

Experimental and theoretical investigations on the photophysical and electronic properties of new synthesized organic small molecule for optoelectronic applications

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Abstract

In the present work, we report the chemical synthesis of a newly π -conjugated system using a Wittig reaction. The chemical structure of the synthesized molecule named 1,4-Bis((*E*)-2-(1-methyl-pyrrol-2-yl)vinyl)benzene (**BisPyrBz**) was supported by Fourier transform infrared spectroscopy. The optical properties were investigated first using optical absorption (O.A) and steady-state photoluminescence (PLs) tools. Otherwise, transient photoluminescence (TRPL) and quantum yield measurements (PLQY) are present in a diluted solution and condensed state. Theoretical investigations on the synthesized molecule were performed using density functional density (DFT). Experimental and theoretical data show the formation of a planar π -conjugated system. The obtained molecule presents a blue emission with high PLQY, at around 35% in the solution state. The emission is red-shifted to the green color, with a drastic decrease of the PLQY to around 1% indicating a possible aggregation-caused quenching behavior in the condensed state. The use of the synthesized **BisPyrBz** as a π linker in a newly designed A- π -D small molecule permits to obtain a newly near-infrared absorbing material with a weak energy gap $E_g = E_{LUMO} - E_{HOMO}$, which is at around 1.93 eV, and a weak optical band gap which is estimated to be 1.67 eV.

Keywords: π -conjugated system, optical absorption (O.A), steady-state photoluminescence (PL), dye, density functional density (DFT).

I-Introduction

Since the discovery of new classes of semiconducting organic material, the scientific community (physics and chemistry) focused their attention on the preparation of new organic molecules combining high flexibility and low cost with their modifiable photophysical properties, which permitted several applications, such as organic light emitting diode (OLEDs), organic solar cells (OSCs)[1-2], organic field effect transistors (OFETs), bioapplications, and many others [3-4]. Several efforts were chemically undertaken to enhance the photophysical properties of the conjugated polymers and the performances of the devices based on the used polymers [5-6]. Else, several chemistries focused their attention earlier, on developing new small organic molecule systems, with short and defined main-chain [7-8]. Switching between the polymeric system to the small organic molecule or oligomeric system is worthwhile for several optoelectronic applications such as OLEDs and organic photovoltaic applications [9-10]. The major reason for the switch is that it is far easier to synthesize and produce, purify, and structurally characterize the small organic systems than the polymeric systems. For these reasons, small molecules offer the opportunity for vast and commercial applications in the field of organic electronics [11-12].

Recently, organic solar cells attracted a great deal of interest, due to the versatility of the used organic dyes. In particular, small organic molecules with a defined molecular structure have been successfully synthesized and developed [13-15]. Besides the general donor- π -acceptor (D- π -A) chemical structure [16], new organic sensitizers with chemical structures such as D- π -A, D- π -A- π -D, D-D- π -A, and D-A- π -A have been also employed as a donor part on a new Donor-acceptor bulk-heterojunction for the next generation of organic solar cells [17-20]. The modification of the acceptor or the donor units [21] or the topologies structures [18]

can improve the photovoltaic performances[18,21]. In addition to the donor and the acceptor units, the π -system plays a crucial role on improving the charge transfer between the acceptor and the donor part of the dye molecule and to extend the absorption range along the visible and infra-red solar irradiation [22].

In this paper, we propose the synthesis of a new small molecule based on phenyl and pyrrole monomers that can be used as π linkers in a new D- π -A organic dye for photovoltaic application. The synthesized molecule named **BisPyrBz** has been characterized structurally by NMR and infrared spectroscopies, whereas the optical properties were studied by steady-state optical absorption and photoluminescence spectroscopies as well as by transient photoluminescence spectroscopy. Experimental studies were combined with theoretical simulations on the studied chemical structure using essentially the density functional theory (DFT) to highlight the investigated material's chemical, optical, and electronic structure.

II- Experimental and theoretical methods

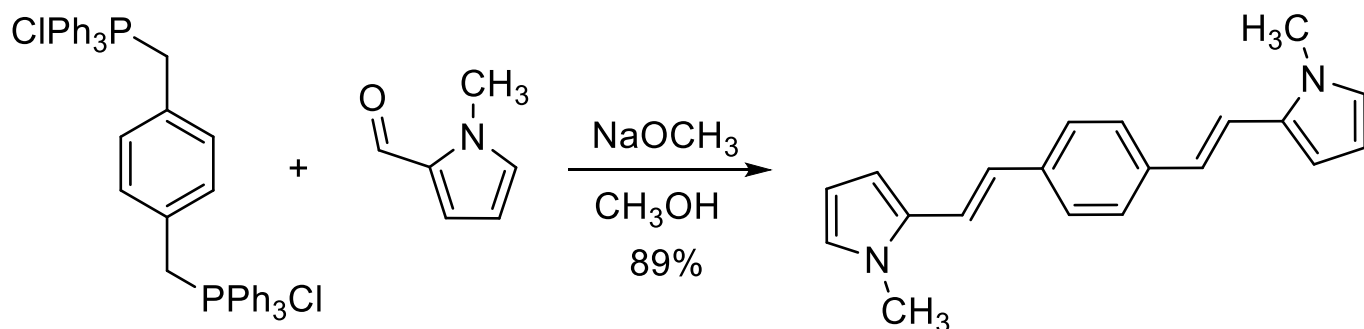
Experimental optical absorption spectra were obtained at room temperature (RT) using a Varian Cary 5G spectrophotometer. Stationary Photoluminescence (PL) and Photoluminescence Excitation (PLE) measurements were carried out at room temperature, using an Agilent spectrophotometer equipped with a 450W Xenon lamp. Fourier-transform infrared analysis (FT-IR) was carried out on a Perkin-Elmer BX FT-IR system spectrometer, and using the FT-IR Attenuated Total Reflectance (ATR) technique. Thermogravimetric analysis (TGA) was obtained on TA Instruments Q50 under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹. The computations on the studied chemical structure were done using density functional theory (DFT) [23] methodologies, implemented in the Gaussian 09 software [24]. The ground state was obtained using the B3LYP functional [25] combined with the 6-31g (d,p) basis set [26]. Simulated vibrational analysis (Frequency) was also recorded at this level of theory. The contour plots of the highest occupied molecular orbital (HOMO) and the lowest unoccupied

molecular orbital (LUMO) of the optimized structure in the ground state were obtained and visualized using the GAUSSVIEW program [27].

III- Synthesis of the BisPyrBz

The synthetic route adopted for the preparation of the compound 1,4-Bis((E)-2-(1-methyl-pyrrol-2-yl)vinyl)benzene (**BisPyrBz**) is shown in Scheme 1. The following procedure was followed: A refluxing solution of p-Xylylenebis(triphenylphosphonium chloride) (1.0 g, 1.42 mmol) and N-Methyl-2-pyrrolecarboxaldehyde (0.34 g, 3.14 mmol) in dry methanol (25 mL) was prepared. Over a period of 0.5 hours, sodium methoxide (1 M in methanol) was added to the solution under an argon atmosphere. The mixture was then heated at reflux for 3 hours. After cooling to room temperature, the reaction mixture was concentrated under vacuum to reduce its volume by half. Distilled water was added, and the resulting solution was extracted multiple times with a large volume of CHCl_3 . The residue obtained after drying and solvent removal was subjected to chromatography on silica gel using cyclohexane/ethyl acetate (95:5, v/v) as the eluent. This yielded 0.36 g of dark yellow powder, with a total yield of 89%.

$^1\text{H NMR}$ (CDCl_3 , ppm) δ : 7.44 (s, 4H, ArH), 6.99 (d, 2H, $J = 16.2$ Hz, C=CH), 6.87 (d, 2H, $J = 16.2$ Hz, C=CH), 6.67–6.66 (m, 2H, PyH), 6.53–6.51 (m, 2H, PyH), 6.20–6.17 (m, 2H, PyH), 3.73 (s, 6H, N-CH₃). $^{13}\text{C NMR}$ (CDCl_3 , ppm) δ : 137.04, 132.53, 126.60, 126.04, 124.05, 116.99, 108.74, 107.14, and 34.53.



Scheme 1: Chemical synthesis of the 1,4-Bis((E)-2-(1-methyl-pyrrol-2-yl)vinyl)benzene (**BisPyrBz**)

IV-Results and discussions

IV-1- Theoretical conformational analysis on the BisPyrBz chemical structure

A conformational analysis of the studied chemical structure is theoretically undertaken. Torsion potential curves of the **BisPyrBz** microstructure are obtained using the DFT/B3LYP/6-31G(d,p) tools of calculation. The studied torsional angles are ($\theta_1(^{\circ})$ and $\theta_2(^{\circ})$), as defined in Figure 1: $\theta_1 = (C7-C8-C9-N16)$ and $\theta_2 = (C6-C5-C7-C8)$.

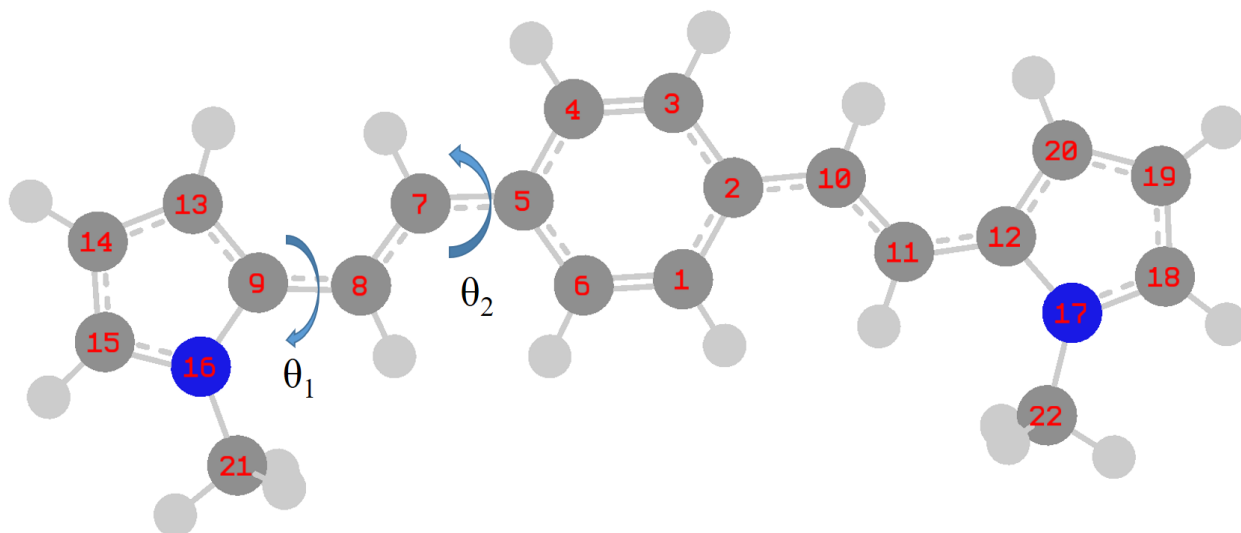


Figure 1: The Chemical structure of the **BisPyrBz**

The relative energies as a function of torsional angles were recorded by varying the torsional angles (θ_1 and θ_2) from 0° to 180° in 10° increments during the scan process. The obtained relative energy as a function of θ_1 is registered and presented in Figure 2.

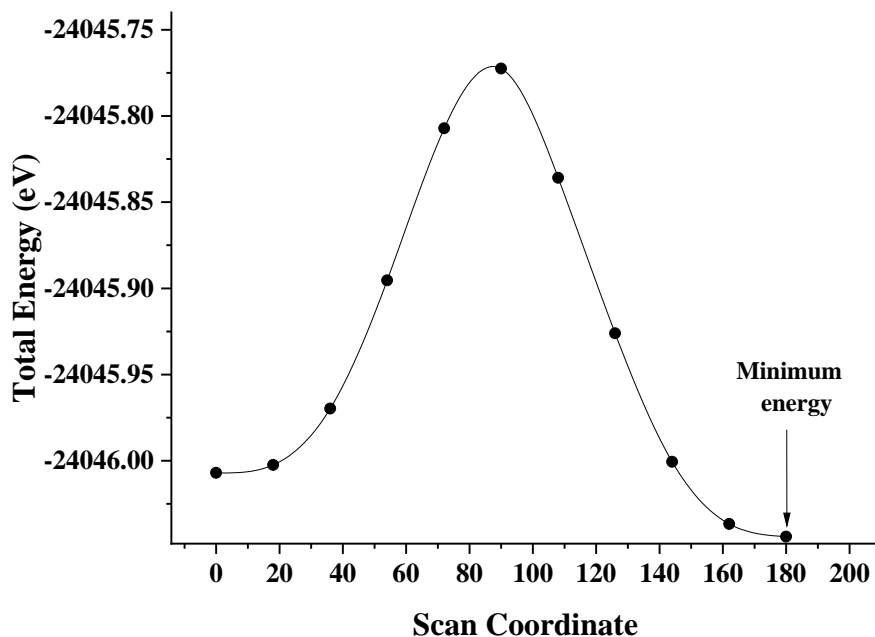


Figure 2: Potential energy curves of **BisPyrBz** as a function of torsional angles θ_1 ($^\circ$)

Figure 2 shows that the minimum energy is achieved at $\theta_1 = 180^\circ$. Meanwhile, the relative energy obtained by varying θ_2 is registered and depicted in Figure 3. From Figure 3, one can deduce that the minimum energy is obtained for $\theta_2 = 0^\circ$. The obtained results show that a planar conformation is obtained in the ground state.

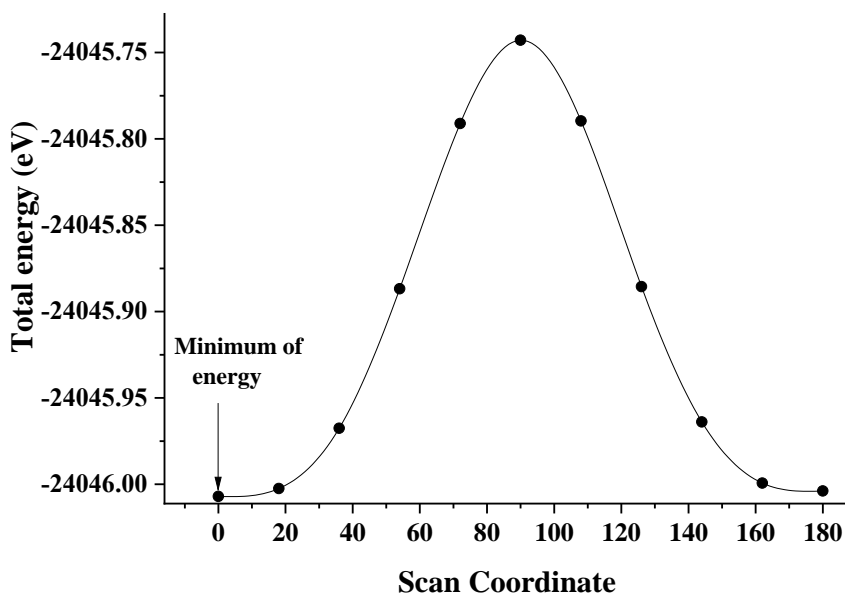


Figure 3: Potential energy curves of **BisPyrBz** as a function of torsional angles θ_2 ($^\circ$)

Based on the conformational analysis, the molecular structure of **BisPyrBz** was optimized on the ground state by the means of the DFT/B3LYP/6-31G(d,p) level of theory, and the resulting

structure is depicted in Figure 4. The figure underlines the planar structure of the dye in the ground state.

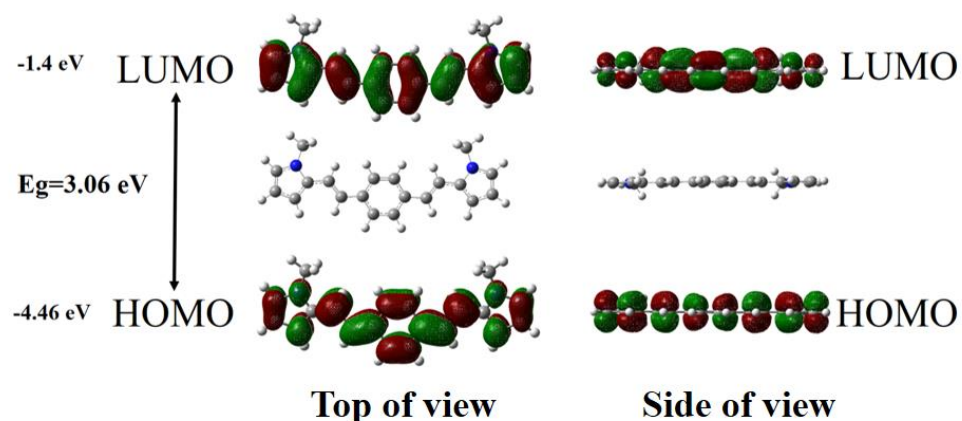


Figure 4: The optimized molecular structure of **BisPyrBz** and their contour plots HOMO and LUMO orbitals obtained by using the DFT/B3LYP/6-31G(d,p) level of theory.

Based on the optimized chemical structure of **BisPyrBz**, the contour plots of HOMO and LUMO orbitals are drawn using Gaussview software and presented in Figure 4. The HOMO and LUMO energies were estimated to be respectively -4.46 eV and -1.4 eV, inducing an energy gap HOMO-LUMO at around 3.06 eV. The planarity of the optimized chemical structure of the **BisPyrBz** permits to obtain a large distribution of the HOMO and LUMO orbitals on all the backbone of the chemical structure in the ground state.

From the DFT/B3LYP/6-31G(d,p) optimized chemical structure of the BisPyrBz on the ground state, the molecular electrostatic potential (MEP) was drawn using Gaussview software and depicted in Figure 5

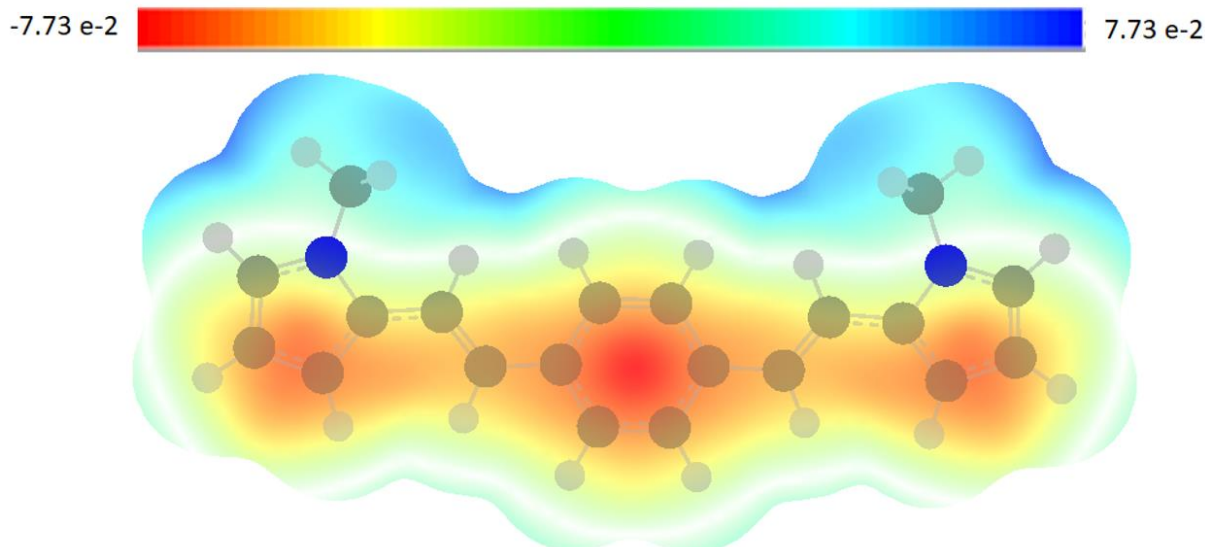


Figure 5: Molecular electrostatic potential (MEP) of **BisPyrBz**

The false color going from blue to red color in the obtained maps shows the abundance of the charge on the presented surface: the surface with blue color is a signature of the absence of electrons, while the surface in red color is due to the abundance of electron in the region [28]. From Figure 5, one can deduce that in the ground state, the electrons are localized into the backbone of the molecule, while the CH₃ molecule presents a blue color as a signature of the abundance of the hole.

IV-2-Vibrational investigations (FT-IR analysis)

The experimental Infrared spectrum of **BisPyrBz** is obtained using the ATR technique. The obtained spectrum is depicted in Figure 6. The most dominant bands are found in the region 500-1780 cm⁻¹. By analyzing the obtained infrared spectrum, we detect characteristic main vibrations of the C-H stretching mode at 690-820, 1065, and 1378 cm⁻¹ [29-30]. The bands detected at 965, 1510, and 1675 are due to the main vibration of the C-C stretching mode of the aromatic phenyl group [28-30]. While the band detected at 1600 cm⁻¹ is assigned to C=C stretching in the phenyl ring [30-31]. The C-N stretching deformation is detected at 1250 cm⁻¹. Added to that intense bands are detected in the range 2850-2956 due to the main vibration of the C-H stretching modes of the methyl (CH₃) group [32].

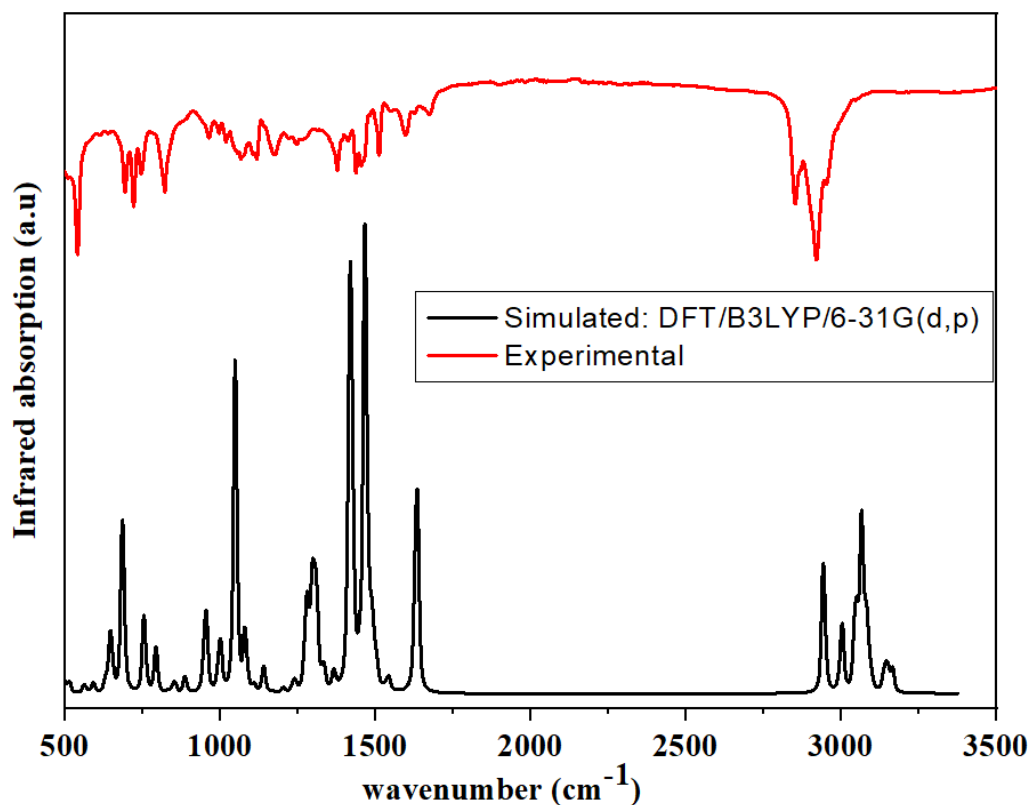


Figure 6: The DFT/B3LYP/6-31G(d,p) simulated and experimental infrared spectra of **BisPyrBz**.

The simulated infrared spectrum is obtained by DFT/B3LYP/6-31G(d,p) level of theory and the obtained spectrum was corrected using the scale factor 0.9668 [33-34] and presented in Figure 6. Notably, no imaginary frequencies were detected in the simulated infrared spectrum. Additionally, the obtained simulated spectrum reproduces the experimental one in terms of the position of the vibrational bands, which confirms the proposed optimized chemical structure of the **BisPyrBz**.

IV-3- Optical properties of the synthesized **BisPyrBz** molecule

IV-3-1- Optical absorption properties of **BisPyrBz**

The optical absorption spectrum of **BisPyrBz** was recorded in CHCl_3 diluted solution (1.5×10^{-5} M) and in thin prepared film. The optical absorption spectra in solution and solid state are presented respectively in Figure 7a and 7b.

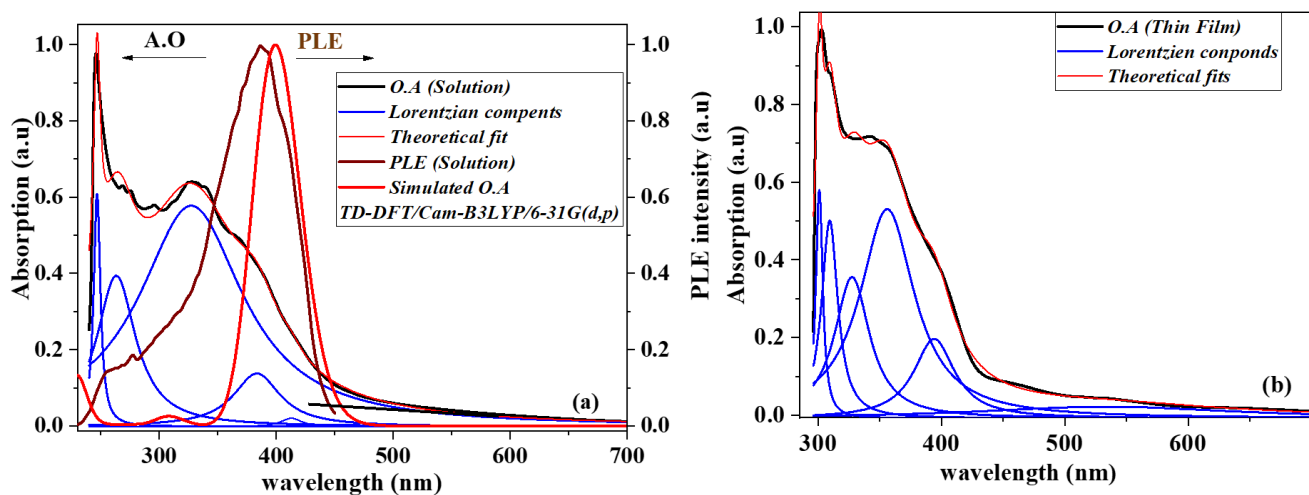


Figure 7: (a) Normalized optical absorption and PLE spectra of **BisPyrBz** recorded in diluted solution ($c = 1.5 \times 10^{-5}$ M). (b) Normalize optical absorption spectrum of **BisPyrBz** thin film

The **BisPyrBz** synthesized molecules absorbs in the ultraviolet (UV) and in the near visible part of the electromagnetic spectrum, in solution and in solid state (thin film). Similar observations are obtained by synthesizing a new small molecules named -N-phenylcarbazole-capped 10-vinylanthracene isomers, absorbing in the UV near visible part [35].

The deconvolution of the optical absorption spectrum recorded in solution state into Lorentzian profiles (Figure 7a) reveals the presence of five absorption transitions, centered respectively at around 246, 264, 328, 383, and 412 nm. Meanwhile, the deconvolution of the optical absorption spectra recorded in solid state into Lorentzian profile (Figure 7b) reveals the presence of five optical absorption transitions centered at around 300, 310, 330, 355 and 400 nm.

Photoluminescence excitation spectroscopy (PLE) was recorded in chloroform diluted solution (Figure 7a) for the maximum emission at 460 nm. The obtained PLE spectra present a maximum at around 380 nm.

Using the TD-DFT/Cam-B3LYP/6-31G(d,p) level of theory, the simulated optical absorption spectra of the **BisPyrBz** molecules was calculated using the chloroform as a solvent and The CPCM as a model, to consider the solvation effect [36]. Using GaussSum software [37], the

simulated optical absorption spectrum is drawn and presented in Figure 7a. The simulated spectrum reproduces the experimental PLE spectrum with a maximum absorption at around 400 nm. Else, using GaussSum software, the optical transitions in solution state are assigned and presented in Table 1.

Experimental wavelength (nm) (Solution)	Simulated wavelength (nm) TD-DFT/CAMB3LYP/6-31G(d,p)	Electronic transition	Oscillator strength (<i>f</i>)	Major contribution
412	400	S ₀ -S ₁	1.9774	HOMO->LUMO (93%)
383	310	S ₀ -S ₂	0.05	H-1->LUMO (70%), HOMO->L+1 (27%)
328	280	S ₀ -S ₃	0.0068	H-5->LUMO (17%), H-1->LUMO (12%), HOMO->L+1 (30%), HOMO->L+2 (32%)
264	255	S ₀ -S ₄	0.0073	H-5->LUMO (13%), H-1->LUMO (13%), HOMO->L+1 (38%), HOMO->L+2 (28%)
246	230	S ₀ -S ₈	0.1997	H-5->LUMO (64%), HOMO->L+2 (33%)

Table 1: Main transitions, assignments, experimental versus simulated wavelengths and oscillator strengths of BisPyrBz

IV-3-2- Steady-State Luminescence properties of the BisPyrBz

Luminescence properties of **BisPyrBz** were first investigated in solution state by steady-state photoluminescence spectroscopy. A diluted solution of **BisPyrBz** ($c = 1.5 \times 10^{-5}$ M) was prepared using CHCl₃ as a solvent and the solution was excited in the UV-visible region (200-

500 nm) under 10 nm steps. A 3-D map was obtained presenting the photoluminescence dependence on the wavelength of excitation (Figure 8).

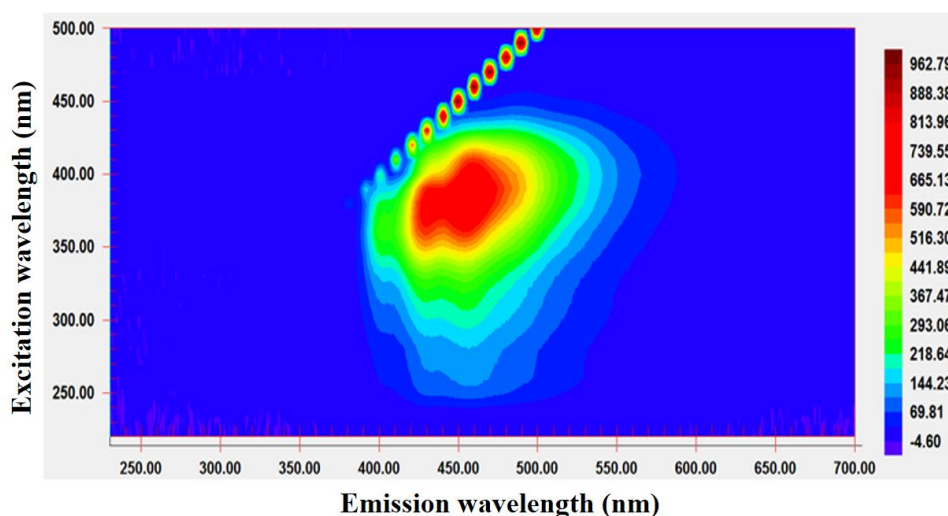


Figure 8: Photoluminescence dependence on the wavelength excitation light: PLE maps of **BisPyrBz** recorded in diluted solution ($c = 1.5 \times 10^{-5}$ M).

In the obtained 3D map, the color goes from blue to red presenting the increase of the PL intensity from low to high emission. From the map, a vibronic emission is obtained, and no emission occurred for the low-wavelength excitations ($\lambda_{exc} < 250$ nm) and under the high-wavelength excitation ($(\lambda_{exc} > 450$ nm). The high-intensity PL is obtained by exciting between 350 and 420 nm (red color), as confirmed by the PLE spectrum reported in Figure 7.

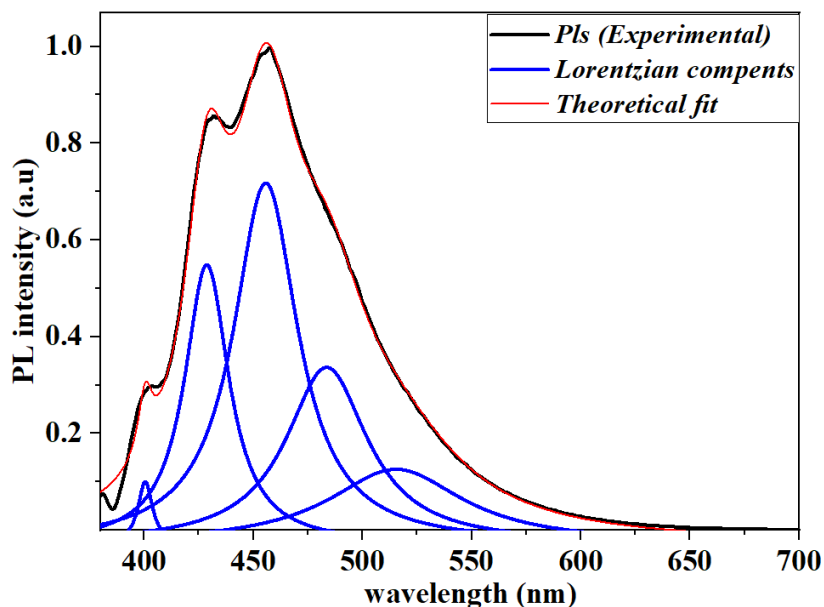


Figure 9: Photoluminescence spectrum of **BisPyrBz** in diluted chloroform solution

$$(\lambda_{\text{exc}} = 380 \text{ nm}, c = 1.5 \times 10^{-5} \text{ M}).$$

Figure 9 depicts the PL spectrum obtained under excitation at the maximum PLE wavelength (380 nm). A vibronic spectrum containing multi-optical transition is obtained. The deconvolution of the obtained PL spectrum into the Lorentzian profile shows the presence of five emission transitions centered respectively at 400, 430, 460, 480, and 520 nm. Similar PL observations are obtained and a broad and vibronic PL spectra were obtained in synthesising a planar small molecule based on phenyl rings [38-39]

Based on the optimized chemical structure on the ground state, the excited state was obtained by the re-optimisation of the chemical structure of the **BisPyrBz** by the TD-DFT/Cam-B3LYP-6-31G(d,p) level of theory. The optimised chemical structure in the first excited state is presented in Figure 10

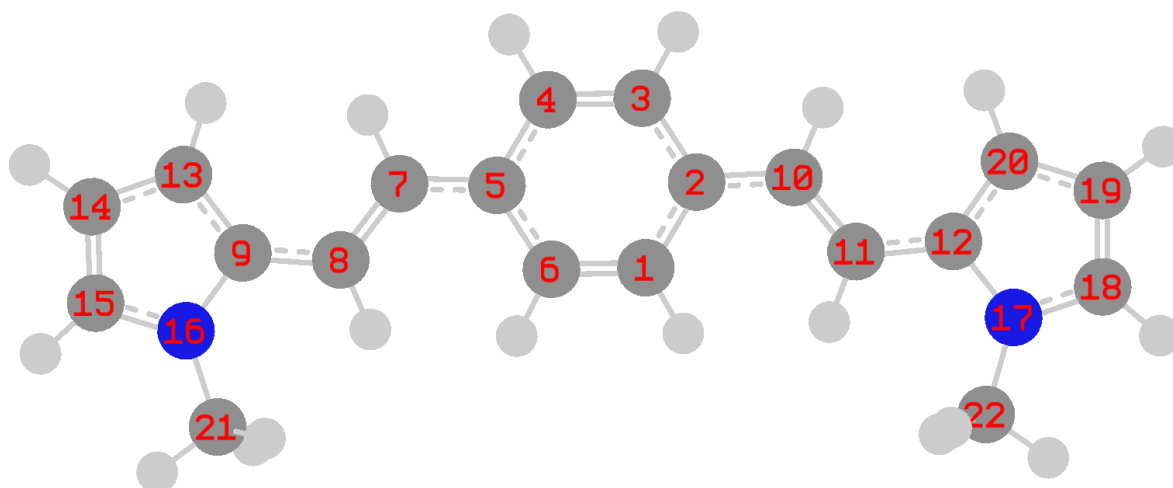


Figure 10: The optimized chemical structure of the **BisPyrBz** in the first excited state (TD-DFT/Cam-B3LYP/6-31G(d,p))

The geometric parameters such as bond length (C_i-C_j) in the ground and excited state are collected and summarized in Table 1a (supporting information). Going from the ground to excited state, a change on the bond length is occurred (see table 1a supporting information). Else, the dihedral angle (°) are collected in table 1b (supporting information). From table 1b we can deduces that a planar chemical structure was obtained in the ground and first excited state (see table 1b supporting information), which favours the formation of the aggregation and non emissive aggregation species in the solid states. From the excited state obtained by TD-DFT/Cam-B3LYP/6-31G(d,p), the simulated PL spectra is obtained and presented in Figure 11

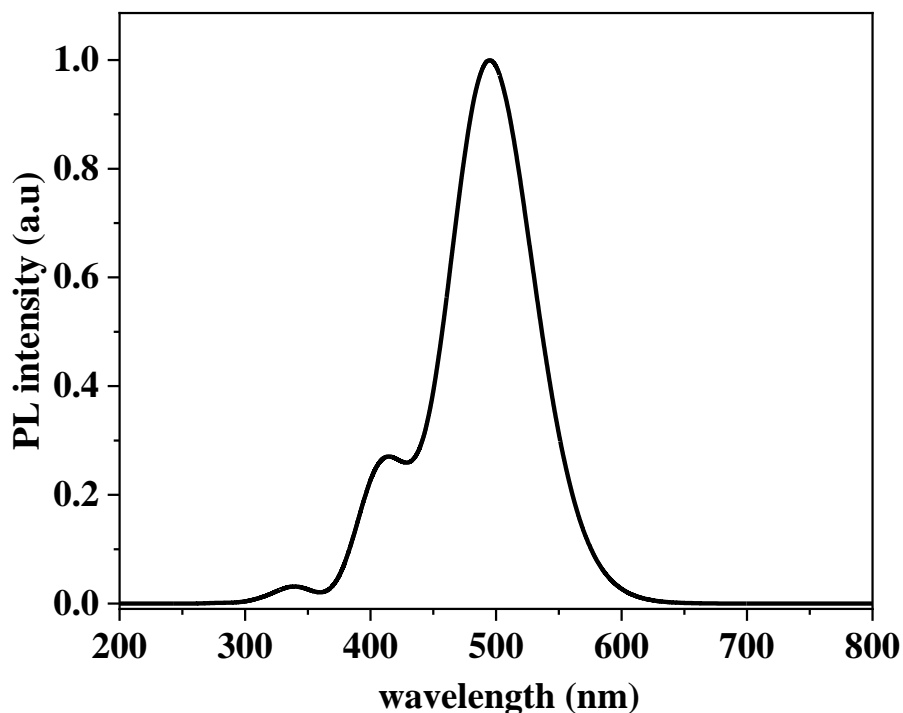


Figure 11: The TD-DFT/Cam-B3LYP-6-31G(d,p) simulated PL spectrum of the **BisPyrBz**

The simulated PL spectra is calculated using the chloroform as a solvent with the CPCM model. Compared to the experimental spectrum, a broad and vibronic spectrum is obtained with multi-optical transition and a maximum emission at around 495 nm.

Afterwards, excitation and emission spectra were recorded at different concentrations (34.6 and 346 μM) to investigate possible aggregation effects, and the results are reported in Figure 12. In solution, both excitation and emission bands are not affected by the increased concentration, with maxima at 380 nm and 450 nm for PLE and PL, respectively. On the contrary, spectra recorded in a solid state appear very different from the solution. The dye in solid state was investigated as powder and thin film. The latter was obtained by drop-casting a solution of dye in polymethylmetacrylate (PMMA) 10 wt% dissolved in chloroform. To prepare the thin film, the PMMA:dye solution was carefully dripped onto a cleaned glass plate (100 μL), and dried at room temperature for several minutes until a homogeneous film was formed.

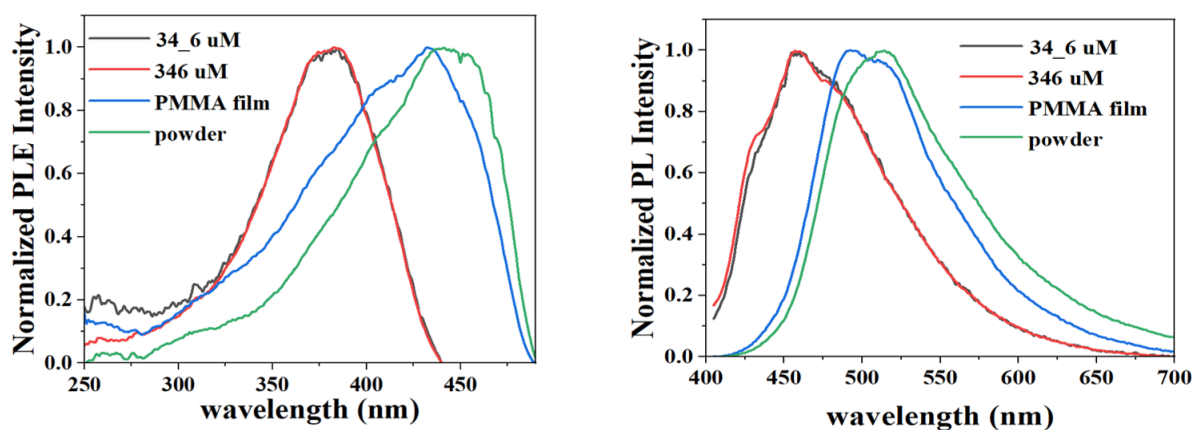


Figure 12. Excitation (PLE, left) and emission (PL, right) spectra of **BisPyrBz** recorded in CHCl_3 at different concentrations, in thin films, and in powder.

PLE and PL in both solid states are red-shifted compared to the solution, suggesting the formation of aggregated structures. The excitation spectrum in powder appears slightly shifted to lower energy compared to the PLE in thin film (440 nm vs. 432 nm, respectively). A more pronounced bathochromic shift is observed in the PL spectra. The maxima of the band are at 492 nm (thin film) and 514 nm (powder), resulting in blue-greenish and green emission colors compared to the blue observed in the solution (see Figure 13).

CIE 1931

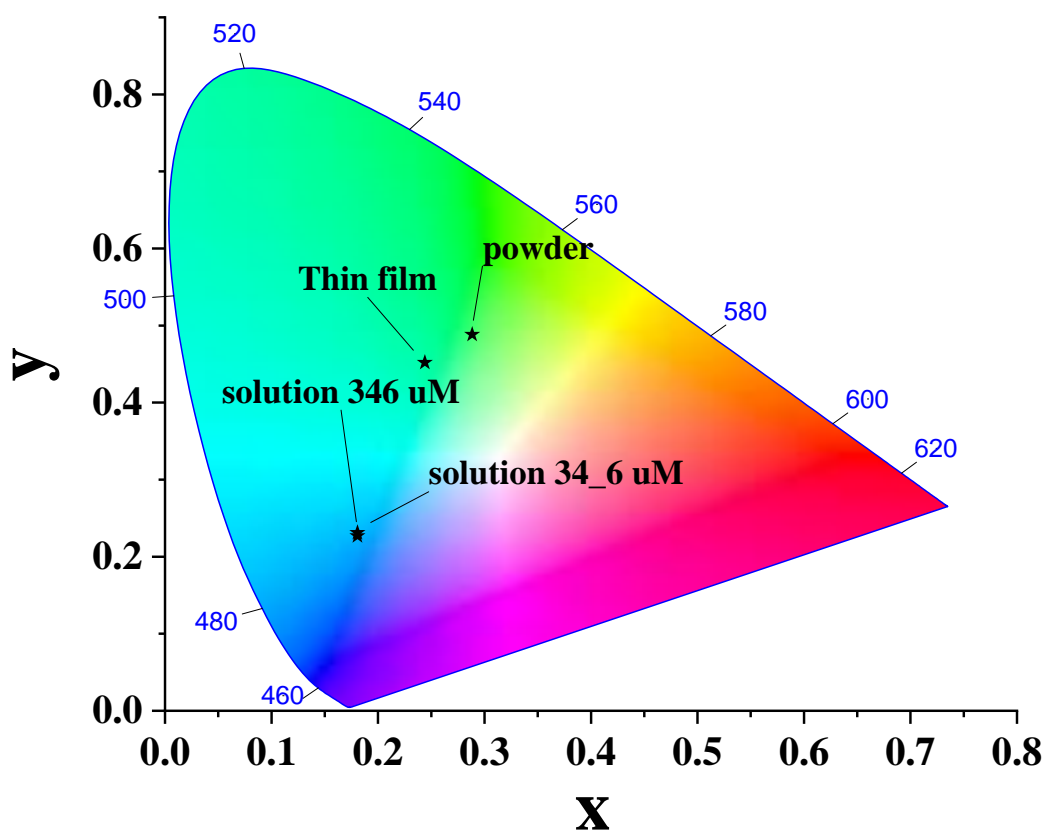


Figure 13. Color coordinates of the studied dye in solution, powder and thin film state in the CIE 1931 diagram

The emission quantum yield (PLQY) decreases dramatically from solution to solid state (from 35% to 1% in both thin film and powder), indicating possible aggregation-caused quenching behavior. The radiative decay in solution appears monoexponential, indicating the presence only of isolated dye as emitting species. In both solid-state forms, the radiative decay becomes multiexponential, further supporting the hypothesis of the presence of aggregates. The observed red shift in the solid state could be associated to the restriction of rotational freedom of the molecule, which hampers the rearrangement of the dye in the excited state to a configuration suitable for an efficient radiative decay. Nevertheless, the formation of some aggregates generating an extended conjugation system cannot be totally excluded. The photophysical data are summarized in Table 2.

BisPyrBz	Abs (nm)	PLE (nm)	PL (nm)	PLQY (%)	τ (ns)
Solution	330, 380sh ^b	380	455	35	0.82
Thin film ^a	-	432	492	1	0.95 ^c
Powder	-	440	514	1	0.68 ^c

a: in PMMA (10 wt%). b: shoulder. c: average value.

Table 2. Summarized photophysical data.

VI- Thermal analysis

Thermal properties of **BisPyrBz** were elucidated by thermogravimetric analysis (TGA) under a nitrogen atmosphere. From the TGA curve (Figure 14), one can deduce that the synthesized material presents good thermal stability. Indeed, the material remains stable until at around 280 °C. Else, a rapid degradation started at around 300 °C (Figure 14), which completely decomposes at around 600 °C.

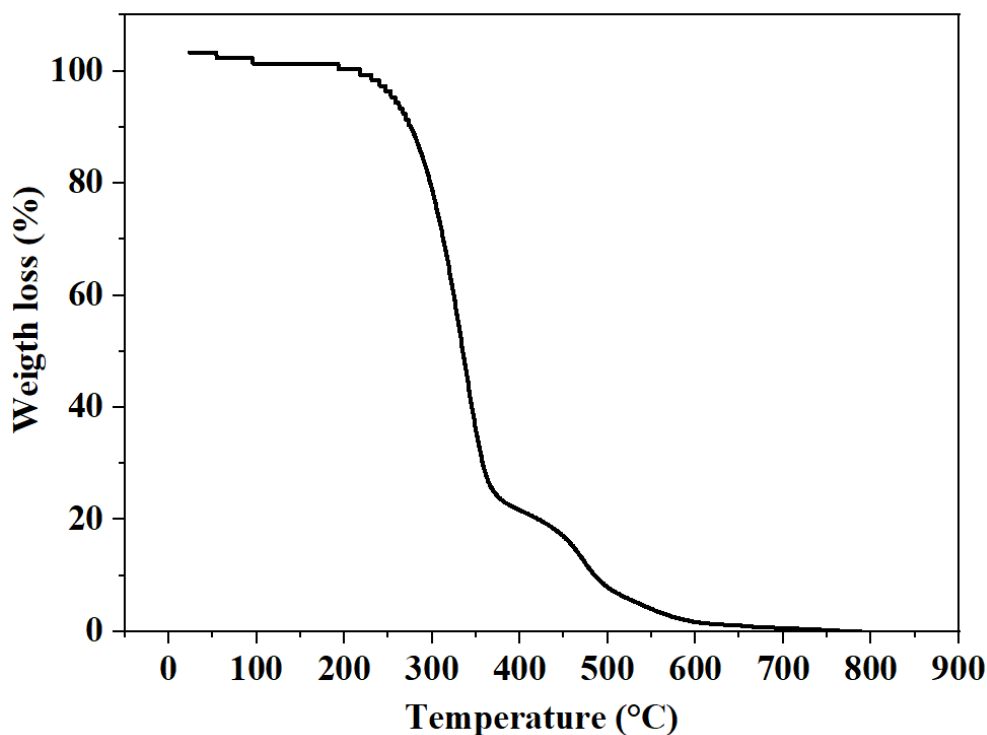


Figure 14: TGA curve of **BisPyrBz**.

V- Designing of new A- π -D absorbing small molecule using the synthesized BisPyrBz as a π linker

In this part, we attempt to design a newly small **A- π -D** small molecule for photovoltaic application. The synthesized **BisPyrBz** is used as a π -linker between a chosen acceptor and donor molecule (See Figure 15). In this work, the donor ring is a carbazole molecule, while the acceptor chosen ring is a benzothiadiazole derivative: 2-methyl-2H-[1,2,3]triazolo[4,5-g]quinoxaline. The designed molecule was optimized by DFT/B3LYP/6-31G(d,p) level of theory, and the optimized structure is depicted in Figure 15. From the optimized chemical structure, the contour plots of HOMO and LUMO orbitals are drawn using Gauss view software [27] and presented with their energies value in Figure 16. The HOMO orbital is localized in the partial part of the donor part, and essentially in the **BisPyrBz** π linker, while the LUMO orbital is localized in the acceptor part, due to a local intramolecular charge transfer occurring into the obtained molecule [40].

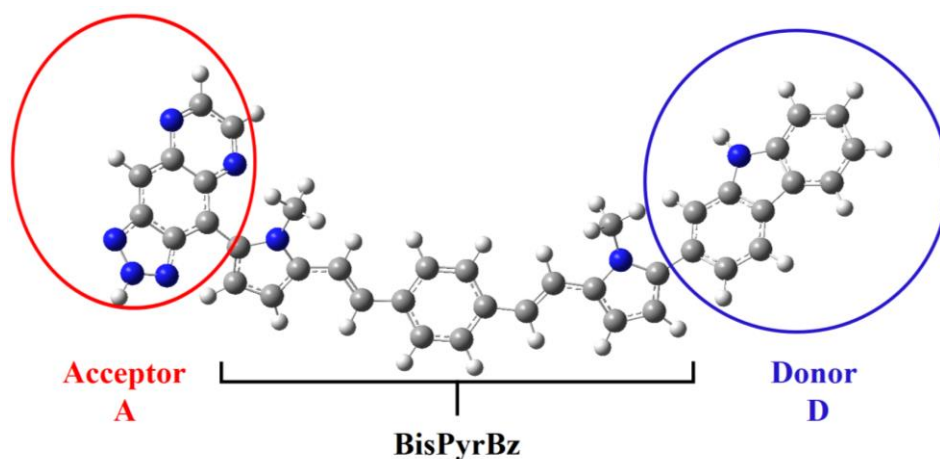


Figure 15: The DFT/B3LYP/6-31G(d,p) optimized chemical structure of the **A- π -D** small designed small molecule based on the synthesized **BisPyrBz** as a π linker.

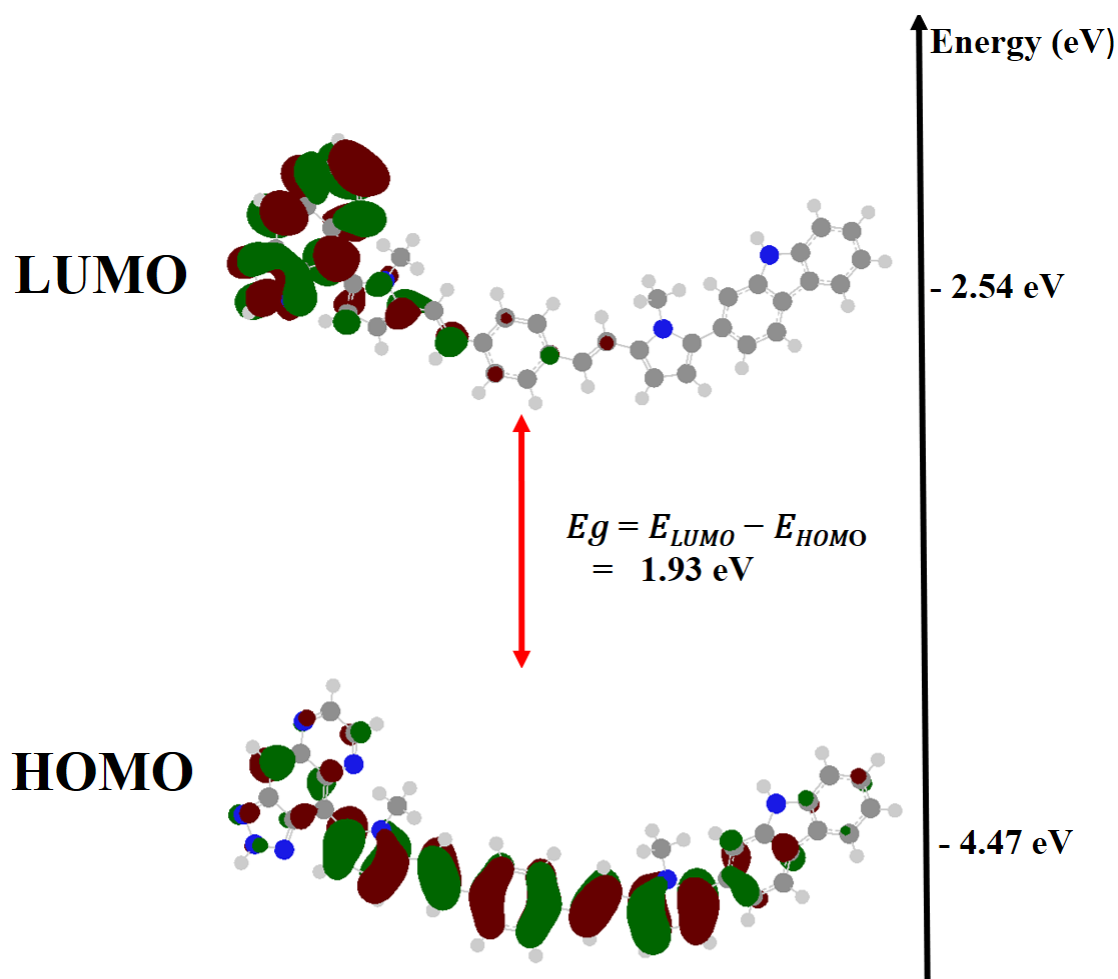


Figure 16: Contour plots of the HOMO and LUMO orbitals of the designed A- π -D small molecule and their energies values deduced from the DFT/B3LYP/6-31G(d,p) level of calculation.

Based on the DFT/B3LYP/6-31G(d,p) level of theory, the HOMO and LUMO energy was calculated and presented in Figure 16. The HOMO presents energy at around - 4.47 eV and The LUMO presents energy at around -2.54 eV, which induces a reduced energy gap $E_g = E_{LUMO} - E_{HOMO}$, at around 1.93 eV. The obtained result reveals that the designed molecule based on the BisPyrBz as a π linker is a good candidate for photovoltaic application.

Based on the DFT/B3LYP/6-31G(d,p) optimized chemical structure, the simulated optical absorption spectrum of the A- π -D designed small molecule was simulated using the TD-DFT/B3LYP/6-31G(d,p) level of theory and drawn using GaussSum software [37].

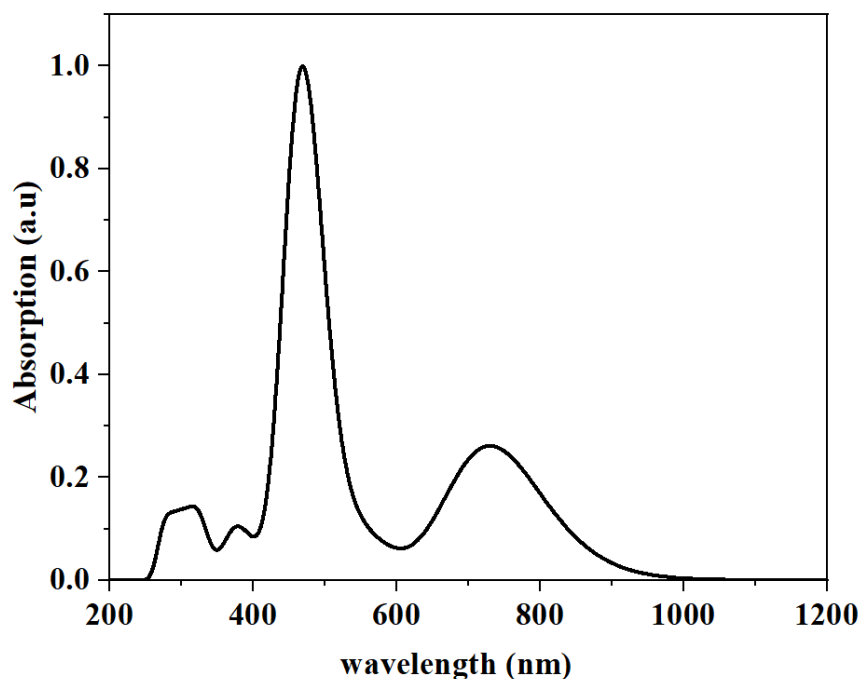


Figure 17: The TD-DFT/B3LYP/6-31G(d,p) simulated optical absorption spectrum of the A- π -D designed small molecule.

The simulated optical absorption spectrum is depicted in Figure 17. The designed molecule presents good absorption in the visible and near-infrared regions (Figure 17), presenting also a near-infrared absorbing A- π -D designed small molecule. Based on the simulated optical absorption spectrum, the simulated optical absorption spectrum is calculated which is at around 1.67 eV.

Conclusion:

In summary, using a Wittig reaction, we have synthesized a new small organic molecule based on pyrrole and phenyl group named **BisPyrBz**. Based on experimental investigation and quantum chemical simulation, the structural and electronic properties were examined. DFT investigations show a planar chemical structure was obtained which induces an extension of the HOMO and LUMO orbitals until the formed backbone of the **BisPyrBz**. The high planarity of the obtained π system induces a high degree of the π - π stacking in the condensed state, which induces a high degree of possible aggregation. Consequently, a strong quenching of the luminescence is observed in the condensed state and a high decrease of the PLQY from 35% in

solution to 1% in thin prepared film. The high planarity of the synthesized π -system combined with the good thermal stability encourages the endorsement of the synthesized molecule on a newly A- π -D system. Otherwise, using DFT methodology, a new A- π -D system using the synthesized **BisPyrBz** molecule as a π linker was theoretically established. The use of the **BisPyrBz** molecule as a π linker permits a good charge transfer between the chosen acceptor (A) and the donor (D), which permits to obtain a new molecule with an energy gap HOMO-LUMO at around 1.93 eV and presenting a high absorption in the visible and near-infrared part.

Author Contributions: All authors contributed to the study design and analysis. The initial draft of the manuscript was collectively authored by all contributors. Subsequently, all authors reviewed and endorsed the final version

Funding: The authors have not disclosed any funding.

Data Availability Statement: The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

Acknowledgments: The authors gratefully acknowledge the support of King Abdulaziz University's High-Performance Computing Centre (Aziz Supercomputer) for facilitating the computational DFT calculations conducted in this study. The authors are grateful to ing Aida Ben Mansour for their help in the stationary photoluminescence measurements.

Conflicts of Interest: The authors assert that they have no competing interests

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