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Synthesis and properties of novel near-infrared dye based on BODIPY and diketopyrrolopyrrole units



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ABSTRACT

A novel near-infrared dye of DPP-BODIPY with a diketopyrrolopyrrole (DPP) central unit and two 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) flanking units has been synthesized and characterized. Its quasi-planar structure was confirmed by X-ray diffraction and panchromatic absorption from 300 nm to 1000 nm was exhibited both in solution and in solid state. Near-infrared emission at about 804 nm and low LUMO energy level at -3.93 eV are observed. Furthermore, ambipolar charge transporting properties with hole mobility of $1.5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ and electron mobility of $2 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ S}^{-1}$ were obtained in thin films.

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1. Introduction

Photoactive organic dyes with absorption/emission features in the near infrared (NIR) between 700 and 1100 nm have attracted considerable interest because their optical property are appealing to a variety of applications such as organic semiconductor devices [1], energy conversion [2], biomedical sensing [3], and photodynamic therapy [4]. To date, various NIR absorbing/fluorescent materials based on metal complexes, ionic dyes, and extended π -conjugated chromophores have been reported [5,6]. Among them, 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY) derivatives have become one of the most fascinating family of NIR dyes due to their excellent stability, high fluorescence, and tunable optophysical properties via molecular functionalization [7–9].

Inspired by the strategies for low-band gap materials with conjugated donor–acceptor (D–A) systems, a wide range of D–A [10–12], A–D–A [13,14] and A–D–A–D–A [15–17] dyes have been

reported. Considering that diketopyrrolopyrrole (DPP) is a widely used acceptor building block for organic semiconductor dyes [18], in particular when substituted with thiophene donor groups, due to strong charge-transfer transition and good π -delocalization, herein, we designed a novel A–D–A–D–A NIR dye of DPP-BODIPY, in which DPP and BODIPY units were used as the acceptor building blocks and bithiophene groups were employed as the donor bridges. To ensure good solubility of DPP-BODIPY in organic solvent, 2-ethylhexyl chains were grafted onto the central DPP unit. We envisioned this molecule would present excellent NIR characteristics due to efficient intramolecular charge transfer transitions. For this reason, in this context, the relationship between the DPP-BODIPY structure and optophysical property were explored. And its organic field-effect transistors (OFET) were fabricated to evaluate the charge transport properties of this material.

2. Results and discussion

Materials: All reagents were purchased from Aldrich, Acros and TCI companies and used as received. All reactions and manipulations were carried out under N_2 atmosphere with the use of standard inert atmosphere techniques. The procedures of **2** and **3** are described in the supporting information.

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Synthesis of DPP-BODIPY: A mixture of compound **3** (98 mg, 0.1 mmol) and 2,3,5,6-tetrachlorocyclohexa-2,5-diene-1,4-dione (54 mg, 0.22 mmol) in CH_2Cl_2 (10 mL) was stirred for 8 h at room temperature under N_2 atmosphere. Then, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (1 mL) was added. After 5 min, triethylamine (2 mL) was added, and the reaction mixture was stirred for a further 3 hours, after which it was quenched with water. The organic layer was separated, dried over MgSO_4 , filtered, and evaporated. The crude compound was purified by column chromatography on silica (CH_2Cl_2) to afford a purple powder. Yield: 71%. ^1H NMR (400 MHz, CDCl_3) δ 8.97 (s, 1H), 7.95 (s, 2H), 7.57 (s, 1H), 7.48 (s, 2H), 7.35 (s, 2H), 6.62 (s, 2H), 4.08 (s, 2H), 1.93 (s, 1H), 1.35 (d, $J=35.0$ Hz, 8H), 0.93 (dd, $J=17.3, 10.3$ Hz, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ : 161.52, 144.04, 142.28, 140.72, 139.41, 138.22, 136.66, 134.85, 134.33, 134.05, 130.96, 126.34, 125.94, 118.64, 109.25, 46.15, 39.40, 30.46, 29.68, 28.60, 23.62, 23.07, 14.02, 10.61. MALDI-MS (m/z): 1068.94; Found: 1068.39, 1049.37 [M-F].

3. Results and discussion

As shown in Scheme 1, we obtained the DPP-BODIPY dye via a three-step synthesis route. Compound **1** was obtained according to

previous literature [19]. Then, Pd-catalyzed Suzuki coupling between compound **1** and 5-formylthiophen-2-ylboronic acid afforded compound **2** in 65% yield. Compound **3** was synthesized by the condensation of **2** with pyrrole in the presence of $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ in catalytic amount with good yield of 64%. Finally, chelating reaction

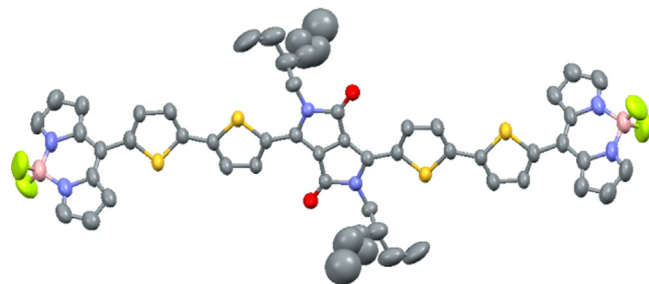
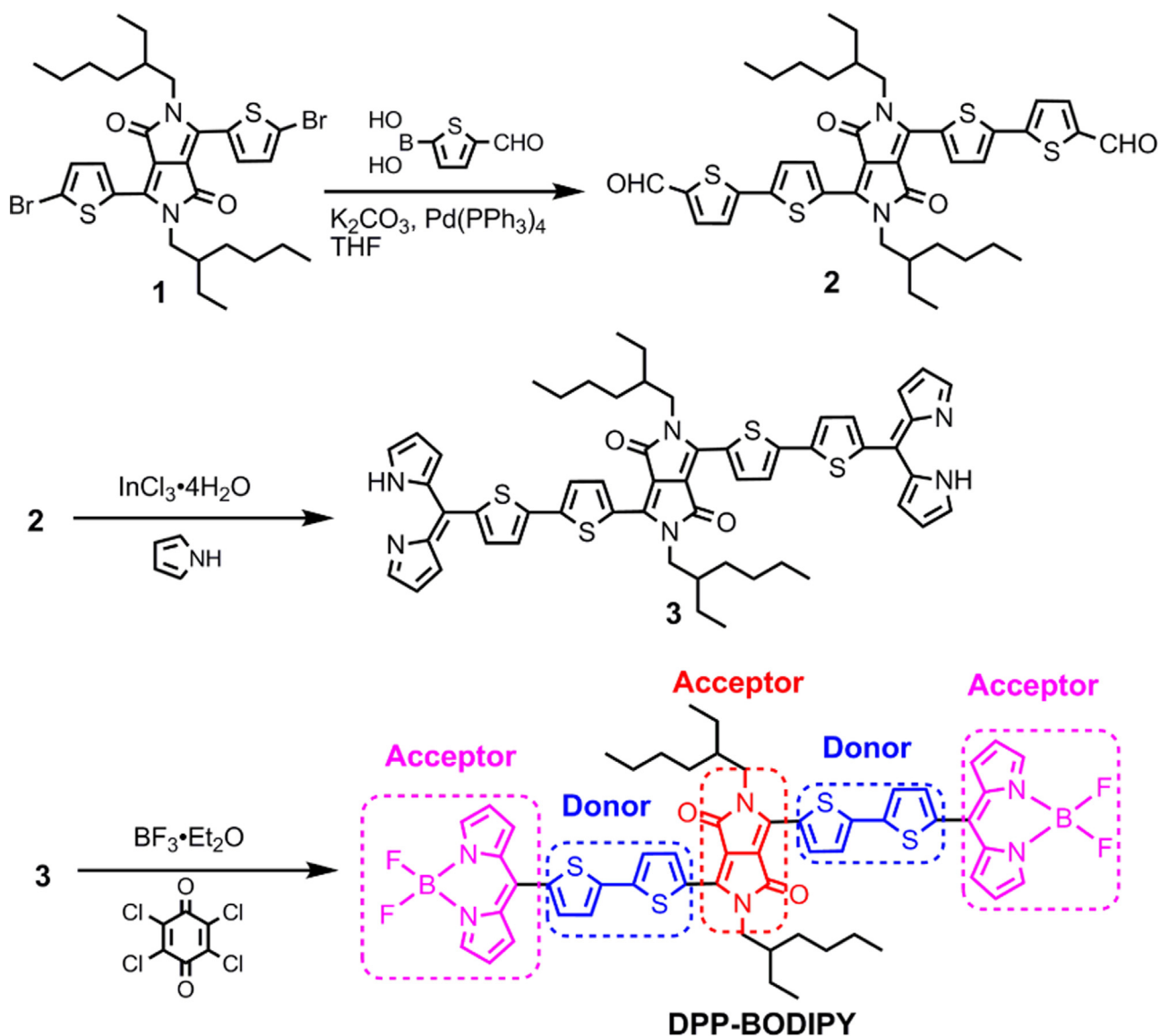


Fig. 1. ORTEP view of DPP-BODIPY (50% displacement ellipsoids). H atoms are omitted for clarity. C, gray; O, red; N, blue; B, pink; F, green. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)



Scheme 1. Synthetic route of DPP-BODIPY.

between compound **3** and $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in the presence of chloranil led to the target compound DPP-BODIPY as a purple solid in 71% yield. The structure of the resulting molecule was confirmed by ^1H NMR, ^{13}C NMR and TOF-Mass (Fig. S1, ESI).

To investigate the molecular structure along with the packing structure in solid state, single crystal of DPP-BODIPY used for X-ray diffraction analysis has been grown by slow evaporation of its CH_2Cl_2

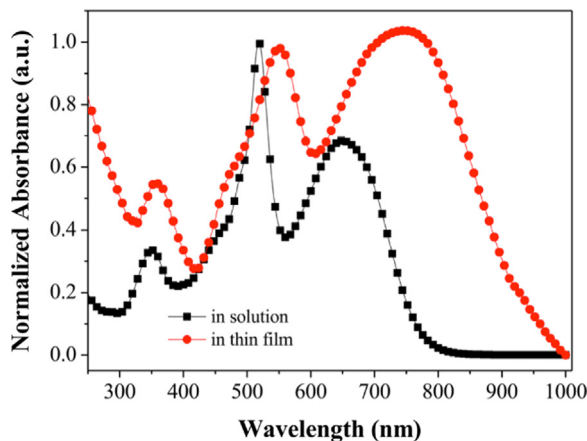


Fig. 2. UV/vis absorption spectra of DPP-BODIPY in chlorobenzene (black) and as a thin film (red). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

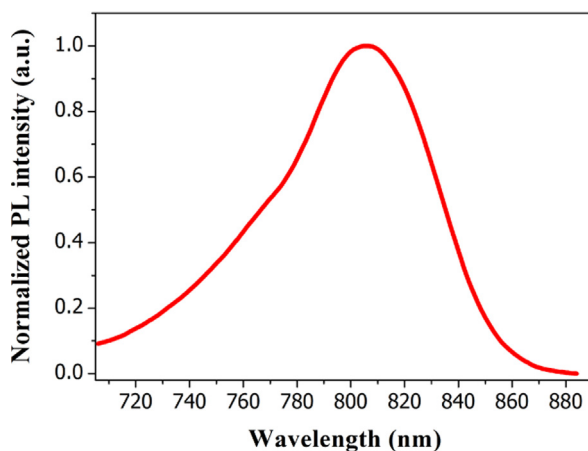


Fig. 3. PL spectra of DPP-BODIPY in chlorobenzene.

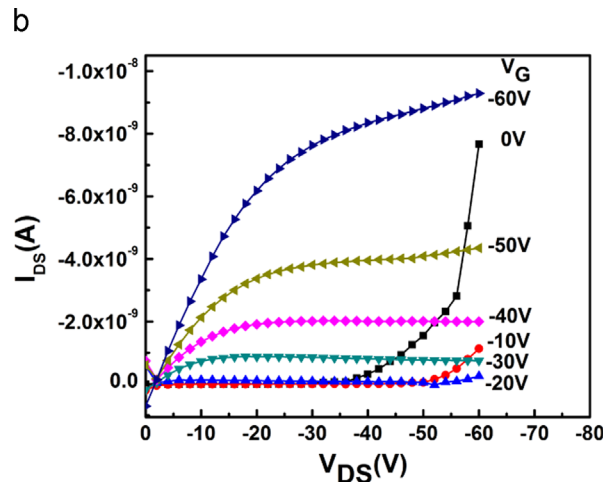
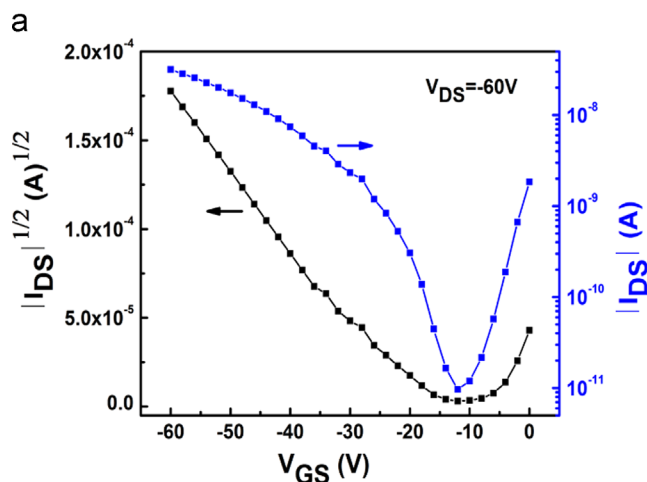


Fig. 4. (a) Transfer curves and (b) output characteristics of OFET devices.

solution. As shown in Fig. 1 and Fig. S2, the DPP core and thiophene parts display a quasi-planar structure with torsion angle low than 10° between the rings. However, both flanking BODIPY units are tilted by about 47° from the bithiophene-DPP plane owing to significant steric hindrance between the neighboring hydrogen atoms on the BODIPY and the thiophene units. The molecules are packed in a slipped arrangement with close contact (3.5 \AA) between a bithiophene of one molecule and the DPP unit of another one (see ESI).

Fig. 2 shows the UV-vis absorption spectra of DPP-BODIPY in chlorobenzene ($10^{-5} \text{ mol L}^{-1}$) solution and its thin film. A broad absorption profile from 250 nm to 800 nm is observed in solution. Two absorption peaks located at 350 nm ($2.8 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) and 522 nm ($8.74 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) are assigned to the π - π^* transition of the BODIPY moiety [20]. The broad absorption band at low energy (670 nm, $6 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) is attributed to an intramolecular charge transfer (ICT), which is more intense than that of A-D-D-D-A-type BODIPY dyes [21]. To further explore the relationship between structure and absorption, the temperature-dependent and concentration-dependent absorption spectra were studied (Fig. S3, ESI). As temperature increased from 25°C to 95°C , the broad absorption band at 670 nm is hypsochromically shifted, but the narrow band at 520 nm undergoes virtually no change. At the same time, no change is observed for the absorption spectra at different concentrations. It implies that no aggregation occurs in solution. On the contrary, in thin film, the absorption spectrum significantly expands to near-infrared area. This is attributed to aggregation in solid state and additional ICT transitions.

At the 517 nm excitation wavelength, the DPP-BODIPY presents an NIR photoluminescent emission at 804 nm in chlorobenzene solution (Fig. 3). The PL spectra display minor changes in solution with increasing temperatures (Fig. S4), further indicating that no aggregation occurred in solution. However, no emission is detected up to 900 nm (limit of the instrument) in the film.

The electrochemical properties of DPP-BODIPY were measured in solution in dichloromethane by cyclic voltammetry. As shown in Fig. S5, DPP-BODIPY displays two clear irreversible oxidation peaks and one reduction peak with onset potential of 0.34 V, 0.44 V and -0.87 V vs Fc^+/Fc , respectively (ESI). According to the equations of $E_{\text{HOMO}} = -(E_{\text{ox}} + 4.8)$ and $E_{\text{LUMO}} = -(E_{\text{red}} + 4.8)$, the HOMO and LUMO energy levels were calculated to be -5.14 eV and -3.93 eV [22]. Compared to the reported DPP derivatives, DPP-BODIPY has a lower LUMO energy level due to the enhanced acceptor strength of the dual BODIPY unit. Interestingly, the electrochemical bandgap of 1.21 eV matches well with the onset of absorption in thin film (1.24 eV).

To further investigate the electronic structure of DPP-BODPY, density functional theory (DFT) calculations at the B3LYP/6-31G (d) level were carried out. The electron density distribution patterns of the HOMO and LUMO of DPP-BODIPY are shown in Fig. S6. As expected, the HOMO of DPP-BODIPY is mainly located on the DPP central unit while the LUMO is largely concentrated on the BODIPY unit. Accordingly, the HOMO and LUMO energies were evaluated to -4.982 eV and -4.098 eV, respectively, in line with the experimental results.

Charge carrier mobilities in DPP-BODIPY were investigated via bottom-contact organic field effect transistors (OFET). This dye showed ambipolar charge transporting character with both medium electron and hole mobilities (Fig. 4). The maximum hole mobility and electron mobility was determined to be $1.5 \times 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $2 \times 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, respectively. To probe the reasons for the relatively low mobilities, the surface morphology of this compound was explored by atomic force microscopy (AFM). As shown in Fig. S7, the DPP-BODIPY film exhibits a poor crystallinity, which is adverse for charge mobilities, leading to the non-ideal OFET [23].

4. Conclusion

In summary, a novel NIR dye based on a central DPP acceptor unit connected to two BODIPY acceptor units through donor bithiophene bridges was prepared. The DPP-BODIPY dye exhibited a planar structure and the NIR emission in solution, as well as a low LUMO energy level. Most interestingly, panchromatic absorption up to 1000 nm was observed in thin film. Ambipolar charge transporting properties was achieved due to the introduced push-pull unit.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at <http://dx.doi.org/10.1016/j.matlet.2014.10.043>.

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