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Proceeding Paper

α-Substituted BODIPY Molecules: A Photophysical Comparison Between Pyrrolyl and Thienyl Substituted BODIPY [†]

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Abstract: This study explores the photophysical properties of two α-substituted BODIPY dyes: thienyl-substituted (DTPBDP) and pyrrolyl-substituted (DPyPBDP). Both dyes were synthesized and analyzed in spin-coated polystyrene films using absorption, emission, and amplified spontaneous emission (ASE) measurements. DTPBDP exhibited efficient ASE with a red-shifted emission under 640 nm excitation, while DPyPBDP required higher excitation energy and degraded. These results emphasize the impact of α-substituents on ASE performance and suggest DTPBDP's potential for laser applications, contributing to the development of sustainable, high-performance optoelectronic materials.

Keywords: BODIPY dyes; Amplified Spontaneous Emission (ASE); ultrafast spectroscopy

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1. Introduction

The rapid advancement of emerging technologies, from nanomedicine and personalized medicine to stimuli-responsive smart materials and organic electronics [1,2], presents unparalleled opportunities for progress across various fields, while also addressing urgent societal needs. However, the highest-performing materials currently in use often rely on rare elements like lanthanide-based metal complexes [3,4], which do not align with the sustainability requirements essential for modern society. In this context, organic dyes have garnered significant attention, as their production does not depend on the extraction of non-renewable rare earth elements. As a result, they represent a more accessible and environmentally friendly alternative for meeting the increasing demand for high-performance materials.

Despite their potential, several challenges remain, like the development of organic dyes that can absorb and emit light in the red and near-infrared regions. One particularly promising material in this respect is 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) [5]. This fluorescent organic chromophore has attracted substantial interest due to its versatile properties and wide range of applications [5,6]. The chemical structure of BODIPY is defined by a boron–dipyrrin core, which offers several advantages: strong absorption and emission in the visible-to-red region of the spectrum, high fluorescence quantum yields, excellent stability, and tunable optical properties via structural modifications.

Over the years, numerous synthetic strategies have been developed to fine-tune the optoelectronic properties of BODIPY. By modifying the position and type of substituents, key parameters such as the delocalization of π-electrons in the molecule and the supramolecular organization and morphology of solid thin films can be adjusted [7]. The

BODIPY core has eight reactive positions that can be exploited to tailor its optical properties: two α-positions; four β-positions, which strongly influence electronic delocalization; and the meso- and boron positions, which primarily impact steric hindrance and, consequently, thin-film properties. One of the most common strategies for red-shifting the absorption and emission spectra involves substituting the α-position of the molecule with electron-rich moieties [8–10], or substituting the carbon in meso position with a nitrogen (AZA-BODIPY) [11,12].

In this study, we have synthesized and explored the photophysical properties of a symmetric thienyl-substituted (DTPBDP) BODIPY alongside a pyrrolyl-substituted BODIPY (DPyPBDP). Thiophene and pyrrole are both five-membered aromatic heterocycles, but they differ in their electronic properties, particularly pyrrole shows a stronger electron-donating ability compared to the thiophene ring. Since the BODIPY unit is generally considered an electron acceptor, this characteristic allows for a redshift in the absorption and emission of the final molecule. By comparing their absorption and emission spectra, amplified spontaneous emission, and stability characteristics, we aim to elucidate how these α-modifications, specifically the introduction of a stronger electron rich moiety, influence their performance. This research not only contributes to the fundamental understanding of BODIPY chemistry but also to the developing of enhanced fluorescent probes with tailored functionalities for diverse applications in advanced sensing technologies and high-performance optoelectronic devices.

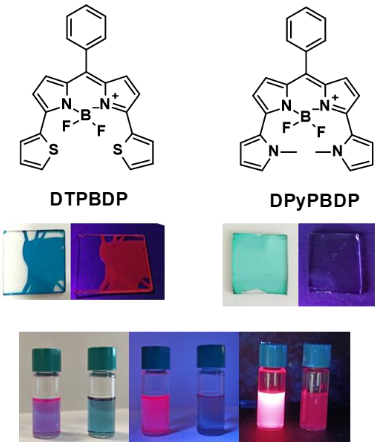


Figure 1. The structures of the two BODIPY molecules, the spin-coated films of the dyes dispersed in polystyrene matrix under visible and UV light and the chloroform solutions of the dyes under visible light, 400 nm and 366 nm.

2. Materials and Methods

General information for synthesis. All reagents were purchased from commercial source and used without further purification. All solvents have been distilled prior to use. All reaction were carried out in inert atmosphere. The ^{1}H NMR spectra were recorded with a Bruker ARX 400 MHz spectrometer (Bruker, Karlsruhe, Germany). Gas-phase mass determination was carried out using the Agilent Technologies 7890A GC System (Santa Clara, CA, USA) coupled with an Agilent Technologies 5975C VL MSD (Santa Clara, CA, USA) with a triple-axis mass detector.

*Synthesis of monomer **M1**.* Benzaldehyde (1 g, 9.4 mmol) was dissolved in excess of pyrrole (25.2 g, 40 eq). The resulting mixture was degassed for 30 min by nitrogen and then 100 μL of trifluoracetic acid were added. The reaction was stirred at room temperature for an hour and the crude product was diluted with dichloromethane and washed three times with sodium hydroxide (NaOH) aq. 0.1 N and dried on magnesium sulphate. The solvent was removed under reduced pressure. The product was purified by column chromatography on silica gel using hexane/ethyl acetate 9:1 as eluent. The pure product was obtained as a brown powder with a yield of 66% (1.360 g). Purity controlled with GC-MS (*m*/*z* = 222.1).

Synthesis of monomer ***M2***. Monomer M1 (600 mg, 2.7 mmol) was dissolved in dry THF and cooled down to −78 C under nitrogen. N-Bromosuccinimide (961 mg, 5.4 mmol) was added portionwise in three time over 10 min. After one hour, the reaction mixture was controlled by GC/MS, showing only the dibromoderivative and a slight amount of mono-brominanted compound. The reaction mixture was then warmed to room temperature. A solution of dry THF (15 mL) and DDQ (612 mg, 2.7 mmol) was added dropwise to the reaction mixture in 10 min. After 10 min, the solvent was removed and the crude product was quickly purified on silica gel using dichloromethane as eluent. The compound was then redissolved in dry toluene (35 mL), DIPEA (1640 g, 12.69 mmol) was added and the mixture stirred at room temperature for 90 min. Finally the boron trifluoride diethyl etherate (5.7 mL) was added and the mixture was stirred at 80 °C for 2 h and then cooled at room temperature. The crude product was washed with water and dried on magnesium sulphate. The solvent was removed under reduced pressure and the product was purify by silica gel chromatography using a mixture of hexane/ethyl acetate 8:2 as eluent. The pure product was obtained as shine dark violet crystalline powder with a yield of 49% (561 mg). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50–7.45(m, 5H) 6.84(d, J = 4.3 Hz, 2H), 6.54 (d, J = 4.3 Hz, 2H).

Synthesis of ***DTPBDP***. Monomer M2 (100 mg, 0.24 mmol), $Pd(PPh_3)_4$ (15% mol, 41 mg) and 2-(tributylstannyl)thiophene (4 eq., 360 mg) were refluxed in dry toluene (10 mL) under nitrogen and under stirring. After 24 h the reaction mixture was diluted in dichloromethane and filtered on celite pad. The solvent was removed under reduced pressure and the crude product purified by silica gel chromatography using hexane/dichloromethane 7:3 as eluent. The pure product was obtained as shine dark blue crystalline powder with a yield of 60%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.2(d, J = 3.8 Hz, 2H) 7.55–7.50 (m, 5H) 7.48(d, J = 4.3 Hz, 2H) 7.20 (t, J = 4.3 Hz, 2H) 6.81–6.78 (m, 4H).

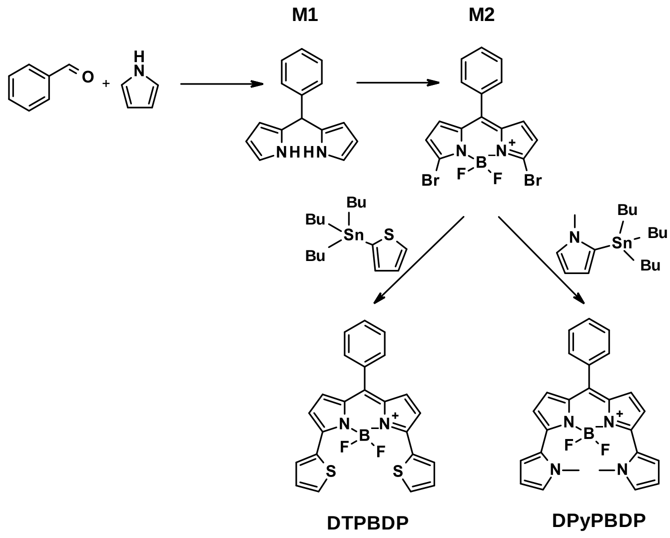
Synthesis of ***DPyPBDP***. Monomer M2 (100 mg, 0.24 mmol), tetrakis(triphenylphosphine) palladium(0) $Pd(PPh_3)_4$ (15% mol, 41 mg) and 1-methyl-2-(tributylstannyl)pyrrole (4 eq., 350 mg) were refluxed in dry toluene (10 mL) under nitrogen and under stirring. After 24 h the reaction mixture was diluted in dichloromethane and filtered on celite pad. The solvent was removed under reduced pressure and the crude product purified by silica gel chromatography using hexane/dichloromethane 7:3 as eluent. The pure product was obtained as dark blue crystalline powder with a yield of 55%. ^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58–7.51 (m, 5H) 7.06 (d, *J* = 2.4 Hz, 2H), 6.83 (d, *J* = 4.2 Hz, 2H), 6.81–6.78 (m, 2H), 6.53 (d, *J* = 4.2 Hz, 2H), 6.25 (t, *J* = 2.6 Hz, 2H), 3.7 (s, 6H).

Film Preparation. The films were prepared on quartz glass by spin-coating a solution (100 mg/mL) at 1500 rpm for 60 s in toluene of DTPBDP (10% *w*/*w*) and PS (Aldrich, Darmstadt, Germany, Mn 140,000, Mw 230,000).

ASE Measurements with Femtosecond Excitation. ASE was obtained by pumping the film at 400 nm, 630 nm and 640 nm with rectangular stripe spot excitation with a length of 1.05 mm and a width of 0.140 mm (1.5×10^{-3} cm^2). The emitted spectrum was collected at the edge of the film with the help of a spectrograph (Princeton Instruments SP2150, Acton, MA, USA, 300 g/nm) coupled with a CCD camera (Princeton Instruments pixis 256). The spectral resolution was 0.5 nm. All the measurements were performed in air.

3. Results and Discussion

DTPBDP and DPyBDT (Scheme 1) were synthesized according to our previously published procedure [13].



Scheme 1. Reaction scheme for the synthesis of DTPBDP and DPyPBDP.

The bromination of phenyl dipyrromethane (M1) was directly followed by oxidation with 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) without any additional purification steps. The cycle was then closed using boron trifluoride diethyl etherate, resulting in the formation of dibromo-BODIPY (M2). The α-substituted BODIPY were synthesized via Stille Coupling.

In order to avoid aggregation-caused quenching (ACQ) and the reabsorption of fluorescence due to the high planarity of the molecules and the small Stokes shift, we have dispersed the BODIPYs in polystyrene (PS) matrix. The resulting films exhibit a homogeneous dispersion of the dye (Figure 1) [14,15].

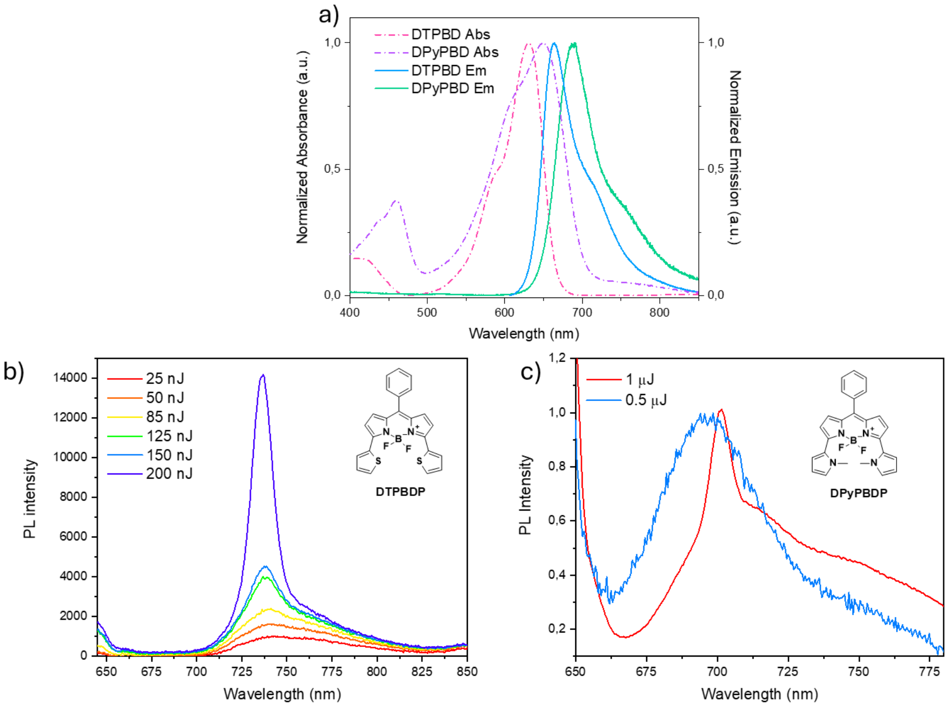


Figure 2. (**a**) Absorption and emission spectra of DTPBDP and DPyPBDP dispersed in PS matrix. (**b**) amplified spontaneous emission spectra at different pump excitation of DTPBDP in PS matrix under 640 nm laser. (**c**) amplified spontaneous emission spectra at different pump excitation of DPyPBDP in PS matrix under 630 nm laser.

The absorption and emission spectra of DTPBDP and DPyBDT of the spin-coated film (10% dye in PS) are reported in Figure 2a. The molecule DTPBDP show two absorption maxima in the visible region: one peak at 400 nm and one peak at 631 nm, with a vibronic replica at 585 nm and an emission maximum at 660 nm. These band can be attributed at the S0-S1 transition (631 nm) and S0-Sn transition (400 nm). DPyBDT show a similar spectrum, but the two peak are slightly red shifted: the first maximum is at 460 nm (S0-Sn transition), the second is at 650 nm (S1-S0 transition) with a vibronic at 610 nm, while the emission maximum is at 687 nm.

In order to prove a possible application in laser, we performed amplified spontaneous emission (ASE) measurements on the samples [16]. Both samples, DTPBDP and DTPBDP, did not show any ASE under 400 nm excitation pump, but they show ASE signals when excited at 640 nm and 630 nm respectively, with spot size 1.5×10^{-3} cm^2.

As we can see in Figure 2b, the spectra of DTPBDP exhibit a red shift in the spontaneous emission peaks (from 660 nm to 740 nm) that can be attributed to the strong self-absorption within the film.

When the excitation exceeds 150 nJ, a narrow band start to emerge at 735 nm, progressively dominating the spectra. Under the laser excitation, the sample did not show any degradation.

Molecule DPyBDT, on the contrary did not show any ASE emission until the excitation exceed 1 μJ, 5 times higher than the energy needed for DTPBDP. Under the laser excitation an ASE band start to arise peaked at 700 nm, but the high energy of the laser cause degradation of the sample.

4. Conclusions

Here we have presented two symmetrical α-substituted BODIPY dyes, one with thiophene substituents and one with pyrroles. We have study the photophysical properties of the dyes dispersed in inert matrix, expecting a similar behavior. However, we found that only the thiophene substituted molecule was able to have ASE, while the pyrrole substituted needed a laser excitation energy too much high, which has degraded the sample. The mechanism under the different behavior is under studying however, it could be attributed to the stronger electron-donating nature of pyrrole, which enhances the charge transfer characteristics of the molecule, leading to a redshift in both absorption and emission. However with the enhancement of the intramolecular charge transfer process, the overlap between the emission and charged excited state absorption spectra is enlarged, with the consequent increase of the ASE threshold as previously reported in literature [17]. We hope our findings will help to have a deeper understanding of the photophysics of this class of molecules, contributing to the design of higher-performance materials tailored for laser applications.

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References

1. Squeo, B.M.; Gregoriou, V.G.; Avgeropoulos, A.; Baysec, S.; Allard, S.; Scherf, U.; Chochos, C.L. BODIPY-Based Polymeric Dyes as Emerging Horizon Materials for Biological Sensing and Organic Electronic Applications. *Prog. Polym. Sci.* **2017**, *71*, 26–52. https://doi.org/10.1016/J.PROGPOLYMSCI.2017.02.003.
2. Vodyanova, O.S.; Kochergin, B.A.; Usoltsev, S.D.; Marfin, Y.S.; Rumyantsev, E.V.; Aleksakhina, E.L.; Tomilova, I.K. BODIPY Dyes in Bio Environment: Spectral Characteristics and Possibilities for Practical Application. *J. Photochem. Photobiol. A Chem.* **2018**, *350*, 44–51. https://doi.org/10.1016/J.JPHOTOCHEM.2017.09.049.
3. Destri, S.; Pasini, M.; Porzio, W.; Rizzo, F.; Dellepiane, G.; Ottonelli, M.; Musso, G.; Meinardi, F.; Veltri, L. New Erbium Complexes Emitting in Infrared Region Based on Oligothiophene and Thiophenefluorene Carboxylate. *J. Lumin.* **2007**, *127*, 601–610. https://doi.org/10.1016/J.JLUMIN.2007.03.018.
4. Dang, S.; Yu, J.B.; Wang, X.F.; Guo, Z.Y.; Sun, L.N.; Deng, R.P.; Feng, J.; Fan, W.Q.; Zhang, H.J. A Study on the NIR-Luminescence Emitted from Ternary Lanthanide [Er(III), Nd(III) and Yb(III)] Complexes Containing Fluorinated-Ligand and 4,5-Diazafluoren-9-One. *J. Photochem. Photobiol. A Chem.* **2010**, *214*, 152–160. https://doi.org/10.1016/J.JPHOTOCHEM.2010.06.019.
5. Loudet, A.; Burgess, K. BODIPY Dyes and Their Derivatives: Syntheses and Spectroscopic Properties. *Chem. Rev.* **2007**, *107*, 4891–4932. https://doi.org/10.1021/CR078381N/ASSET/IMAGES/LARGE/CR078381NC00020.JPEG.
6. Bañuelos, J. BODIPY Dye, the Most Versatile Fluorophore Ever? *Chem. Rec.* **2016**, *16*, 335–348. https://doi.org/10.1002/TCR.201500238.
7. Poddar, M.; Misra, R. Recent Advances of BODIPY Based Derivatives for Optoelectronic Applications. *Coord. Chem. Rev.* **2020**, *421*, 213462. https://doi.org/10.1016/J.CCR.2020.213462.
8. Rihn, S.; Retailleau, P.; Bugsaliewicz, N.; Nicola, A.D.; Ziessel, R. Versatile Synthetic Methods for the Engineering of Thiophene-Substituted Bodipy Dyes. *Tetrahedron Lett.* **2009**, *50*, 7008–7013. https://doi.org/10.1016/J.TETLET.2009.09.163.
9. Leushina, E.A.; Usol'Tsev, I.A.; Bezzubov, S.I.; Moiseeva, A.A.; Terenina, M.V.; Anisimov, A.V.; Taydakov, I.V.; Khoroshutin, A.V. BODIPY Dyes with Thienyl- and Dithienylthio-Substituents—Synthesis, Redox and Fluorescent Properties. *Dalton Trans.* **2017**, *46*, 17093–17100. https://doi.org/10.1039/C7DT03801A.
10. Llano, R.S.; Zaballa, E.A.; Bañuelos, J.; Durán, C.F.A.G.; Vázquez, J.L.B.; Cabrera, E.P.; Arbeloa, I.L.; Llano, R.S.; Zaballa, E.A.; Bañuelos, J.; et al. Tailoring the Photophysical Signatures of BODIPY Dyes: Toward Fluorescence Standards across the Visible Spectral Region. *Photochem. Photophysics—Fundam. Appl.* **2018**. https://doi.org/10.5772/INTECHOPEN.74848.
11. Virgili, T.; Ganzer, L.; Botta, C.; Squeo, B.M.; Pasini, M. Asymmetric AZA-BODIPY with Optical Gain in the Near-Infrared Region. *Molecules* **2022**, *27*, 4538. https://doi.org/10.3390/MOLECULES27144538/S1.
12. Mróz, W.; Squeo, B.M.; Vercelli, B.; Botta, C.; Pasini, M. AZABODIPY Aggregates as a Promising Electroluminescent Material for Sustainable NIR OLED Applications. *Mater. Adv.* **2023**, *4*, 1702–1710. https://doi.org/10.1039/D3MA00006K.
13. Virgili, T.; Ganzer, L.; Squeo, B.M.; Calzolari, A.; Pasini, M. Interplay between Theory and Photophysical Characterization in Symmetric α-Substituted Thienyl BODIPY Molecule. *Molecules* **2024**, *29*, 2625. https://doi.org/10.3390/MOLECULES29112625/S1.
14. Vu, T.T.; Dvorko, M.; Schmidt, E.Y.; Audibert, J.F.; Retailleau, P.; Trofimov, B.A.; Pansu, R.B.; Clavier, G.; Méallet-Renault, R. Understanding the Spectroscopic Properties and Aggregation Process of a New Emitting Boron Dipyrromethene (BODIPY). *J. Phys. Chem. C* **2013**, *117*, 5373–5385. https://doi.org/10.1021/JP3097555/SUPPL_FILE/JP3097555_SI_002.CIF.
15. Shimizu, K.; Kitagawa, D.; Kobatake, S. Solid Emission Color Tuning of Polymers Consisting of BODIPY and Styrene in Various Ratios. *Dye. Pigment.* **2019**, *161*, 341–346. https://doi.org/10.1016/J.DYEPIG.2018.09.055.
16. Mróz, M.M.; Perissinotto, S.; Virgili, T.; Gigli, G.; Salerno, M.; Frampton, M.J.; Sforazzini, G.; Anderson, H.L.; Lanzani, G. Laser Action from a Sugar-Threaded Polyrotaxane. *Appl. Phys. Lett.* **2009**, *95*, 31108. https://doi.org/10.1063/1.3179689/131975.
17. Li, Y.; Han, P.; Zhang, X.; Zhou, J.; Qiao, X.; Yang, D.; Qin, A.; Tang, B.Z.; Peng, J.; Ma, D. Effect of Intramolecular Charge Transfer Processes on Amplified Spontaneous Emission of D–π–A Type Aggregation-Enhanced Emission Molecules. *J. Mater. Chem. C Mater.* **2023**, *11*, 3284–3291. https://doi.org/10.1039/D2TC04683K.