



Derivatives of diphenylamine and benzothiadiazole in optoelectronic applications: a review

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Abstract

Light-emitting conjugated organic compounds have found special interest among researchers. Because of their adjustable optoelectronic properties they can be applied in e.g. field-effect transistors, sensors, light-emitting diodes or photovoltaic cells. In order to develop high-performance systems, it is important to understand the relationship between the structure and the photophysical properties of the material used. One of the employed strategies is to decrease the band gap of conjugated compounds, often achieved through a “donor–acceptor” approach. One of the popular groups applied as an electron-accepting unit are benzothiadiazoles, while diphenylamine exhibits good electron-donating ability. The functional groups can affect the energy levels of materials, influencing the color of the light emitted. This work presents a review of research focused on the structure-properties relationship of diphenylamine and benzothiadiazole derivatives with optoelectronic applications.

Keywords Diphenylamine derivatives · Benzothiadiazole derivatives · Optoelectronics · Organic semiconductor · Donor–acceptor polymer

Introduction

Conjugated organic compounds, due to their tunable optical and electronic properties, have become promising materials for applications in devices such as field effect transistors [1–3], photovoltaic cells [4–8], light-emitting diodes [9–13], sensors [14–16], and others. Understanding the relationship between the structure and optoelectronic properties of organic semiconductors is essential when designing the architecture of the above-mentioned devices in order to achieve their optimal parameters, including high efficiency [17]. The most advantageous solution in optoelectronics design strategies is a “donor–acceptor” (D-A) or “push–pull” structural motif in organic semiconductors, due to the ability to control the band gap width [18–20]. So far, various groups of donors, acceptors, and π bridges have been combined in the research, e.g. diphenylamine (DPA), carbazole, and benzothiadiazole (BTD) groups, which serve as D-A electron pairs, and benzene and thiophene rings act as π bridges. Benzothiadiazoles

are a popular electron-accepting unit in D-A copolymers, especially with non-functionalized or functionalized oligothiophene units, that also exhibit electrochromic and electrofluorochromic effects [21]. 2,1,3-benzothiadiazole derivatives are promising candidates for efficient solid-state emitters due to their strong electron-withdrawing effect, highly polarized properties, and easy crystallinity [22–24]. On the other hand, diphenylamine groups, due to the lone pair of electrons in nitrogen, have a high electron donation ability, thanks to which these derivatives are widely used in optoelectronics [25–30]. DPA as an electron donor increases the HOMO energy, while the use of an electron acceptor unit (e.g. BTD) can lead to a decrease in both HOMO/LUMO (HOMO-Highest Occupied Molecular Orbital; LUMO-Lowest Unoccupied Molecular Orbital). For this reason, with the help of individual units in the structure of the entire semiconductor system, we can manipulate the ground state energy level in materials and thus influence the color of the emitted light and the mobility of electrons/holes.

Organic chemistry deals with the synthesis of polymers used in widely understood consumer electronics. The electronics market is growing steadily, and its most promising area is OLEDs (organic light-emitting diodes). Their commercialization is displacing standard displays and they are considered excellent candidates for new lighting technology.

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The structural core of such diodes is the emission layer. It determines the color that will be emitted and the light flux. In addition, the electrode contains a transparent anode and a metal cathode, a hole injection layer, a hole transport layer, an electron transport layer, and an electron injection layer [31]. The disadvantage of OLEDs is the low external quantum efficiency of 20–25% [32], so reducing the amount of light trapped inside the device is a task for future years of optoelectronics research.

This review provides an overview of the diphenylamine and benzothiadiazole derivatives that have been reported over the past decade and focuses primarily on the dependence of the physicochemical properties on the structure of the above-mentioned systems. The work concerns compounds that have been used mainly in optoelectronic devices due to their properties.

Diphenylamine derivatives

The use of diphenylamine (Fig. 1) has been the subject of much research aimed at using it and its derivatives for modern biosensors and optoelectronic devices. Previous reports confirm many properties of DPA derivatives that account for their use in optoelectronics. Diphenylamine is a rigidly structured compound, which increases its solubility in organic solvents. It is also thermally stable. DPA, as an electron donor unit, is combined in many experiments with various electron acceptors, thanks to which the resulting structures show fluorescence and non-linear optical properties. Electron transport in chemistry is extremely important, so DPA is an ideal candidate for the synthesis of optoelectronic materials [33].

Structure modifications in the design strategy of conjugated polymer materials

The design strategy of conjugated polymer materials with a narrow band gap should focus on an appropriate molecular energy level of the compounds, an effective π -conjugated system, a good coplanar backbone structure, good solubility, etc.

Obtaining a low-energy gap is a challenge during the synthesis of DPA derivatives. The relevance of such compounds

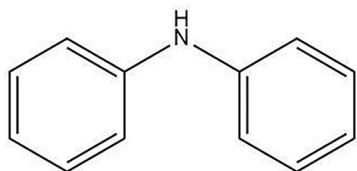


Fig. 1 Structure of diphenylamine [33]

is extremely important in charge transfer from the donor side to the acceptor side.

Researchers at the Vellore Institute of Technology [33] synthesized three donor–acceptor molecules (DPA-PA) based on Knoevenagel condensation. In the reactions, the electron donor was DPA and the acceptors were pyridine-acetonitrile (PA) groups. The DPA-PA-1, DPA-PA-2, and DPA-PA-3 molecules (Fig. 2) were obtained with yields of 75%, 70%, and 73%, respectively. The compounds exhibited excellent solubility in toluene, dichloromethane, and tetrahydrofuran, and a low band gap, which was 1.8 eV for DPA-PA-3 and 1.9 eV for DPA-PA-1 and DPA-PA-2 (Fig. 2) [33].

Also important for optoelectronic studies are the cyano-vinylene bonds formed in compounds DPA-PA 1–3 (Fig. 2) [33], which increased the flexibility of energy levels and improved optoelectronic properties. They were confirmed by the FTIR spectrum with a peak of 2215 cm^{-1} , and a singlet of 8.3 ppm in $^1\text{H NMR}$. The properties of these bonds were also noticed by Iqbal and his team [34]. In this study, they described the properties of a small D-A molecule, a DPA derivative (M-3) (Fig. 3). Because the system was strongly conjugated, it exhibited a high degree of polarity in the ground state. A lower band gap of 2.0 eV was achieved, compared to compounds presented in Fig. 2 [34]. Furthermore, the electron distribution in the HOMO orbital is uniform, which translates to a uniform distribution of hole density in both the excited molecule and the charge-separated hole carrier. The energy of this orbital is high (-5.08 eV) due to the presence of methoxy groups [34].

A higher but still satisfactory calculated band gap value was obtained by Bella et al. [35] in compound BT-3 (Fig. 4C). Due to the HOMO–LUMO energy gap of 3.29 eV, it is also an excellent candidate for optoelectronics applications.

In addition, the compounds studied by the team of Bella et al. [35], whose biphenyl group was replaced by a bipyrrrole group (Fig. 5), exhibited a wide bandgap, which is a desirable feature for use as a supercapacitor electrode. They were classified as promising compounds in this field. Each of the mixed-valence compounds studied by Bella

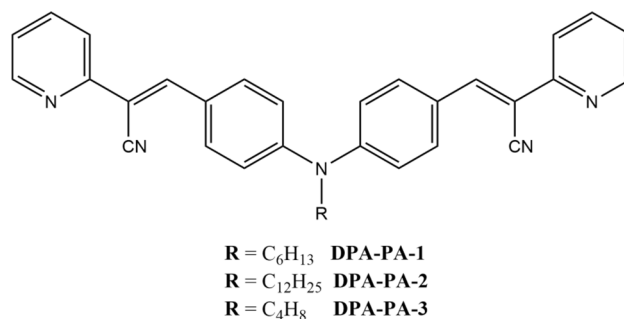


Fig. 2 Chemical structure of DPA-PA compounds [33]

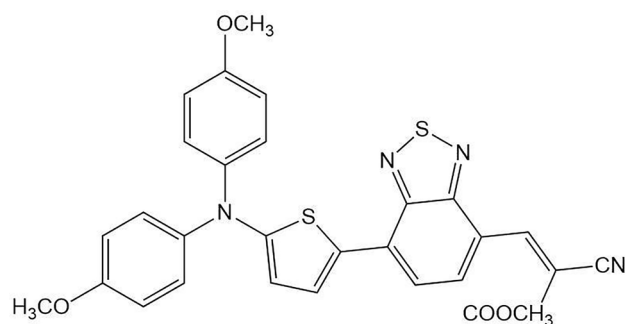


Fig. 3 Chemical structure of M-3 [34]

et al. [35] exhibited good electron delocalization and high redox potential values, which is important for optoelectronic applications.

Bella et al. [35] investigated a total of 12 valence compounds based on DPA, whose optoelectronic properties were confirmed by density functional theory (DFT) and time-dependent density functional theory (TD-DFT) methods. The calculated C–C bond lengths in the range of 1.38–1.4 Å

suggest that the discussed compounds exhibit excellent delocalization of π electrons in the molecules. An important discovery was the results of FMO (Frontier Molecular Orbital) analysis, which showed effective stabilization of HOMO and LUMO by the donor and acceptor, respectively. (Fig. 6).

The FMO also confirmed the photophysical properties of bithiophene-substituted compounds (Fig. 4; BT-1, BT-2, and BT-3), which show higher absorption, the lowest HOMO–LUMO energy gap, and higher wavelength of maximum absorption (λ_{\max}) compared to other π -acceptors (Fig. 6). For BT-3 λ_{\max} was 451 nm, for BT-2 – 440 nm, and for BT-1 – 430 nm. The λ_{\max} for the other compounds ranged from 345 to 397 nm. The reason for such results is that bithiophene abolishes the maximum contribution to LUMO and additionally maintains the balance between planarity and π delocalization. It allocates 83% of its LUMO to π -delocalization and outperforms other π -acceptor units in this regard.

Wang et al. [36] confirmed the strong electron-donor properties of the DPA unit in the synthesized compound SM3 (Fig. 7). The electrons of the HOMO orbital were mainly

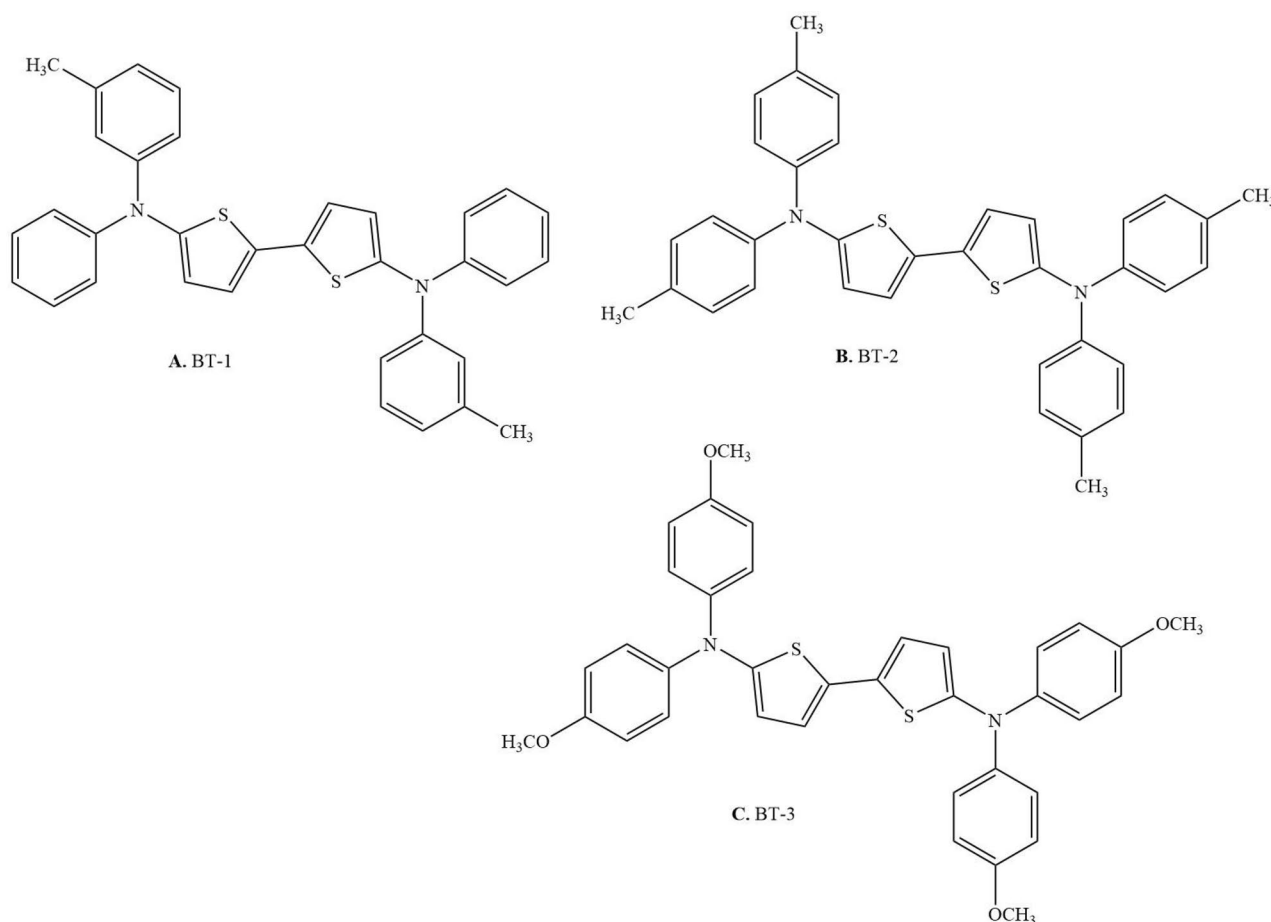


Fig. 4 Chemical structure of BT 1–3 compounds [35]

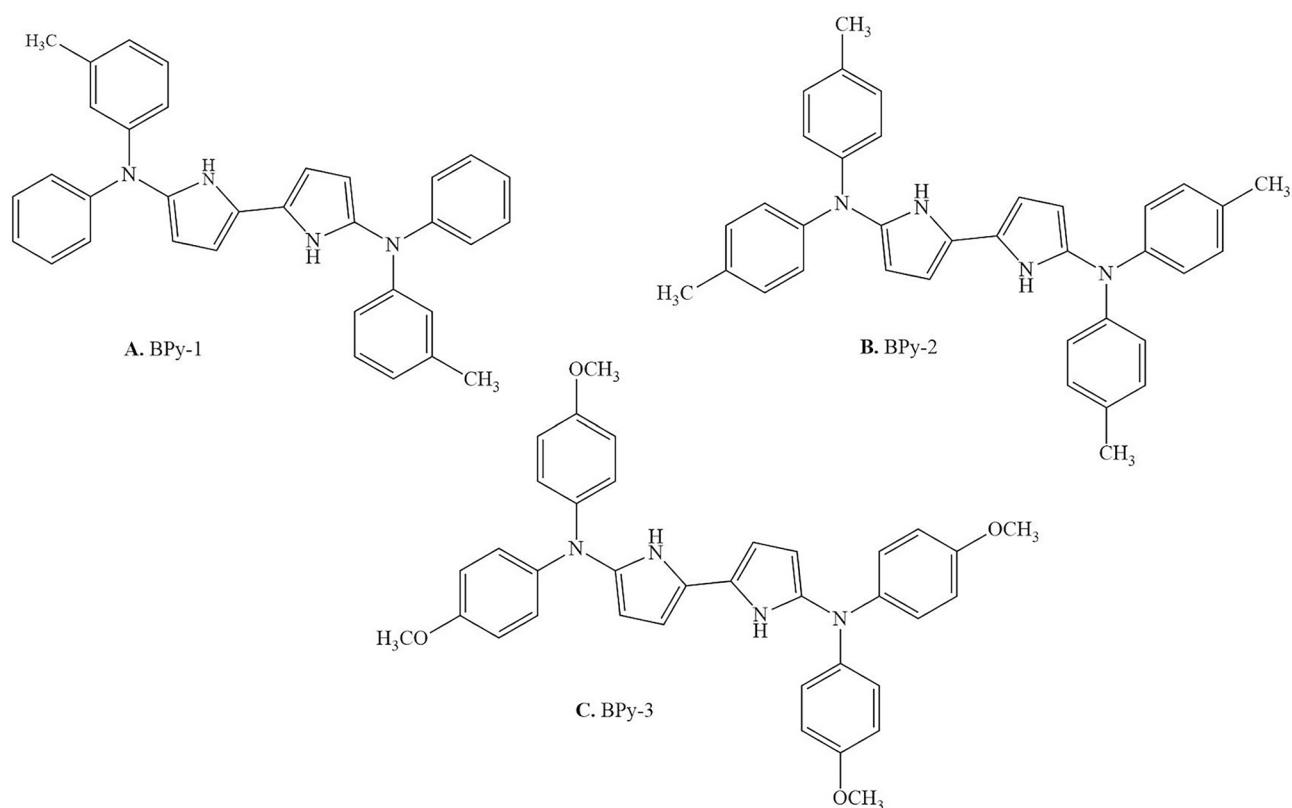


Fig. 5 Chemical structure of BPy 1–3 compounds [35]

located near the central core, while the electron cloud density of the LUMO was distributed throughout the molecule. HOMO was calculated at -5.51 eV and LUMO at -3.68 eV. These are the highest values among the tested compounds, hence the difference between them was only 1.83 eV. Due to the high value of LUMO energy, the V_{oc} (open circuit voltage) reached 0.96 V. The obtained compound is important for the construction of efficient organic solar cells (OSCs).

D-A and D-A-D type compounds (Fig. 8) developed by I. Danyliv et al. based on PFBP (per-fluorobiphenyl; acceptor) and DPA (donor) are also promising in modern OLED technology. Their synthesis was based on a one step, catalyst-free aromatic nucleophilic substitution reaction (Scheme 1) [37].

HOMO values were -5.9 eV and -5.7 eV, while LUMO values were -2.1 eV and -1.9 eV (for DPA-PFBP-A and DPA-PFBP-B, respectively). Compared to the compound SM3 (Fig. 7), the HOMO orbitals were delocalized throughout the molecule, and due to the high electronegativity of the fluorine atoms, the LUMO orbitals were mainly on the PFBP fragment [37].

Electroluminescence

Electroluminescent (EL) is the emission of light in response to the application of an electrical current or a strong electric field. Since 1963, due to wavelength tunability, and narrow, intense, stable photoluminescent behavior, organic

Fig. 6 Chemical structure of π -acceptor units [35]

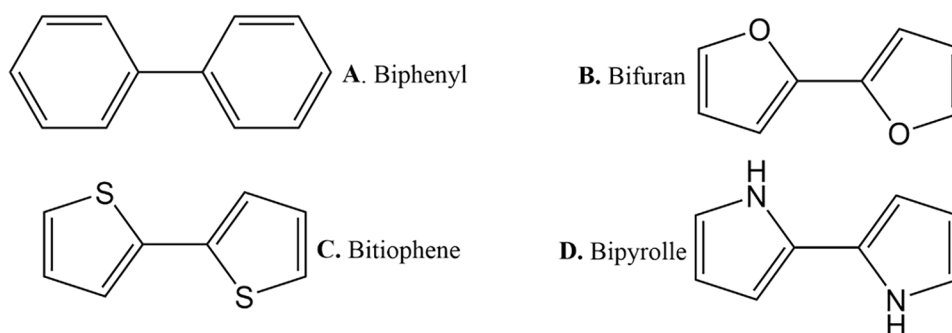
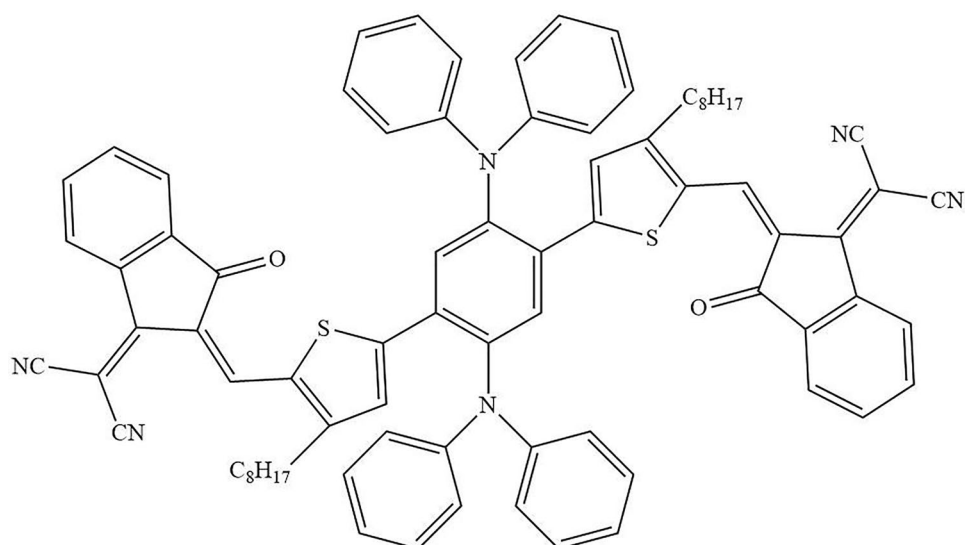


Fig. 7 Chemical structure of SM3 [36]

compounds have been intensively researched for use in electroluminescent devices [38–40].

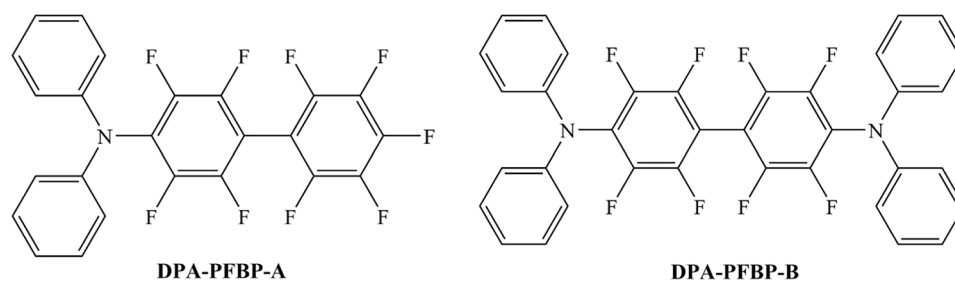
Zhou et al. [31] described a D-A blue phosphor based on phenyl(3-phenylimidazo[1,2-a]pyridin-2-yl)methanone (pBZ), an azarylketone derivative (Fig. 9a). A two-step synthesis used diphenylamine as the electron-rich donor and pBZ as the electron-deficient acceptor. The use of pBZ can result in strong fluorescence or mechanochromic luminescence. The obtained (4-(diphenylamino)phenyl)(3-phenylimidazo[1,2-a]pyridin-2-yl)methanone (pBZ-DPA) (Fig. 9b) can be used as a blue emitter and starting material for OLED applications. It exhibits blue electroluminescence color, peaking at 472 nm, with CIE coordinates (0.16, 0.25) (CIE—the International Commission on Illumination). It has a high decomposition temperature (421 °C). Para-phenylene acting as a pi-linker is useful for fine-tuning the molecular coupling and charge transfer range, and consequently for modulating the emission properties. Furthermore, the obtained pBZ-DPA was used as the host for the red lumiphore bis(2-methyldibenzo[*f,h*]quinoxaline)(acetylacetonate) iridium(III) (Ir(MDQ)₂(acac)) due to its wide energy gap. The obtained OLEDs exhibited red fluorescence with external quantum efficiencies of about 20% [31].

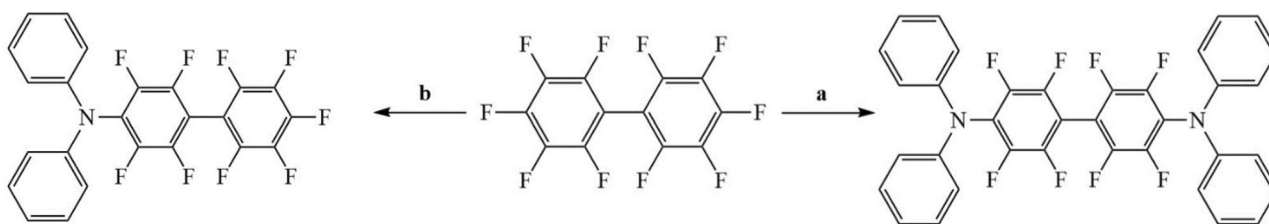
Mahesh et al. [33] confirmed that the reported molecules (Fig. 2) can exhibit green fluorescence in nonpolar solvents

in the range of 498–499 nm. The change in fluorescence color to yellow and orange occurs with increasing solvent polarity. Compounds synthesized by Knoevenagel condensation also exhibit positive solvatochromism as the emission maximum shifts towards 530 nm in DMF with increasing solvent polarity. Significantly, the Stokes shift for the reported DPA compounds 1–3 (Fig. 2) was 113, 108, and 110 nm in THF solution. These are higher values compared to other studied thiophene and carbazole derivatives [41, 42], making them promising compounds for applications in light-emitting diodes. The authors also confirmed that for the fluorescence to be as high as possible and the electrochemical bandgap to be as small as possible, DPA must be coupled to a good electron acceptor. Such conjugated molecules are of interest to many research teams due to their optical, morphological, and electrical properties.

Electrofluorochromism

Electrofluorochromic (EFC) materials should contain fluorophores with high and reversible fluorescence in response to electrochemical redox. Such compounds are promising for applications in sensors, displays, or memory devices. The team of Sun et al. reported a new polyamide (Fig. 10)

Fig. 8 Chemical structure of DPA-PFBP-A and DPA-PFBP-B [37]



Scheme 1 Synthetic route of DPA-PFBP-A and DPA-PFBP-B [37]

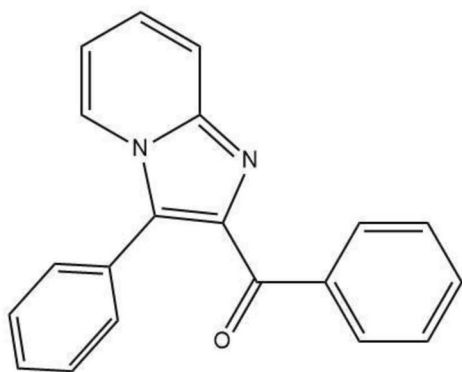
with DPA and tetraphenylethylene (TPE) units, which has promising applications in electrofluorochromism [42].

The reported compound in the case of a solid polymer layer exhibited aggregation-induced emission (AIE) with a high fluorescence quantum yield of 69.1% and was also stable during multiple electrochemical cycles. As an on/off compound, it exhibited an on/off fluorescence contrast ratio of up to 417, which is the highest value obtained to date. The use of DPA as an electroactive unit along with TPE afforded a polymer with a high fluorescence contrast. DPA

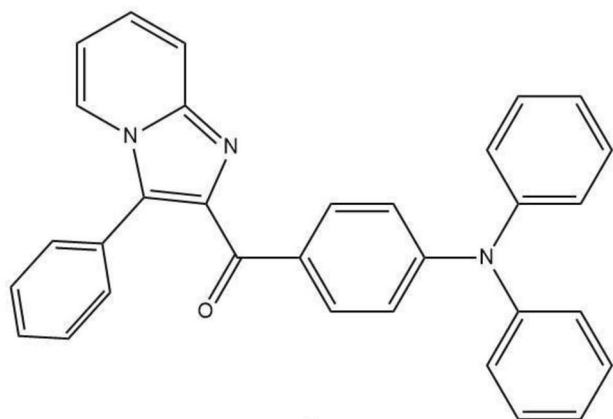
as an electrodonor group acted as a strong fluorochrome and greatly improved the fluorescence of the DPA-TPE [42].

The area of scientific research in the synthesis of heterocyclic compounds and their optoelectronic properties is used in different scientific fields, among others, in biosensors. An example in this area may be research on one of the diphenylamine derivatives, polydiphenylamine (PDPA) (Fig. 11a). The backbone of polydiphenylamine is composed of repeating sequences of two aromatic rings. It can take on many oxidation states. Moreover, PDPA is a derivative of polyaniline (PANI) (Fig. 11b) and compared to it, it is characterized by higher thermal stability and solubility in organic solvents, such as chloroform or tetrahydrofuran [43]. PDPA has a high sensitivity to many bioanalytes, which is an advantage in designing biological sensors used in medicine and industry [44]. This conductive polymer, compared to PANI, has a wider pH range in which it is stable, which is also an advantage [45]. Good electrochemical and optical properties of PDPA have been reported, which translates into application and proper influence on the properties of the synthesized PDPA/PANI composite forms used in optoelectronics [43].

Muthusankar et al. [44] presented the results of their research, in which they obtained a glucose biosensor with a 5 s response time, in the concentration range from 1 to 10 μM ,



a



b

Fig. 9 **a** Chemical structure of azaryl ketone (pBZ) [31]. **b** Chemical structure of (4-(diphenylamino) phenyl) (3-phenylimidazo [1,2-a] pyridin-2-yl) methanone (pBZ-DPA) [31]

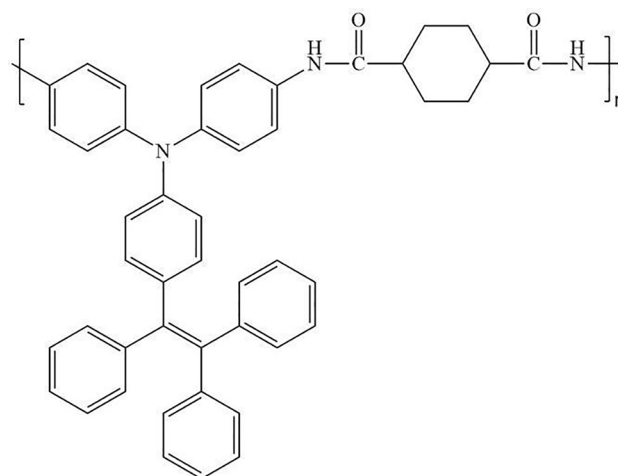


Fig. 10 Chemical structure of EFC polymer [42]

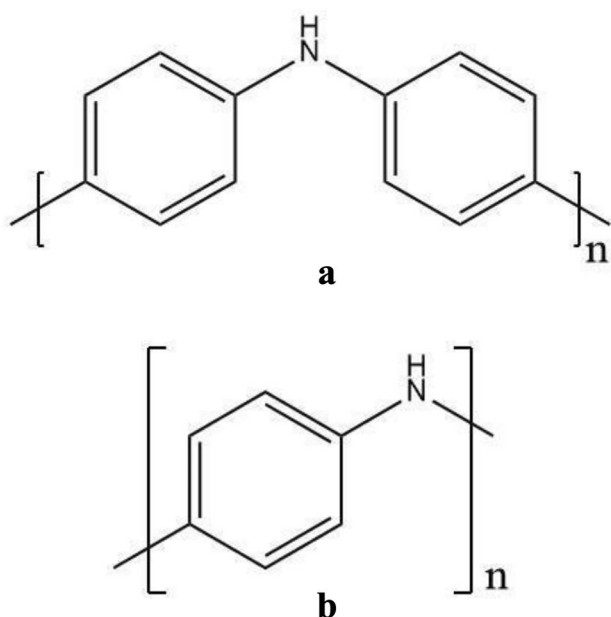


Fig. 11 **a** Chemical structure of polydiphenylamine [43]. **b** Chemical structure of polyaniline (PANI) [43]

with a sensitivity of $0.51 \mu\text{A}/\mu\text{M}$. Each of the results confirmed the stability and repeatability of the obtained biosensor. The three-step synthesis led to excellent electron transfer kinetics from glucose oxidase (GOx) through the copolymer and graphene sheets, which was confirmed by the electrocatalytic studies performed. In the CV studies, $\text{Fe}(\text{CN})_6^{3-/4-}$ was used as a redox indicator. The modified ITO/Gra-PANI-co-PDPA electrode (ITO-Indium-doped Tin Oxide; Gra-graphene) exhibited higher peak current densities for $\text{Fe}(\text{CN})_6^{3-/4-}$ redox peaks than the comparative ITO/Gra-PDPA and ITO/Gra-PANI electrodes. In addition, amperometric and interference studies confirmed its practical application. The stability of ITO/Gra-PANI-co-PDPA/GOx was tested for 20 days at 4°C . The biosensor maintained 94% current for $1.0 \mu\text{M}$ glucose at 0.52 V . By combining graphene with a copolymer, the biosensor can determine glucose over a wide range of concentrations.

A similar biosensor for urea detection was obtained by electrochemical deposition [46]. This is the first attempt to prepare an ITO/PDPA/PTA/Gra-ME (PTA- Phosphotungstic Acid, ME-Modified Electrode) layered electrode using this method. Scanning electron microscopy (SEM) with 15 kV was used to study the morphology of the conductive surface of the polymer nanohybrid. Atomic force microscopy (AFM) was also used to determine the thickness of the surface coating. The obtained biosensor was sensitive to urea concentration in the range of $1\text{--}13 \mu\text{M}$ and exhibited sensitivity at the level of $1.085 \mu\text{A}/\mu\text{M cm}^2$. Due to the interaction of tungsten atoms and layered PDPA/graphene, high electrocatalytic activity was achieved. This solution provided reversible multi-electron redox behaviors that result in fast

electron transfer. Produced nanohybrid can be widely used in electrocatalysis.

Benzothiadiazole derivatives in optoelectronics

Solid derivatives

In 2020 Zhao et al. conducted a study [47] on the optical properties of solid benzothiadiazole derivatives. Despite the unpredictability and complex modulation of solid organic substances, the versatility of use in optoelectronics, as well as greater sensitivity in comparison with the same liquid derivatives, did not allow this topic to be bypassed.

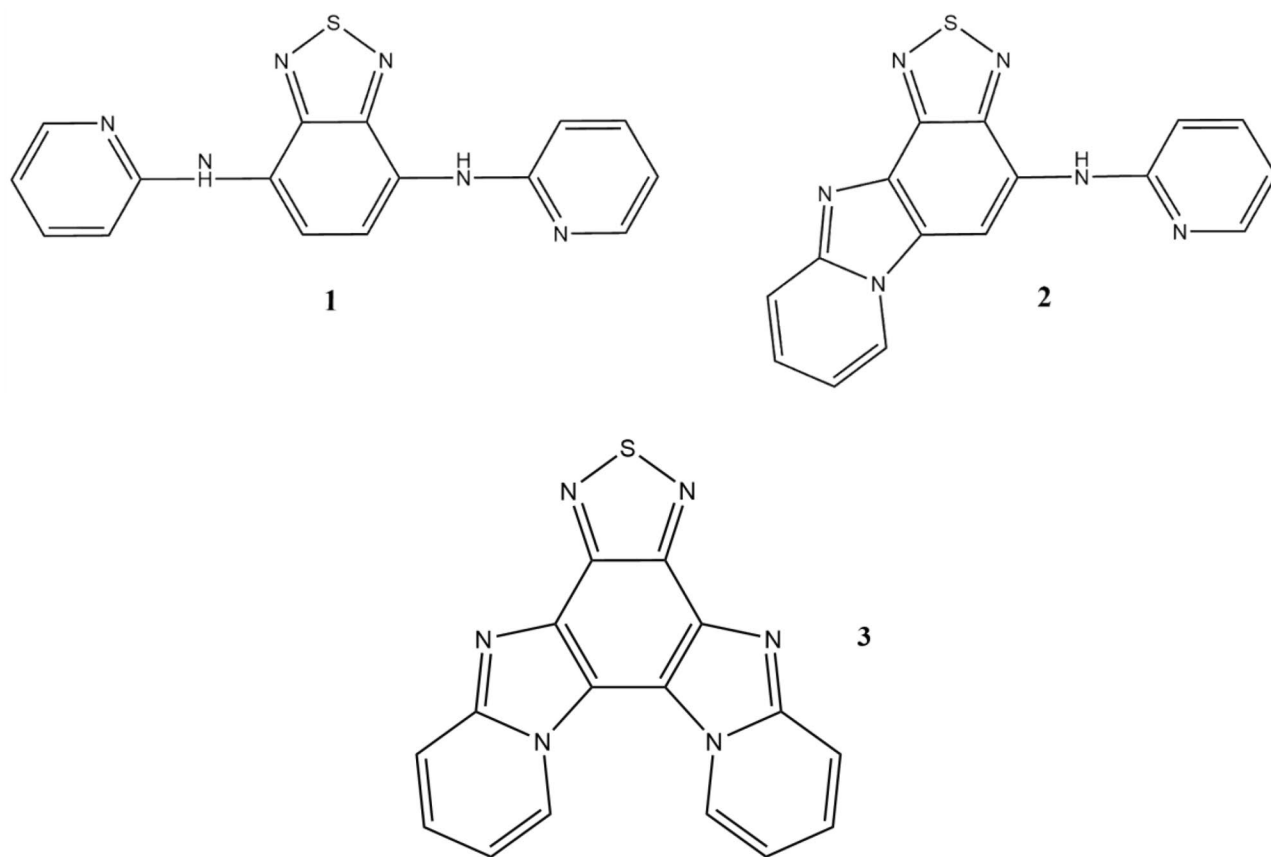
To investigate the effect of the molecular structure on the optical properties, three BTD derivatives were obtained (Scheme 2).

The first compound (1) was obtained by the Buchwald-Hartwig reaction and further crystallized by the slow evaporation method in ethyl acetate or petroleum ether [48]. Compound 2 was synthesized from the first one using 20% CuBr_2 and acetonitrile. The third compound (3) with an efficiency of 88% was obtained from the first and second substances by different reactions.

After several necessary experiments, the scientists learned the basic optoelectronic properties of the obtained substances. The first experiment concerned studies of photoluminescent properties in solid and liquid states. Photoluminescence spectroscopy showed the shifted lowest energy absorption band: compound 1 from 495 nm (in the dichloromethane (DCM) solution) to 472 nm (in crystal), compound 2 – from 461 to 487 nm , while the third compound showed a result from 430 to 427 nm . Thus, the wavelength of maximum absorption of the first substance in this experiment decreased by 23 nm compared to the results above, compound 2 increased to 487 nm , and for substance 3 the difference is insignificant (Table 1).

A study of the aggregate state of substances 1 and 2 was also conducted. The phenomenon of self-assembly was not detected at the initial stage in DMF. The changes began to manifest themselves with the addition of water. Photophysical studies of the sediment of both derivatives showed the same results as those for the crystalline form. This explains the differences in photoluminescence of solutions and crystals.

For the concept of the relationship between crystal luminescence and molecular structure, new studies have been conducted, namely, the effect of hydrostatic pressure on substances. The results showed that under pressure all three derivatives behaved similarly and as soon as the pressure ceased to act, absorption and emission were restored to their original parameters. During the experiment, 1–3 derivatives demonstrated reversible red-shifted piezochromic behaviors with significant sensitivities, and in particular 2



Scheme 2 Chemical structure of benzothiadiazole derivatives compounds [47]

showed orange to near-infrared (NIR) region (700–2500 nm) piezochromism. Cationic dimers have demonstrated red-shifted luminescence compared to the photoluminescence dimer, which gives a new insight into the development of new materials emitting NIR in OLED displays. Interestingly, photoluminescence microscopy indicated that the morphology of the first substance differs from the derivatives 2 and 3. According to the literature [49], it can be concluded that such benzothiadiazole derivative can be used in organic micro-lasers.

Elastic derivative

Shotaro et al. in 2017 conducted their study of benzothiadiazole derivatives [50]. One of the priority characteristics was elasticity. The main substance of the experiments was 4,7-dibromo-2,1,3-benzothiadiazole (Fig. 12).

During the experiments, it turned out that in the crystalline state, the derivative exhibits impressive flexibility and fluorescence. Such results were achieved by forming a 1 cm long needle from a crystal. The needle was able to withstand the applied force with the ability to return the shape and

Table 1 Selected absorption peaks of benzothiadiazole derivatives in solution and solid state; λ_{\max} -wavelength of maximum absorption [47]

Compound	System	Solvent	λ_{\max} (abs)/nm
1	Solution	DCM	495
	Single crystal	-	472
2	Solution	DCM	461
	Single crystal	-	487
3	Solution	DCM	430
	Single crystal	-	427

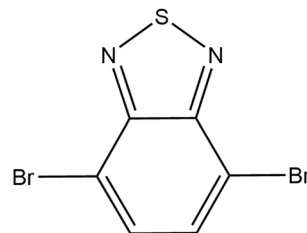
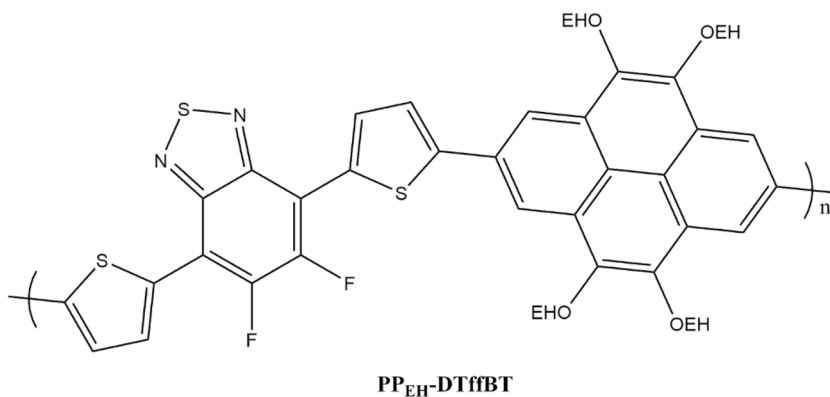
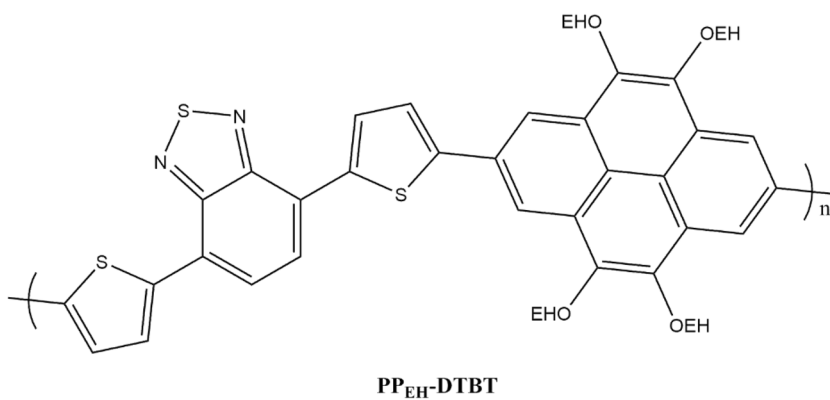
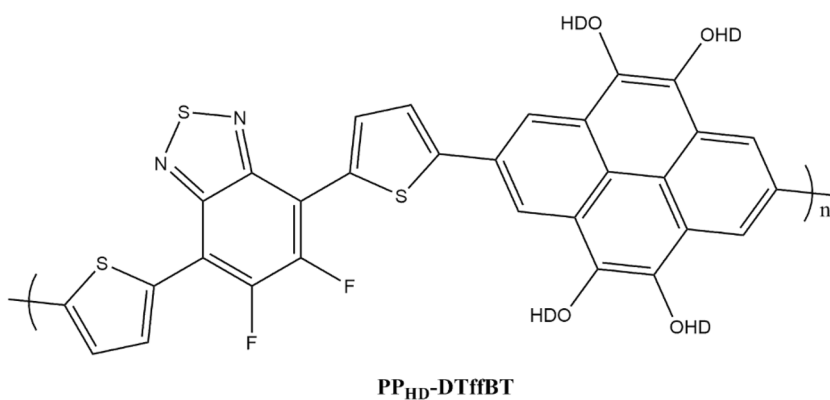
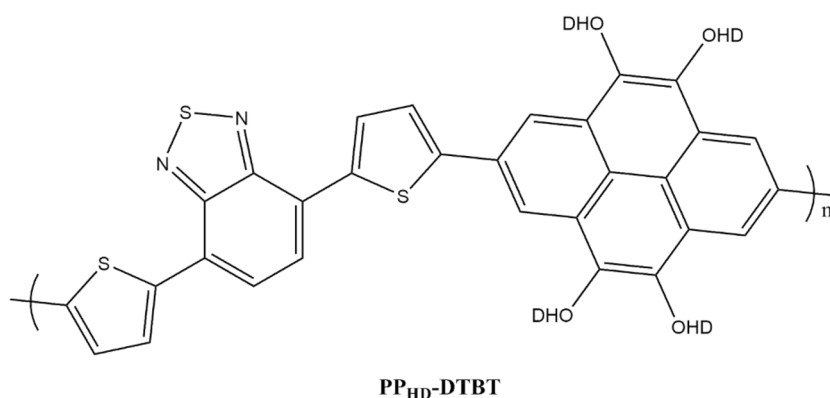


Fig. 12 Chemical structure of 4,7-dibromo-2,1,3-benzothiadiazole (DBBT) [50]

Fig. 13 Structural formulas of Poly{4,5,9,10-tetrakis[(2-hexyldecyl)oxy]pyrene-2,7-diyl-alt-[4,7-dithiophen-2-yl]-2',1',3'-BT-5,5-diyl} (PP_{HD}-DTBT), poly{4,5,9,10-tetrakis[(2-hexyldecyl)oxy]pyrene-2,7-diyl-alt-[5,6-difluoro-4,7-di(thiophen-2-yl)-2',1',3'-BT-5,5-diyl]} (PP_{HD}-DTffBT), poly{4,5,9,10-tetrakis[(2-ethylhexyl)oxy]pyrene-2,7-diyl-alt-[4,7-dithiophen-2-yl]-2',1',3'-BT-5,5-diyl} (PP_{EH}-DTBT), and poly{4,5,9,10-tetrakis[(2-ethylhexyl)oxy]pyrene-2,7-diyl-alt-[5,6-difluoro-4,7-di(thiophen-2-yl)-2',1',3'-BT-5,5-diyl]} (PP_{EH}-DTffBT) [53]



fluorescence to its original state. A centimeter-straight shape was obtained using an ethanol solution containing DBBT (1.0 M) and slow crystallization for 1 day.

To obtain the necessary information about the substance, several experiments were conducted. To ensure immobility, the crystal was fixed with adhesive tape on a test tube. With the help of tweezers, pressing on the end of the crystal was created. The needle was bent and unbent as many times as this manipulation was done with it. This proves the elasticity of the crystal of DBBT. The bending angle of the crystal reached 30°. The crystal was bent in the vertical direction and later it was found that its flexibility is similar to rubber. Unfortunately, the needle can be bent only in the vertical direction, since organic crystals are anisotropic and solid DBBT crumbles when bent diagonally.

Another experiment was the measurement of the fluorescence of crystal, crystal powder, and DBBT in dichloromethane. The solution showed blue fluorescence with a peak at 434 nm, the crystal showed a red shift at 513 nm, and the powder showed a blue shift at 490 nm. These results suggest that the crystal changed its molecular packaging during the grinding of the powder. Further, the fluorescence was checked in a normal, bent, and relaxed state using a single-crystal X-ray diffraction and a polyethylene (PE) film to bend the crystal. In the bent state, the fluorescence of the crystal showed a blue shift at 505 nm, which is similar to the results with powder; it can be concluded that the molecular packaging changes during bending. The relaxed state after removal of the PE film showed red fluorescence identical to the normal state of the crystal, which proves the recovery properties of the crystal.

Surprisingly, in the crystalline state DBBT shows its elasticity, while usually organic crystals are inflexible, and flexible polymers are not crystalline [51, 52]. Balance between elasticity and crystalline state is a big problem in organic materials. The study of flexible crystals with optical abilities can change the view of electronic devices and solve this problem.

Pyrene-based benzothiadiazole derivatives

The main criteria for optoelectronics manufacturers are materials that are inexpensive and nontoxic, have a high absorption coefficient, and can be easily recycled. In 2016 Alqurashy et al. decided to use a pyrene particle to improve the quality of polymers from benzothiadiazole [53]. Pyrene molecules exhibit a strong degree of crystallinity and electron saturation, which facilitates polymerization using electron-deficient units. The addition of a substance with

different substituents in positions 4,5,9- and 10- can positively change its optical and electronic properties.

Researchers have developed four polymers (Fig. 13) using Stille polymerization. Pyrene was oxidized in the positions indicated earlier using $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ and NaIO_4 . The products of these reactions were brominated at positions 2- and 7- with *N*-bromosuccinimide. The final stage was the addition of alkyl chains.

After synthesis, several studies were conducted to find some properties of the new polymers. Using UV-vis spectroscopy, the results of the absorption of derivatives in chloroform solution and in the film state were obtained and are shown in Table 2. Interestingly, polymers with short 2-ethylhexyl chains showed red-shifted absorption in comparison with their analogues with 2-hexyldecyl chains. Also, fluorinated derivatives showed a hypsochromic shift when the others did not, which is described in previous work of the same authors [54].

The thermal abilities of the obtained substances were investigated using thermogravimetric analysis (TGA), which showed that the average value of the degradation temperature is approximately 320 °C (Table 2). It was noticed that 2-ethylhexyl derivatives lost significantly in mass at 513–520 °C, while both $\text{PP}_{\text{HD}}\text{-DTBT}$ and $\text{PP}_{\text{HD}}\text{-DTffBT}$ did so at a lower temperature, which is due to the different structures of alkyl chains.

By powder X-ray diffraction, scientists were able to learn more about the molecular organization of the obtained polymers in the solid state. The results showed that the packaging of $\text{PP}_{\text{EH}}\text{-DTBT}$ and $\text{PP}_{\text{EH}}\text{-DTffBT}$ is denser between the layers than that of their analogues with 2-hexyldecyl chains, as well as that substances with substituents in the form of fluorine have a smaller stacking distance, which means they adopt a more crystalline structure in the solid state.

Dense packing of the material should improve charge extraction and mobility in photovoltaic devices; therefore, the use of polymers with shorter chains like in $\text{PP}_{\text{EH}}\text{-DTBT}$ and $\text{PP}_{\text{EH}}\text{-DTffBT}$ is recommended.

Table 2 Results of UV-vis spectroscopy and thermogravimetric analysis (λ_{max} -wavelength of maximum absorption; T-temperature of degradation) [53]

Polymer	λ_{max} (nm)		T (°C)
	Chloroform solution	Film	
$\text{PP}_{\text{HD}}\text{-DTBT}$	531	571	328
$\text{PP}_{\text{HD}}\text{-DTffBT}$	526	562	328
$\text{PP}_{\text{EH}}\text{-DTBT}$	538	585	322
$\text{PP}_{\text{EH}}\text{-DTffBT}$	521	564	320

Theoretical derivatives

In 2019 Karcimi et al. [55] conducted theoretical studies on the topic of benzothiadiazole derivatives for photovoltaic use. The purpose of the experiment was to find out the change in efficiency after replacing some thiophene molecules with benzothiadiazole. Theoretical methods such as

density functional theory (DFT) and time-dependent density functional theory (TD-DFT) were used. The main use of such polymers as semiconductors could be organic solar cells, especially bulk-heterojunction (BHJ) solar cells, since the charge is generated in them using the "donor-acceptor" approach between two semiconductors. Another optoelectronic application is an organic light-emitting diode since

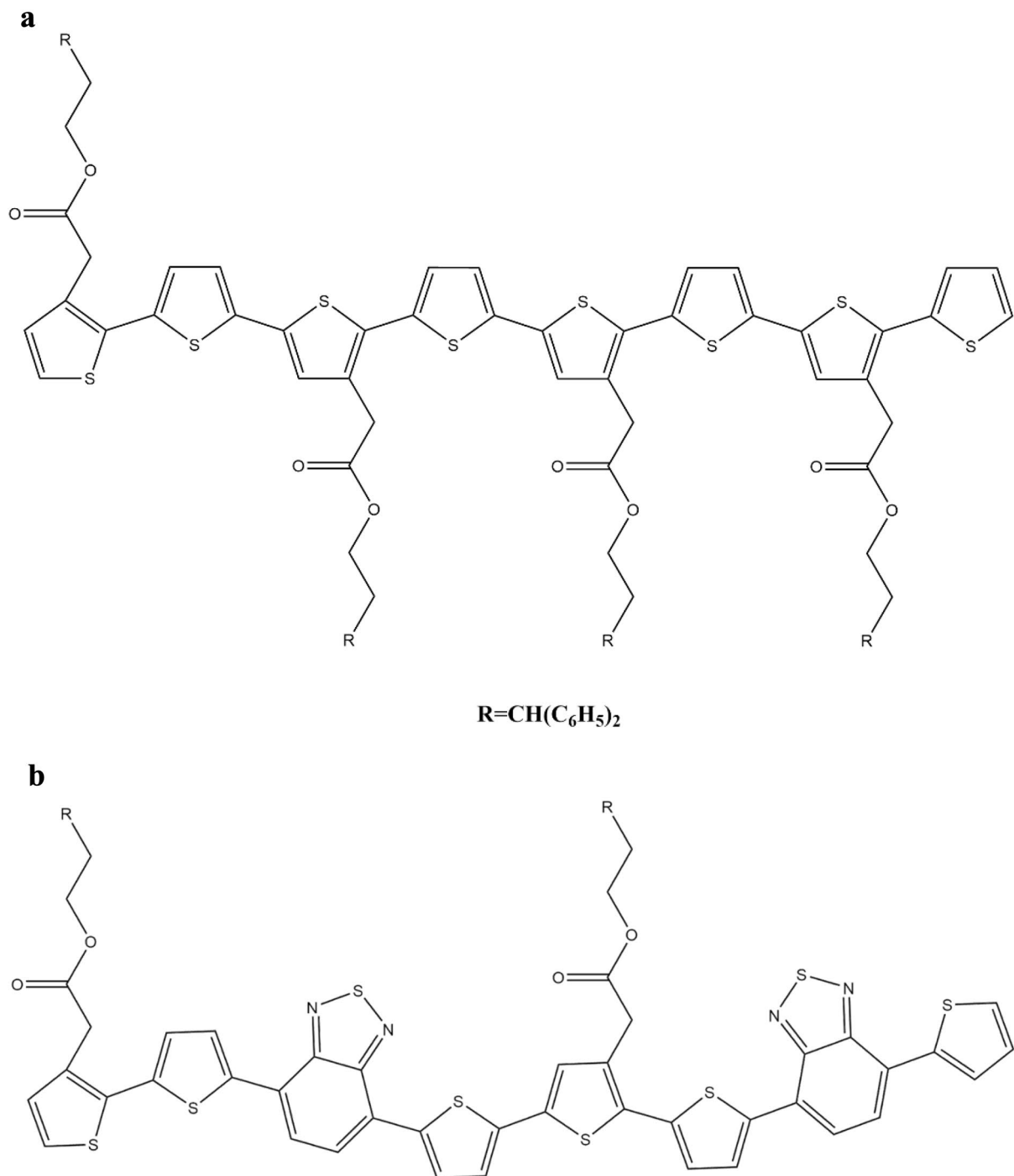


Fig. 14 Chemical structure of studied compounds **a** and **b** [55]

benzothiadiazole derivatives have long been used as building blocks for electron-transport materials [56].

Two polymers containing phenyl ester (Fig. 14) were investigated using DFT and TD-DFT at the CAM-B3LYP/6-31G(d, p) level by presenting to different donor molecules. The optimization results showed that the corresponding binding distances in these substances are similar. It was also noticed that alkyl groups distort the torsion angles between thiophene rings by repulsion from each other, which affects the electronic properties of the substance, therefore, in places of distortion, these groups were replaced by benzothiadiazole. This is not the first time that benzothiadiazole has become a substitute for other molecules. For example, Mancilha et al. [57] in 2006 conducted a quinoxaline replacement experiment. The results showed that benzothiadiazole derivatives have better fluorescence values than quinoxaline derivatives and are thus more suitable for use in OLED devices.

The electronic properties of polymers were also investigated. The electronic properties experiments aimed to find out the effect of benzothiadiazole on these properties using the study of the HOMO and LUMO in comparison to values of C₆₀[6, 6]-phenyl-C61-butyric-acid methyl ester (CB PCBM C₆₀) and energy gap (E_{gap}) as the difference between HOMO and LUMO. As can be seen in Table 3, the energy gap of substance *a* is greater than that of substance with benzothiadiazole (*b*), which is explained by weaker conjugation caused by a distortion of aromatic rings. However, the LUMO of substance *b* is larger than that of substance *a*, which indicates a better binding character between the acceptor and the donor. Together, these results suggest that polymer *b* is a better candidate for use in optoelectronics.

After conducting optical experiments, the results showed that the profile of the spectra of both substances are very similar, since the molecules are not flat, the possible presence of steric effects by alkyl groups is confirmed. The results also indicate that the absorption of substance *b* is higher than substances without benzothiadiazole (Table 4), which indicates greater steric effects and weaker conjugation.

In conclusion, it is important to note that substance *b* has a better binding character, high absorption, and good solubility. These qualities make it an excellent candidate

Table 3 Electronic properties parameters of the studied molecules obtained by B3LYP/6-31G methods (E_{HOMO} – energy of the highest occupied molecular orbital, E_{LUMO} – energy of the lowest occupied molecular orbital, E_{gap} – energy gap) [55]

Compounds	E_{HOMO} (eV)	E_{LUMO} (eV)	E_{gap} (eV)
<i>a</i>	-4.948	-2.031	2.917
<i>b</i>	-4.852	-2.767	2.085
PCMBC ₆₀	-6.100	-3.470	-

for use as a material in OSCs. After conducting theoretical experiments, the scientists hope that their work will help in the development of other organic materials to increase the efficiency of photovoltaics.

Polymer dots based on benzothiadiazole

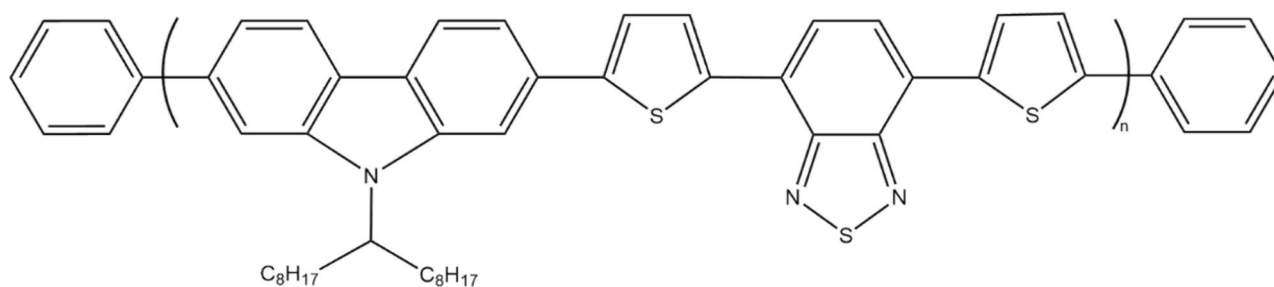
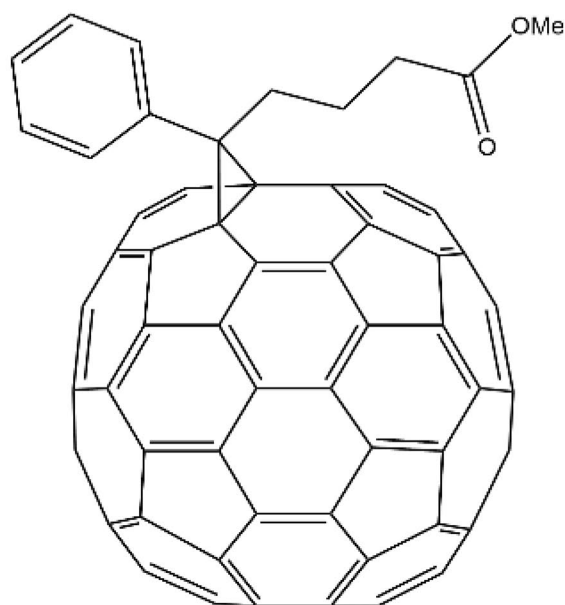
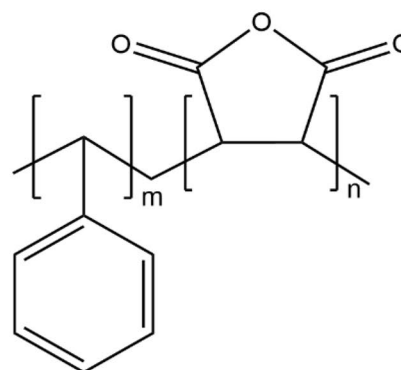
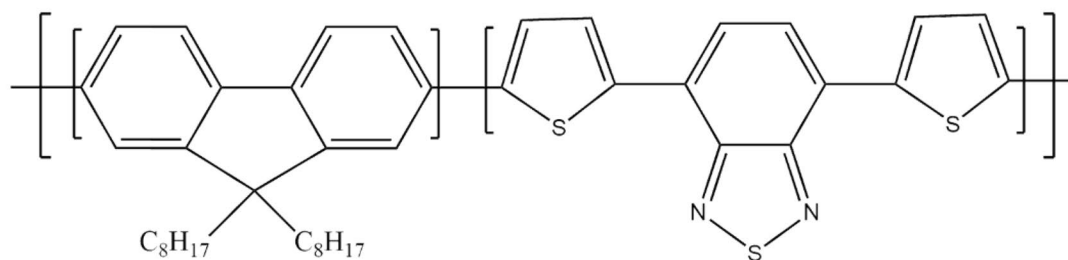
In the joint work of Chinese and American universities in 2015 Li et al. [58] managed to develop polymer dots based on benzothiadiazole with high efficiency for solar cells. Two polymers: poly[N-9"-hepta-decanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole) (*PCDTBT*) and [6, 6]-phenylC₇₁ butyric acid methyl-ester (*PC₇₁BM*) were doped with another pair of polymers: poly(9,9-dioctylfluorene)-co-(4,7-di-2-thienyl-2,1,3-benzothiadiazole) (*PF-5DTBT*) and poly(styrene-co-maleic anhydride) (*PSMA*) as the active layer of organic solar cells. Molecular structures of the polymers are represented in Fig. 15. Thanks to polymer dots, it was possible to increase power conversion efficiency by 29%. High efficiency is achieved by increasing the short-circuit current and the fill factor.

The chemical synthesis of PF-5DTBR was based on the 2004 work of Hou et al. [59]. Two polymers were prepared with THF and reacted under the action of ultrasound in deionized water for 5 min. After removing THF with nitrogen gas, mixtures were concentrated under heating and filtered to remove large particles. Dots were added to the PCDTBT:PC₇₁BM solution and a special device was made. The device consisted of several layers: nanocrystals of Indium Tin Oxide, titanium oxide (TiO₂), an active layer (PCDTBT and PC₇₁BM in a solution of dichlorobenzene with dots of different sizes), molybdenum oxide (MoO₃), and silver. The average size of the dots on the active layer was 5 nm. This device, along with the same one but without the dots, was further investigated for photovoltaic properties.

In the course of experiments and based on other studies [60, 61], it was observed that the addition of polymer dots can increase the short-circuit current. The results of the photon-to-current efficiency (IPCE) spectra showed that the maximum value of a standard device is about 65% at 490 nm, while the manufactured one is 15% higher at 500 nm, which means more efficient use of photons. Also, after conducting reflection studies, it turned out that the addition of dots reduced the reflectivity, which favorably affected the absorption of photons by the active layer. To better understand the influence of dots, the researchers traced the dependence of

Table 4 Results of the maximum absorption obtained by CAM-B3LYB calculations [55]

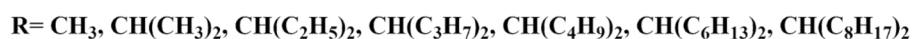
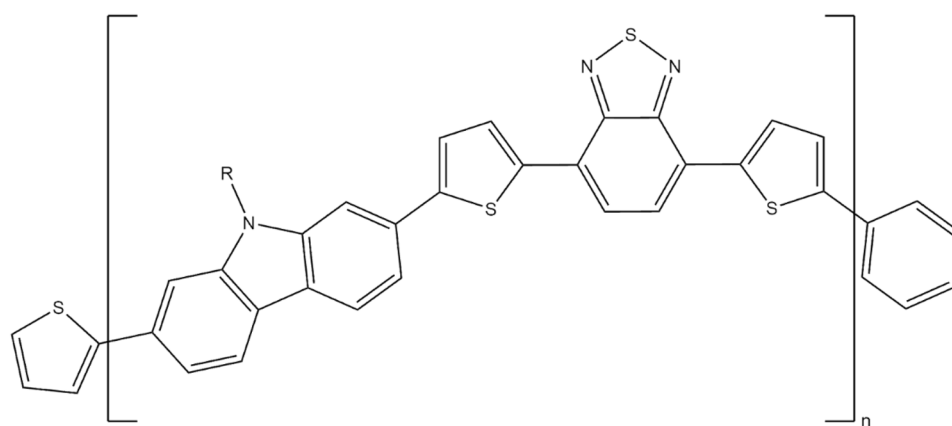
Compounds	λ_{max} (nm) CAM-B3LYB
<i>a</i>	407.09
<i>b</i>	521.13

**PCDTBT****PC₇₁BM****PSMA****PF-5DTBT****Fig. 15** Molecular structure of PCDTBT, PC₇₁BM, PSMA, and PF-5DTBT polymers [58]

photocurrent density (J_{ph}) on effective voltage (V_{eff}). After receiving the results, it was found that J_{ph} increases faster for devices with dots on the active layer at low V_{eff} . This proves the effect of changes on charge generation by increasing the

efficiency of solar cells. Thus, the researchers increased the low power conversion efficiency from 5.73% to 7.40% and believe that their work will contribute to the development of OSCs.

Fig. 16 Molecular structure of PCDTBT polymer with variants of different side chains [62]



Carbazole-benzothiadiazole based polymer

Continuing to develop the OSCs industry, Franco [62] decided to find the effect of the length of different alkyl side chains on the optoelectronic properties of the polymer. Poly[N-9'heptadecanyl-27-carbazole-alt-55-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] (PCDTBT) (Fig. 16) was taken as the base using theoretical methods of computer modeling of molecules similar to those mentioned in the work described above.

Thanks to the well-known methods of DFT and TD-DFT, it was possible to calculate the structural and optoelectronic properties of the polymer. Firstly, it was important to investigate the influence of dihedral angles and bond-length alternation (BLA), because their changes can affect optoelectronic properties. Using computer calculations, it was found

that all alkyl side chains are far from the benzothiadiazole and thiophene rings, regardless of the length of the alkyl chain, which proves that the dihedral angles do not depend on the length of the alkyl side chain. The values of BLA for all variants of side chains were confirmed by calculating the binding energies of the alkyl-carbazole unit with neighboring thiophene units. Calculations have shown that their binding energies are constant and range from 5.35 to 5.37 eV. Structural studies have shown that there are no particular differences in the main chain when the side chain changes. When studying optoelectronic properties, such parameters as E_{HOMO} , E_{LUMO} , and E_{gap} were considered. The calculated energies turned out to be the same as in the work of Wu et al. with another similar polymer [63].

The results of the theoretical study suggest that the use of shorter alkyl side chains does not particularly affect the structural and optoelectronic properties of the carbazole-benzothiadiazole polymer. From this, it should be concluded that in the future the use of shorter alkyl chains will not affect the results, and research costs will significantly decrease.

The researcher believes that his work will help to better represent the design of materials with a similar structure and carry out chemical modifications without reducing the optoelectronic properties of polymers.

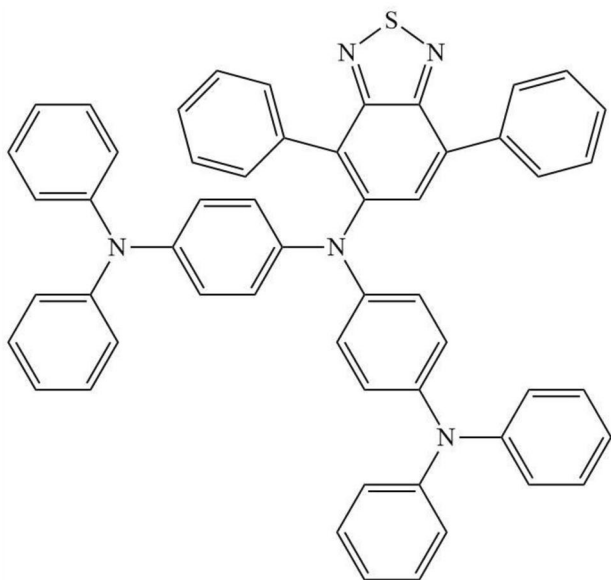


Fig. 17 Chemical structure of 2P-BT-N-2TPA [64]

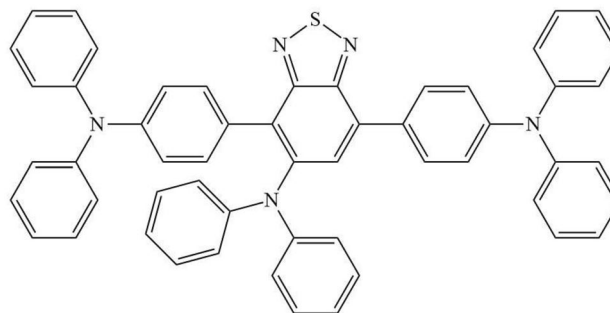
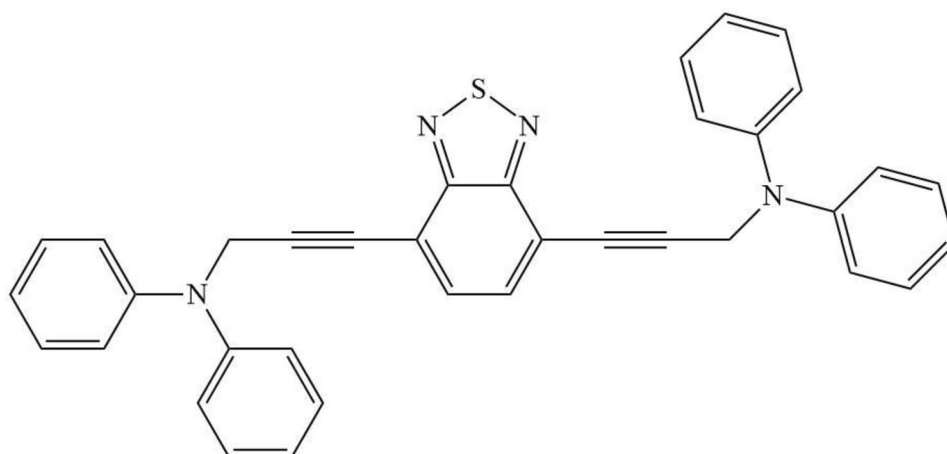


Fig. 18 Chemical structure of 2TPA-BT-N-2P [64]

Fig. 19 Chemical structure of compound 5 [65]



Diphenylamine and benzothiadiazole derivatives

So far, separate use of diphenylamine and benzothiadiazole in donor–acceptor models was described. However, since DPA is an excellent electron donor and BTD is a good acceptor, combining these two molecules should result in a great semiconductor. This section will cover examples of compounds containing both motifs, as several scientific groups have tried to find applications for such substances in optoelectronics.

Orange OLEDs (which are one of the more popular areas of optoelectronics) using phosphorescent dyes have made great strides. The current goal, i.e., is to use orange OLEDs in flat-panel display applications. The work of Yang et al. [64] described the design and synthesis of two isomers with diphenylamine and benzothiazole motif, 2P-BT-N-2TPA (Fig. 17) and 2TPA-BT-N-2P (Fig. 18), which were characterized by Hybridized Local And Charge Transfer (HLCT) properties.

The scientists used 2TPA-BT-N-2P as a dopant to create a doped OLED, which yielded sensational results. The device had an excellent external quantum efficiency (EQE)

of 6.6% with an emission peak at 588 nm. Moreover, the use of 2TPA-BT-N-2P as a pure emissive layer in an undoped OLED resulted in the device achieving EQEs of 5.8% and 5.1% at 100 cd/m² and 1000 cd/m², respectively.

It was found that the aggregation-induced emission enhancement (AIEE) properties that characterize 2TPA-BT-N-2P can effectively inhibit the ACQ (aggregation-induced quenching) effect in the aggregated state. This compound also had an unusually high value in the film in the solid state—its photoluminescence quantum yield (PLQY) reaches up to 91%. Such values show that it is possible to develop efficient orange emitters with AIE-HLCT effects, as well as high PLQY.

Another research team that undertook the synthesis of compounds based on diphenylamine and benzothiazole was Wakabayashi et al. [65]. They described the synthesis and photophysical, electrochemical, and thermal characterization of a BTD core with dual fluorescence emission in the violet-blue and cyan-green-yellow regions. They used propargyl diphenylamine and/or propargyl carbazole as side groups in the Sonogashira reaction.

Fig. 20 Chemical structure of compound 7 [65]

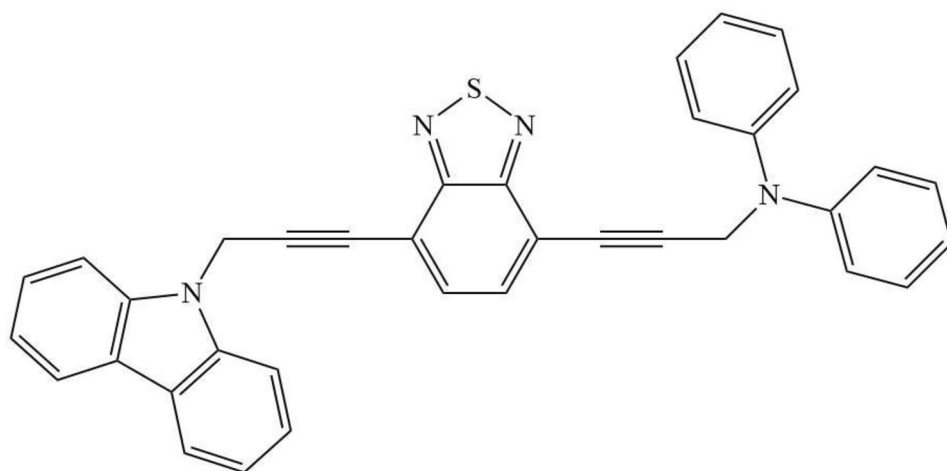
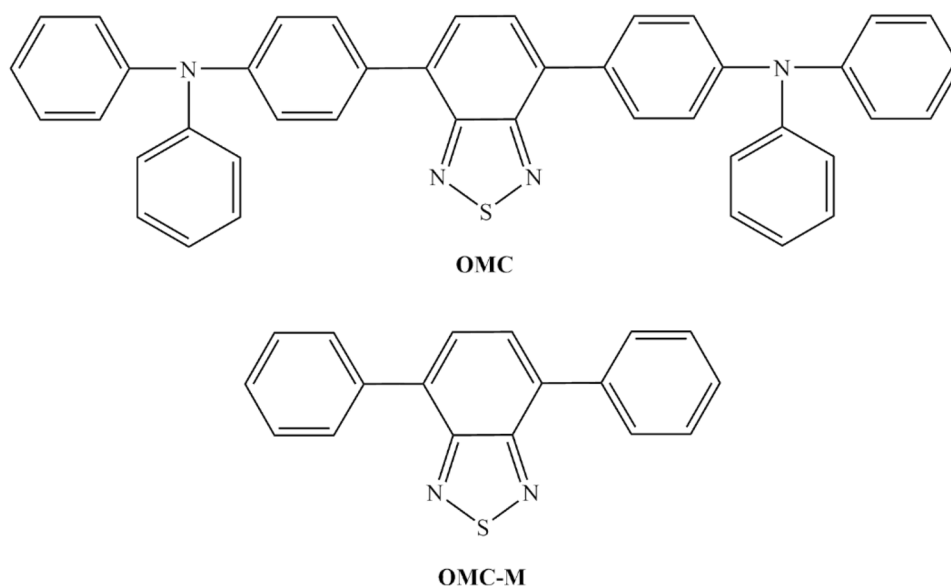


Fig. 21 Chemical structure of compounds OMC and OMC-M [66]



Both fluorophores showed absorption bands in the ultra-violet region with similar absorption maxima—compound 5 (Fig. 19) with a maximum at 380 nm, while fluorophore 7 (Fig. 20) with a maximum at 379 nm. Despite the very low quantum yield of fluorescence in solution, they exhibited the typical phenomenon of aggregation-induced emission. Measured fluorescence showed dual emission through a blue-shifted band at around 425–470 nm and a red-shifted band at around 536–571 nm.

The observed charge transfer characteristics of these compounds correlated with the results of theoretical calculations performed at the CAM-B3LYP/6-31G** level of theory. Moreover, the ordered fluorescence emission in the solid state associated with the AIEE phenomenon was consistent with the fluorescence emission spectra. In addition, the electrochemical band gap of the described compounds 5 and 7 (estimated from redox potentials) was 2.16 eV and 2.17 eV.

Another paper that touches on the topic of semiconductors based on benzothiadiazole and diphenylamine was published in 2011 by Hu et al. [66]. Scientists have conducted theoretical studies on the optical and electronic properties and electron transfer ability of a substance based on DPA and BTD, OMC-M (a derivative of OMC, 4,7-Bis(4-(N,N-diphenylamino)phenyl)-2,1,3-benzothiadiazole) (Fig. 21) to prove good ambipolarity and application in OLEDs. The main goal of the work was to find the relationship between the structure and optoelectronic properties of compounds and to contribute to the development of OLED technologies.

Electronic properties were obtained by DFT. Absorption and emission spectrum were predicted using TD-DFT. Calculations have shown that the E_{HOMO} and E_{LUMO} of OMC-M decrease compared to the values for OMC, this affects the E_g which is higher (4.15 eV) compared to OMC (3.19 eV). The LUMO value for OMC-M compared to OMC have the same

electron density distribution, however, the HOMO value has a different localization: for OMC—on a triphenylamine (TPA) molecule, and for OMC-M on benzene near the benzothiadiazole molecule.

The results of the maximum absorption and emission wavelengths of OMC and OMC-M compounds are shown in Table 5. As can be seen, OMC has a larger Stokes shift than OMC-M.

Charge carrier transfer is an important property in OLED performance. After calculations, it became clear that OMC-M has larger internal reorganization energies for hole and smaller internal reorganization energies for electron as compared with OMC. This leads to a more balanced charge-carrier transport and an increase in the hole-electron recombination rate, thereby increasing the efficiency of OLEDs. In this way compound OMC-M can be used as a better ambipolar charge carrier material in optoelectronic technologies.

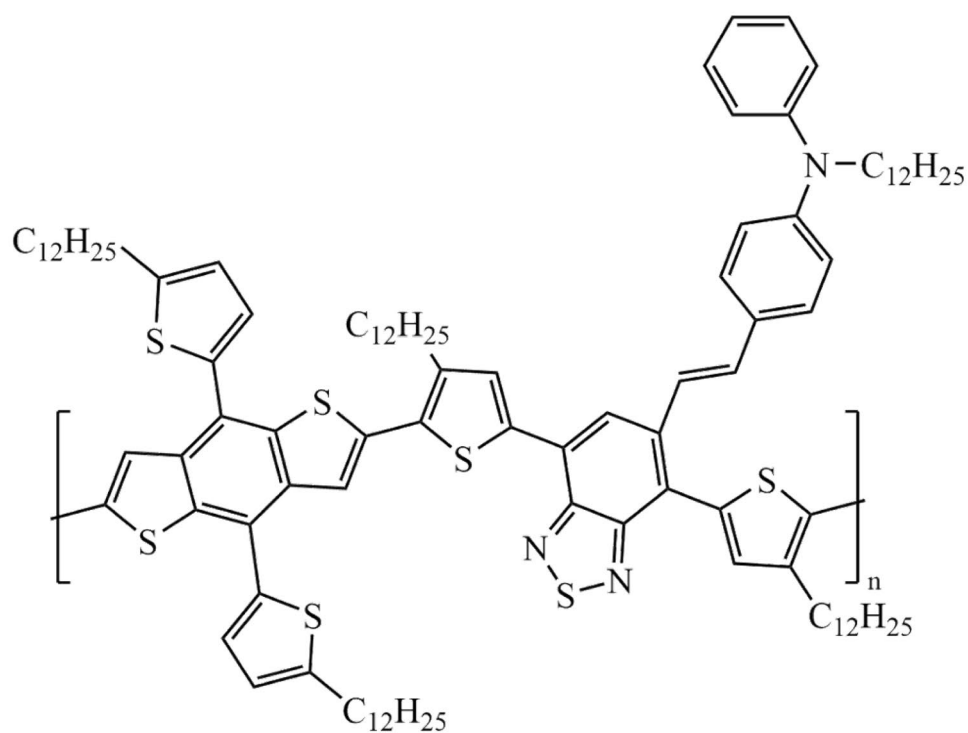
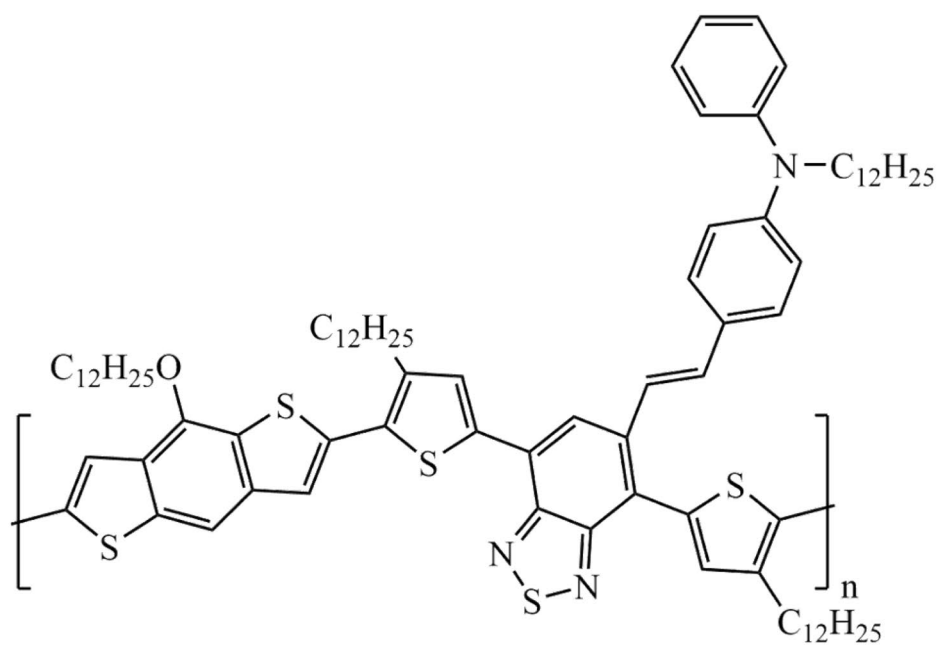
In 2012 Peng et al. [67] decided to investigate the potential use of 2,1,3-benzothiadiazole with diphenylamine-vinyl side chains for polymer solar cells. Two low bandgap copolymers PBTBD1 and PBTBD2 (Fig. 22) were created by Stille coupling polymerization with the expectation that they would have good photovoltaic properties.

After several experiments, scientists have found that these copolymers have excellent solubility in organic solvents and

Table 5 Results of the maximum absorption/emission wavelength of OMC and OMC-M compounds [66]

Compounds	Absorption (λ_{abs})	Emission (λ_{em})
OMC	471	617
OMC-M	359	482

Fig. 22 Chemical structure of compounds PBTBD1 and PBTBD2 [67]



thermal properties. UV–vis measurements have shown that both copolymers exhibit strong and wide absorption in the range of 300 nm to 900 nm. The results also showed that PBTBD2 has a smaller band gap than PBTBD1, which is

a useful property for increasing the short-circuit current in polymer solar cells. Compared with simple benzothiadiazole derivatives, the bandgaps of copolymers are smaller, indicating that increased absorption in the entire visible

wavelength region was achieved due to the side chains of diphenylamine-vinylene, implying that such an improvement is effective.

Experiments on the electrochemical properties of substances were also carried out. The HOMO and LUMO energy levels were measured by cyclic voltammetry experiments and further confirmed using theoretical methods (DFT at the B3LYP/6-31G* level). The results showed that the electron density of LUMO was mainly localized on the benzothiadiazole molecule, while the electron density of HOMO was distributed almost completely over the conjugate molecule, which is an advantageous property for obtaining higher hole mobility. However, in general, the electrochemical parameters are similar between both copolymers and show relatively low HOMO levels, which should affect the stability of substances, as well as photovoltaic properties.

Polymer solar cells were specially made to test the photovoltaic properties. The results of such an experiment showed that both substances have high open-circuit voltages (V_{OC}) of more than 0.9 V and the same external quantum efficiencies (EQEs).

Summarizing, the results of the study showed that these benzothiadiazole-based copolymers PBTBD1 and PBTBD2 with diphenylamine-vinylene side chains can be excellent candidates for efficient polymer solar cells.

Conclusion

Designing narrow band gap heterocycles relies on structural modifications to select the most promising system. For this purpose, individual groups are most often mentioned in the push-pull or donor-link-acceptor systems and the changes in the optoelectronic properties of the entire system are checked. Numerous research centers conduct a series of syntheses, often preceded by quantum-chemical calculations, to obtain heterocyclic structures with appropriate parameters. An example is a group change in bithiophene-substituted compounds (Fig. 4; BT-1, BT-2, and BT-3), which show higher absorption, the lowest HOMO-LUMO energy gap, and higher λ_{max} compared to other π -acceptors (Fig. 6). The reason for such results is that bi-thiophene abolishes the maximum contribution to LUMO and additionally maintains the balance between planarity and π delocalization. It allocates 83% of its LUMO to π -delocalization and outperforms other π -acceptor units in this regard.

Moreover, the compounds studied whose biphenyl group was replaced by a bi-pyrrole group (Fig. 5) exhibited a wide bandgap, a desirable feature for supercapacitor electrode applications, and were classified as promising compounds in this area.

Also important for optoelectronic studies is the type of bond present in the molecule, e.g. cyano-vinylene bonds in compounds DPA-PA 1-3 (Fig. 2), which increased the flexibility of energy levels and improved the optoelectronic properties. As the system was strongly conjugated, it exhibited a high degree of polarity in the ground state. Also, the electron distribution in the HOMO orbital is uniform, which translates to a uniform distribution of hole density in both the excited molecule and the charge-separated hole carrier. The energy of this orbital is high (-5.08 eV) due to the presence of methoxy groups.

Furthermore, it is confirmed that for the fluorescence to be as high as possible and the electrochemical bandgap to be as small as possible, DPA must be coupled to a good electron acceptor. The use of DPA as an electroactive unit along with TPE afforded a polymer with a high fluorescence contrast. DPA, as an electrodonor group, acted as a strong fluorochrome and greatly improved the fluorescence of the diphenylamine TPE.

Another important parameter, e.g. in the design of biosensors, is to obtain a compound showing high thermal stability. An example could be the diphenylamine derivative, polydiphenylamine (PDPA) (Fig. 11a). PDPA has a high sensitivity to many bioanalytes, which is an advantage in the design of biological sensors used in medicine and industry.

An interesting example of the dependence of optoelectronic properties on the structure is that of flexible benzothiadiazole derivatives. In the crystalline state, DBBT shows its elasticity, even though organic crystals are usually inflexible, and flexible polymers are not crystalline. The balance between elasticity and crystalline state is a big problem in organic materials. The study of flexible crystals with optical abilities can change the view of electronic devices and solve this problem. The results showed that the dense packing of the material should improve charge extraction and mobility in photovoltaic devices, therefore, the use of polymers with shorter chains like in PP_{EH} -DTBT and PP_{EH} -DTffBT is recommended.

Moreover, in subsequent research, it was noticed that the addition of dots can favorably affect the increase in the short-circuit current density. The addition of dots reduced the reflectivity, which favorably affected the absorption of photons by the active layer.

Structurally well-defined DPA and benzothiadiazole derivatives display a wide range of interesting physical properties, including good charge transport, electroluminescence, and improved thermal and morphological stabilities. DPA, as an electrodonor group acting as a strong fluorochrome, and benzothiadiazole, as an efficient solid-state emitter, are promising materials for different optoelectronic devices. The full potential of the materials will certainly be studied in future years.

Author contributions Conceptualization: Dorota Zajac; Literature review and data analysis: Marharyta Hancharova, Karolina Mazur, Kinga Halicka, Dorota Zajac; Writing original draft preparation: Marharyta Hancharova, Karolina Mazur, Kinga Halicka, Dorota Zajac; Writing review and editing: Marharyta Hancharova, Karolina Mazur, Kinga Halicka, Dorota Zajac; Supervision: Dorota Zajac.

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Declarations

Conflict of interest The authors declare that they have no conflict of interest.

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