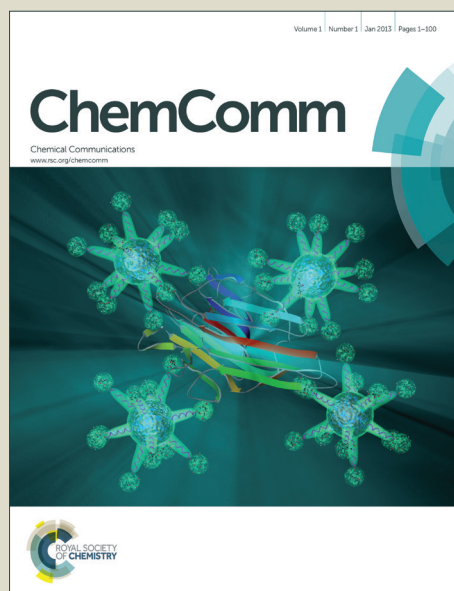


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# Thienyl-BOPHY Dyes as Promising Templates for Bulk Heterojunction Solar Cells

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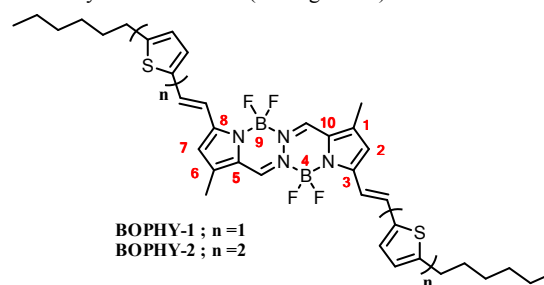
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**Abstract.** The synthesis and characterization of bis(difluoroboryl)-1,2-bis((1*H*-pyrrol-2-yl)methylene)hydrazone functionalized with two lateral vinyl-thienyl modules and exhibiting strong absorption in the 400–800 nm window in thin films is reported. Bulk heterojunction solar cells assembled with these dyes and a fullerene derivative (PC<sub>71</sub>BM), using very small quantities of the additive diiodooctane, give a power conversion efficiency as high as 4.3% with short-circuit current values of 10.9 mA/cm<sup>2</sup>, an open-circuit voltage of 0.7 V and external quantum efficiencies higher than 70% over a broad range of wavelengths (580 to 720 nm).

Organic photovoltaic (OPV) research is a rapidly advancing field and impressive conversion efficiencies of over 10% with either polymer<sup>1</sup> or small-molecule-based materials have been achieved for BHJ solar cells.<sup>2</sup> Recently, attention has been focused on small molecule systems due to the facts that they are monodisperse, can be highly soluble and that their energy levels (HOMO/LUMO) can be easily tuned by modifying the nature of the chemical constituents. Most have been built around oligothiophene modules that may be either flexible,<sup>3</sup> or fused into rigid benzodithiophene,<sup>4</sup> *S*<sub>2</sub>*N*-heteropentacene,<sup>5</sup> or *Si*-bridged bithiazole units.<sup>6</sup> One of the key points in their design has been the use of electron withdrawing groups (benzothiadiazole, oxothiazolidine or dicyanomalonitrile...) to adjust the LUMO energy of the dye with respect to that of the LUMO of the electron acceptor and thus to favor exciton dissociation. Other dyes employed have included diketopyrrolopyrrole (DPP),<sup>7</sup> squaraine,<sup>8</sup> hexabenzocoronene,<sup>9</sup> merocyanine,<sup>10</sup> donor-acceptor oxoindane,<sup>11</sup> thiadiazolo-bithienyl,<sup>12</sup> and boron dipyrromethene (BODIPY)<sup>13</sup> derivatives, with impressive efficiencies being attained in recent years. The BODIPY family holds especial promise because it meets many of the key

requirements for the engineering of high performance solar cells such as large extinction coefficients, appropriate HOMO/LUMO levels distribution, and self-organization of the molecules in the solid state to guarantee well-ordered packing favoring intrinsic mobility of charges.<sup>13</sup> Bis(difluoroboryl)-1,2-bis((1*H*-pyrrol-2-yl)methylene)hydrazone, termed BOPHY, and its derivatives are dinuclear boron(III) complexes of ligands prepared by double-condensation of pyrrolic aldehydes with hydrazine which have been introduced recently with the aim of producing highly fluorescent architectures,<sup>14</sup> and to tailor the bandgap energy for better harvesting of NIR radiation.<sup>15</sup> Recent reports have suggested that in dyes of this type containing  $\pi$ -conjugated ligands coordinated to multiple Lewis-acidic B(III) centers, the unsaturated framework is constrained so as to enhance electron-transport properties.<sup>16</sup> We were intrigued by this concept and the fact that these compounds are analogues of BODIPY dyes but have not yet been appropriately functionalized by thienyl residues for OPV applications.

Herein we describe for the first time BOPHY dyes functionalized in the 3,8-positions by vinyl-thiophene-bearing solubilizing chains at the periphery and investigate their salient physical and optoelectronic properties as well as their performances as active materials in both field-effect transistors and organic solar cells. The preparation of the target molecules is based on a double Knoevenagel condensation of thienyl aldehydes with 1,3,6,8-tetramethyl-BOPHY under conditions we have previously established.<sup>17</sup> The resulting highly soluble dark violet BOPHY-1 and dark blue BOPHY-2 dyes (Fig. 1) display well-defined NMR spectra in keeping with an average *C*<sub>2h</sub> molecular structure. Diagnostic signals are found in the NMR spectrum of BOPHY-2 for the 6,6' ( $\delta$  7.92) and 4,4' ( $\delta$  6.70) protons. Styryl protons signals at  $\delta$  7.33 and 7.12 exhibit a coupling constant of 16.3 Hz, demonstrating the trans configuration of the double bonds. The spectrum of BOPHY-1 shows closely similar features (see Figure S1).



**Figure 1.** Molecular structures of BOPHY-1 and -2.

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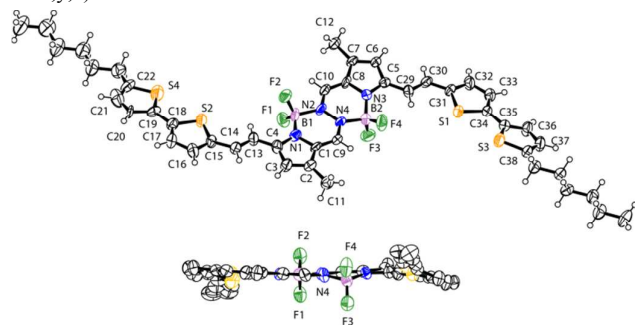
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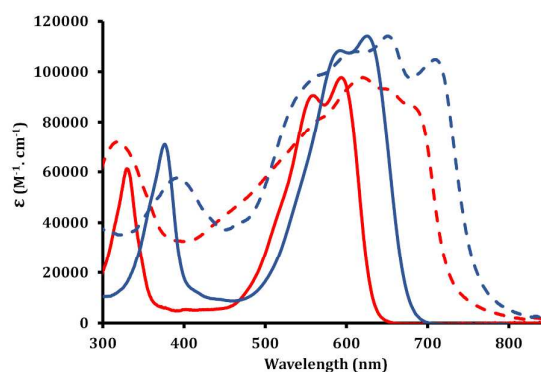
We elucidated the structure of BOPHY-2 via single-crystal X-ray diffraction in order to scrutinize the packing of the dyes in the solid state. The structure belongs to the triclinic space group  $P\bar{1}$  and the molecular structure and partial views of the lattice are shown in Figures 2 and S9. The molecular structure is Z-shaped and has very close to twofold symmetry. The molecules are essentially planar, lying parallel to the (1 2 -4) crystallographic plane, with the long chains barely deviating from the plane of the central quadricyclic with dihedral angles of 15.1-19.9(2)°, the boron atoms also being slightly displaced from the least-squares mean plane (rmsd 0.075 Å) by -0.147 Å and -0.410 Å. The lateral arms with the thiophene groups head-to-head are aligned side-by-side along the [3 -1 0] direction pointing the terminal C atom of the hexyl chain toward the BF<sub>2</sub> group of the inversion-related molecule with an F...H distance of 2.55 Å. This arrangement forms a zipper-like motif with 18 Å-wide sheets involving alkyl-alkyl interactions along the [2 1 1] direction, and orthogonally bordered by the tetracycles (Figure S9). In the third dimension,  $\pi$ - $\pi$  stacking are only found between inversion-related pairs of thiophene vinyl-pyrrole moieties at general position and at position 1-x, 1-y, -z with average centroid distances of  $3.5 \pm 0.05$  Å between the two hetero five-membered rings. Otherwise the adjacent layers have interaction through alkyl groups contacts and other CH<sub>3</sub>...F<sup>1</sup> hydrogen bonds (F...H 2.48 Å symmetry code i: -1+x,y,z).



**Figure 2.** ORTEP representation of BOPHY-2. Displacement ellipsoids are drawn at the 50% probability level, and H atoms are shown as small spheres of arbitrary radii. Below a view perpendicular to the BOPHY median N-N axis, highlighting the planar structure without the hydrogen atoms. Selected geometric parameters: bond lengths B–F 1.388(8)-1.366(9)/1.379(8)-1.370(8); B–N 1.522(10)-1.576(9)/1.522(9)-1.586(9); N–N 1.396(7); N–C 1.400(8)-1.376(7)/1.394(8)-1.367(7) Å; bond angles F–B–F 109.0(6)/110.9(6); N–B–N 108.0(6)/106.0(6); N–B–F 112.1(5)-107.1(5)-112.5(5)-108.0(5)/111.4(5)-108.1(5)-112.4(5)-107.8(5).

The electronic absorption spectra of BOPHY-1 and BOPHY-2 dyes in dilute THF solution and in thin films are displayed in Figure 3. Broad absorption bands with maxima at 595 nm ( $\epsilon = 97,000 \text{ M}^{-1}\text{cm}^{-1}$ ,  $fwhm$  at  $2,900 \text{ cm}^{-1}$ ) and 626 nm ( $\epsilon = 113,000 \text{ M}^{-1}\text{cm}^{-1}$ ,  $fwhm$  at  $3,000 \text{ cm}^{-1}$ ) were found for BOPHY-1 and -2 in THF solution respectively. In both cases, excitation at the onset of the low energy absorption band gave structured emission profiles with maxima at 627 and 674 nm and quantum yields of 13 and 10% for BOPHY-1 and -2, respectively (Figures S10 and S11). The short lifetimes (nanosecond regime) are in keeping with singlet state emission (Table S2).

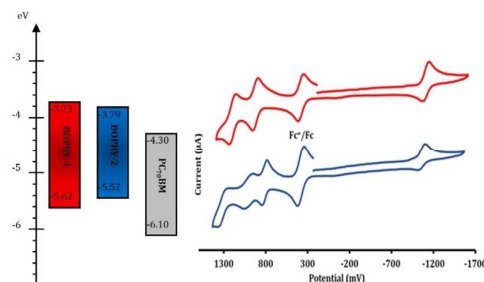
In a solid film, the spectrum for both dyes was red-shifted by 30 nm and greatly broadened ( $fwhm$  of  $7,000 \text{ cm}^{-1}$ ), possibly reflecting the influence of the stacking array seen in the three dimensional packing of the molecules in the X-ray crystal structure (vide supra). The optical gaps estimated from the onset of the film absorption were 1.69 eV and 1.62 eV for BOPHY-1 and -2, respectively.



**Figure 3.** Electronic absorption spectra of BOPHY-1 (plain red trace) and BOPHY-2 (plain blue trace) in THF solution at RT and thin films (dashed traces). The absorption of the films (optical density about 0.5) is normalized to the absorption in solution.

Cyclic voltammetry was used to estimate the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels. All potentials were calibrated using ferrocene (Fc) and taking an ionization potential of -4.78 eV below the vacuum level for the Fc/Fc<sup>+</sup> redox system.<sup>18</sup> Interestingly, for both new dyes the first oxidation and reduction processes are quasi-reversible (Figure 4) allowing calculation of the HOMO/LUMO levels from the oxidation and reduction peaks (Table S3). Notice that the 108 mV anodic shift of the oxidation wave of BOPHY-2 with respect to that of BOPHY-1 is likely due to a better delocalization by extending the  $\pi$ -system of the dye. For BOPHY-1 the HOMO lies at -5.62 eV and the LUMO at -3.73 eV, while for BOPHY-2 the HOMO lies at -5.52 eV and the LUMO at -3.79 eV, providing redox gaps of respectively 1.89 and 1.73 eV (Figure 4). These gaps are in agreement with optical gaps determined above and mean that compared with the energy levels of PC<sub>71</sub>BM (HOMO at -6.10 and LUMO at -4.30 eV), both dyes are potential donor materials. Density functional theory (DFT) calculations at the B3LYP/6-311+G\* level of theory in vacuum are consistent with the cyclic voltammetry data, with a HOMO frontier orbital mostly localized on the thienyl and BOPHY  $\pi$  core and the LUMO orbital localized on the central core (see Figures S12, S13 for details).

The thermal properties were characterized by differential scanning calorimetry. Both materials exhibit crystalline behavior with melting temperatures of 204 °C and 244°C, for BOPHY-1 and -2, respectively (see Figure S14 in ESI).



**Figure 4.** Left: Position of the frontier molecular orbital energies of the BOPHY dyes versus PC<sub>71</sub>BM. Right: cyclic voltammetry of BOPHY-1 (red trace) and BOPHY-2 (blue trace). Genuine ferrocene was added at the end of the CV measurements.

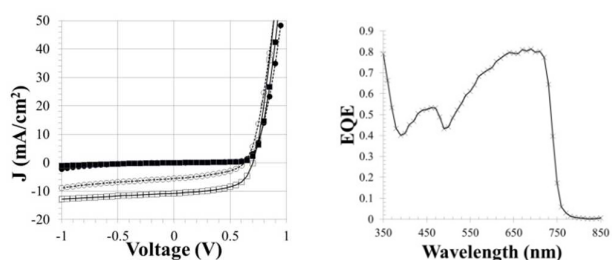
Charge carrier mobilities in the dyes were measured by using them as a semiconductor layer in standard bottom-contact organic field-effect transistors (OFETs). The experimental procedure used for the

device elaboration is given in the ESI and the post-elaboration thermal treatments were chosen accordingly with the best photovoltaic results. Although OFETs probe charge transport under very specific conditions (parallel to the dielectric interface and at high charge carrier densities), the results can give insight into the correlation between the molecular structure and charge transport properties. Both materials exhibit moderate hole mobility values (linear regime) of  $7 \times 10^{-5}$  (without thermal treatment) and  $3 \times 10^{-5} \text{ cm}^2/\text{V s}$  (after a  $70^\circ\text{C}$  for 5 minutes thermal annealing) for BOPHY-1 and BOPHY-2, respectively. However, because these mobilities are related to charge transport properties along the plane of the substrate, the low values recorded are not seen as impeding the utilization of these dyes as donor materials in bulk heterojunction (BHJ) solar cells.

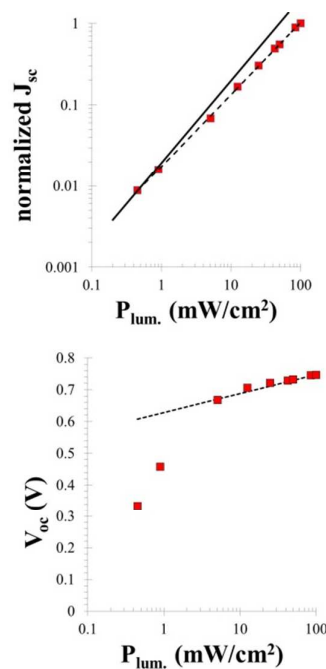
Both molecules were tested as electron donor species in a BHJ active layer, using a standard device structure (ITO/PEDOT:PSS/active layer/Ca/Al) in a blend with  $\text{PC}_{71}\text{BM}$ . After screening of various conditions (see ESI), the optimum ratio was found to be 1:1 for both dyes at a solution concentration of 15 mg/mL in chloroform with 0.5 vol. % of di-iodooctane (DIO) as additive for BOPHY-1, and of 10 mg/mL in chloroform with 0.3 vol. % of DIO for BOPHY-2.

All active layers were sensitive to the presence of DIO as additives (see Figure S16 and Table 1). For both dyes, the use of DIO reduces the leakage current significantly (and consequently leads to an increase in FF) and also reduces the serial resistance (Figure S16). Because its solution was more concentrated, BOPHY-1 needed a higher vol % of DIO (0.5%) than BOPHY-2 (0.3%). However, in all cases, the increase of PCE by using DIO was significant (see Table 1 and Figure 5).

BOPHY-2 shows a higher PCE of around 4.3% after a very short thermal annealing at  $70^\circ\text{C}$ . Such a PCE is promising considering that these are the first photovoltaic trials on BOPHY derivatives. BOPHY-1 shows a lower PCE of only 1.5% at maximum, despite a slightly higher hole mobility (authorizing a thicker active-layer for BOPHY-1). We suggest, based on the different experimental conditions explored (see Table S5), that this efficiency drop is due in part to the weaker absorption features with respect to BOPHY-2 as well as a hypsochromic shift in the solid state as indicated by the  $J_{\text{sc}}$  which is half the one measured for BOPHY-2. In addition, the significantly lower FF measured for BOPHY-1 would mean that the photovoltaic processes including the exciton dissociation at the donor/acceptor interface and the free charge carriers transport and collection are not as efficient as for BOPHY-2. For the optimum conditions using BOPHY-2, the external quantum efficiency is higher than 70% in the 580-720 nm wavelength range with peaks at 80% in the 640-710 nm windows. These high values point out that charge generation at the donor-acceptor interface is highly effective and that the out-of-plane carrier mobility allows efficient charge collection under short-circuit conditions. Moreover, the atomic force microscopy on the best device active layer (Figure S21) showed no macro-phase separation, suggesting a fine mixing of both components, which sustains charge generation. Nevertheless, further measurements as a function of the incident light power have shown that charge-carrier recombination remains important, even in the best-performing BOPHY-2 devices (Figures 6 and S20). A detailed analysis is given in the ESI and indicates that one of the main sources of charge carrier loss is the bimolecular trap-free charge recombination process.



**Figure 5.** Left: Best (J-V) curves measured in the dark (closed symbols) and under standard AM1.5G ( $100 \text{ mW}/\text{cm}^2$ ) conditions (open symbols) using either BOPHY-1 (circles) or BOPHY-2 (squares) as an electron-donor small molecule. Right: External quantum efficiency for BOPHY-2.



**Figure 6.** Top: sub-linear variation of the normalized  $J_{\text{sc}}$  as a function of light power for a cell using BOPHY-2 as electron-donor in blend with  $\text{PC}_{71}\text{BM}$  with a 1:1 ratio. A linear variation of  $J_{\text{sc}}$  as a function of the light power is represented by the continuous line. Bottom: dependence of  $V_{\text{oc}}$  as a function of light power for the same solar-cell. The dotted-line represents the expected variation for trap-free bimolecular recombination.

**Table 1:** Photovoltaic performances measured for BOPHY -1 and -2 blended with PC<sub>71</sub>BM with and without DIO.<sup>a)</sup>

Dye	PC <sub>71</sub> BM ratio	Solution conc. (mg/mL) <sup>b)</sup>	DIO (vol. %)	V <sub>oc</sub> (V)	J <sub>sc</sub> (mA.cm <sup>-2</sup> )	FF (%)	PCE (%)	Thermal Annealing	Active layer thickness (nm)
BOPHY-1	1:1	15	0 %	0.68	3.2	27	0.6	2 min 70 °C	190
BOPHY-1	1:1	15	0.5 %	0.63	5.5	43	1.5	/	190
BOPHY-2	1:1	10	0 %	0.65	10.6	34	2.4	5 min 70 °C	95
BOPHY-2	1:1	10	0.3 %	0.70	10.9	57	4.3	5 min 70 °C	95

<sup>a)</sup> PCE is the power conversion efficiency, FF the filling factor, V<sub>oc</sub> the open-circuit voltage and J<sub>sc</sub> the short-circuit current density.

<sup>b)</sup> Total concentration of the BOPHY and PC<sub>71</sub>BM.

## Conclusions

Two new small molecules (BOPHY derivatives) having two different flexible lateral thiophene modules have been designed, synthesized according a general protocol and fully characterized. These can be used in BHJ solar cells involving PC<sub>71</sub>BM as the electron acceptor to give an average PCE of 4.3% and an external power conversion external quantum efficiency higher than 70% over a large optical window. Decreasing the number of thiophene moieties in the side chains from 2 to 1 decreases the PCE to 1.5% under similar conditions. This new dye has many attractive attributes for increasing the electron density on the flat central core in order to favor packing interactions with PC<sub>71</sub>BM and thus a better exciton dissociation at the interface and charge transport in the respective nano-domains. Increasing the size of central BOPHY core by adding supplementary chelating boron centers to increase the charge transport properties is currently under investigation.

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