of BTBTO₄ as a versatile acceptor unit for the development of printable, solution-processed organic light-emitting materials.

In parallel, the study focused also on molecules based on the BTBT core, with design and synthesis of three new D–A–D molecules, which are the analogous to the BTBTO₄-derivatives, obtained using the same donor units. This larger family of D–A–D molecules was explored by combining experimental and theoretical approaches. Dark-MIS-CELIV measurements revealed an ambipolar charge transport behavior for BTBTO₄-based materials, with a significant p-doping effect, enhancing intrinsic conductivity and suggesting their potential use as dopant-free hole-transporting materials in optoelectronic devices. Conversely, BTBT-based systems exhibited unipolar hole transport with higher mobilities, while MPA₂-BTBT maintained ambipolar characteristics. These results highlight how tuning donor and acceptor combinations can modulate charge transport properties, paving the way for the rational design of high-performance organic semiconductors.

Finally, a new composite organic material, PLA@CR-BI, was developed by incorporating a benzoindolenine-based croconaine dye (CR-BI) into a polylactic acid (PLA) matrix. The design of this composite was guided by the search for an effective photothermal-responsive additive capable of improving the thermal behavior of PLA without compromising its intrinsic properties. The strong affinity between CR-BI molecules and PLA chains led to a homogeneous solid solution, ensuring a uniform distribution of the additive within the polymer matrix in the solid state. Thermal analyses (TGA and DSC) confirmed that the addition of CR-BI does not affect the thermal stability of PLA, while it enhances chain mobility and promotes the formation of more ordered structures, improving the material's ability to store and dissipate thermal energy. Notably, even at only 1% CR-BI, the composite exhibited an over 3.5-fold increase in both thermal conductivity and diffusivity compared to pristine PLA. Electrical measurements showed that the PLA matrix retains its insulating character, demonstrating that CR-BI selectively improves thermal properties without altering electrical insulating

characteristics. These findings identify PLA@CR-BI as a promising photothermal-responsive material with enhanced thermal management capability and preserved mechanical properties, suitable for energy storage and energy saving applications.

Overall, the outcomes of this research contribute to advancing the understanding and design of new functional organic materials with tailored optoelectronic and thermal properties. The different systems developed, luminescent D–A–D emitters, ambipolar charge-transporting materials, and photothermally active composites, represent complementary approaches toward more efficient, sustainable, and multifunctional materials for next-generation energy technologies.

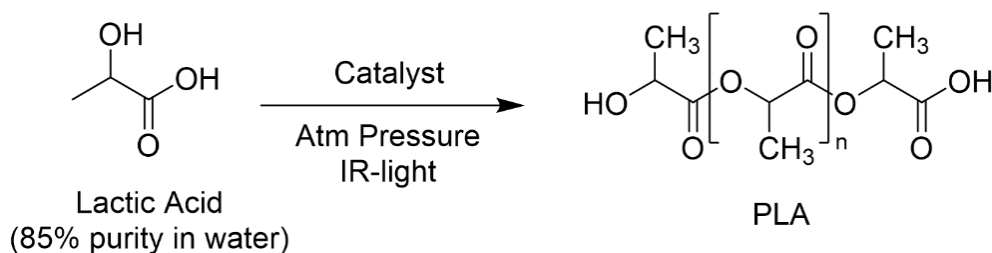
CHAPTER VII

Future Perspectives

The PhD work will be further developed along several complementary research lines. In particular, new molecules belonging to the benzothieno[3,2-b][1]benzothiophene (BTBT) derivative class, both in their oxidized and neutral forms, will be tested as active components in electrochromic devices, with the aim of expanding the potential applications of the studied materials and gaining a deeper understanding of their behavior in advanced optoelectronic systems.

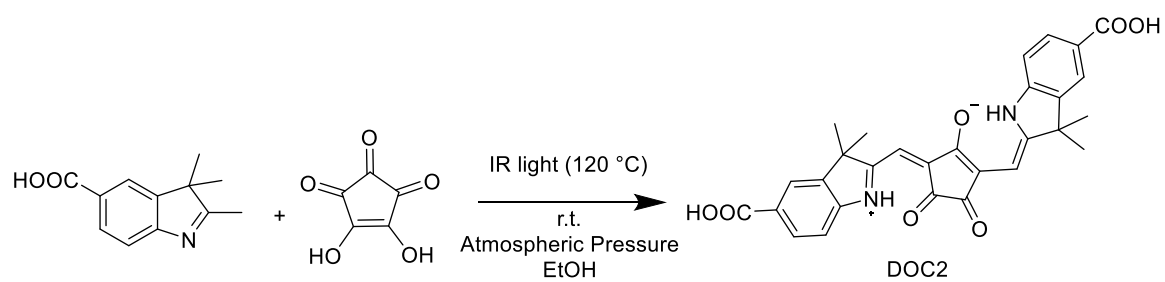
As a natural continuation of the activities carried out during the doctoral program, and within the framework of the current research fellowship, relating to the PERCIVAL project, the PLA@CR-BI composite films obtained will be employed as supports for solid–liquid organic phase change materials (PCMs).

Moreover, in parallel with the research activities carried out during the PhD program, an additional study was conducted to develop sustainable reaction conditions for the synthesis of polylactic acid (PLA) and more generally lactic acid (AL) derivatives. In this context, the conventional reaction conditions, involving high temperatures, vacuum environment, the use of organic solvents, and toxic catalysts, were replaced with more sustainable and environmentally friendly approaches. A direct polycondensation methodology was optimized, based on a condensation reaction employing an alternative heat source (IR light), water-tolerant metal catalysts, and solvent-free conditions (Scheme 5). This approach enabled the synthesis of lactic acid oligomers and polymers with different molecular weights and, consequently, distinct melting points. Among these products, the oligomers obtained as a white solid, exhibiting a melting point in the range of 50–70 °C, will be investigated as a potential organic phase change material (PCM).



Scheme 5. Scheme of sustainable Polycondensation reaction.

Finally, a croconine containing acidic functional groups (labelled as DOC 2) was synthesized, according to the synthesis procedure described for CR-BI in the “Experimental Part”. DOC2 was then reacted with $\text{Zn}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ for the preparation of a new molecular structure (Scheme 6). A preliminary chemical-physical analysis has already been performed, while future investigations will focus on detailed structural characterisation to assess the porosity and potential functional properties of the material.



Scheme 6. Schematic reaction of DOC2.

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