# Synthesis and Characterization of New Push-Pull Chromophores Containing BF₂-Azopyrrole Derivatives

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**ABSTRACT.** Novel push-pull chromophores containing 5'-(4-(bis(9,9-dimethyl-9$H$-fluoren-2-yl)aniline (bisDMFA) as a donor and phenylazo-methylpyrrolyl-boron difluoride (PhAPy-BF$_2$) as an acceptor were designed and synthesized by the Knoevenagel condensation reaction for organic solar cells. Various electron withdrawing moieties were effectively introduced using 2,4-dimethyl-1$H$-pyrrole to afford new asymmetric BF$_2$-azopyrrole molecules that were characterized by UV-vis spectroscopy and cyclic voltammetry measurements.

**Key words:** Organic solar cell, Asymmetric BF$_2$-azopyrrole molecules

## INTRODUCTION

Global warming and the rapid depletion of fossil fuels has led to increased demand for the development of alternative renewable energy sources.[1] Among several such sources, sunlight is one of the most promising candidates for sustainable and clean energy.[2] Recently, organic photovoltaic cells (OPVs) have attracted considerable attention since organic materials are abundant and amenable to solution processing. In addition to obvious advantages such as possibility of mass production and low weight,[3] organic solar cells based on small molecules[4] and polymers can reduce the cost of harnessing solar energy to the level of conventional fuels.

Organic small molecules, which have electron-rich and electron-deficient groups, have been used as electron donor materials with fullerene derivatives as electron acceptors in bulk heterojunction (BHJ) organic solar cells. These systems offer several benefits such as ease of purification and reproducibility of synthesis. These push-pull small molecules can be modified by changing their donor or acceptor units to tune the energy band gap and absorption range of these cells. Consequently, many research groups are trying to optimize push-pull chromophores for such devices as potential alternatives to polymer-based solar cells.[4]

Until now, some fluorine-boron complexes have been synthesized and used in PV devices: these have been reported for use in organic light emitting diodes,[5] field effect transistors,[6] and organic photovoltaics.[7-8] Among fluorine-boron complexes, the BF$_2$-azopyrrole complex contains the azo moiety, which is well known as an organic photoconductive material and is not present in boron dipyrromethene (Bodipy) dye.[9] In 1968, Rau reported azo compounds and their photoconductive properties were observed from thin layers. Several years later, the bisazo pigment as a photogenerating material was reported by Champ and Shattuck. Azo pigments were widely investigated as charge generation materials due to their technological advantages such as high sensitivity, wide spectral range (450–800 nm), and excellent stability.[10] Recently, organic solar cells using small molecules based on the BF$_2$-azopyrrole complex as an electron donor and PCBM as an acceptor have been reported. These cells afford a power conversion efficiency (PCE) of up to 3.15%.[7] Predictably, the thin film absorption spectrum of BF$_2$-azopyrrole complex was broader and showed a lower band gap (1.49 eV) than that of symmetrical bisazopyrrole (1.54 eV).

Our design of new chromophores for small molecule BHJ solar cells has relied on structurally similar organic dyes used in dye-sensitized solar cells (DSSC) as well as push-pull chromophores used in nonlinear optics (NLO).[11] In this study, we incorporated the BF$_2$-azopyrrole moiety as an intramolecular acceptor into the small molecule backbone. Thus, we have synthesized a series of new push-pull chromophores, viz. 2-((5'-(4-(bis(9,9-dimethyl-9$H$-fluoren-2-yl)amino)phenyl)-2,2'-bithiophen-5-yl)ethylene)-4-hexyloxyphenylazo-methylpyrrolyl-boron difluoride (**bisDMFA-diTh-HexPhAPy-BF$_2$**), 2-((5'-(4-(bis(9,9-dimethyl-9$H$-fluoren-2-yl)amino)phenyl)-2,2'-bithiophen-5-yl)ethylene)-phenylazo-methylpyrrolyl-boron difluoride (**bisDMFA-diTh-PhAPy-BF$_2$**), and 2-((5'-(4-(bis(9,9-dimethyl-9$H$-fluoren-2-yl)amino)phenyl)-2,2'-bithiophen-5-yl)ethylene)-
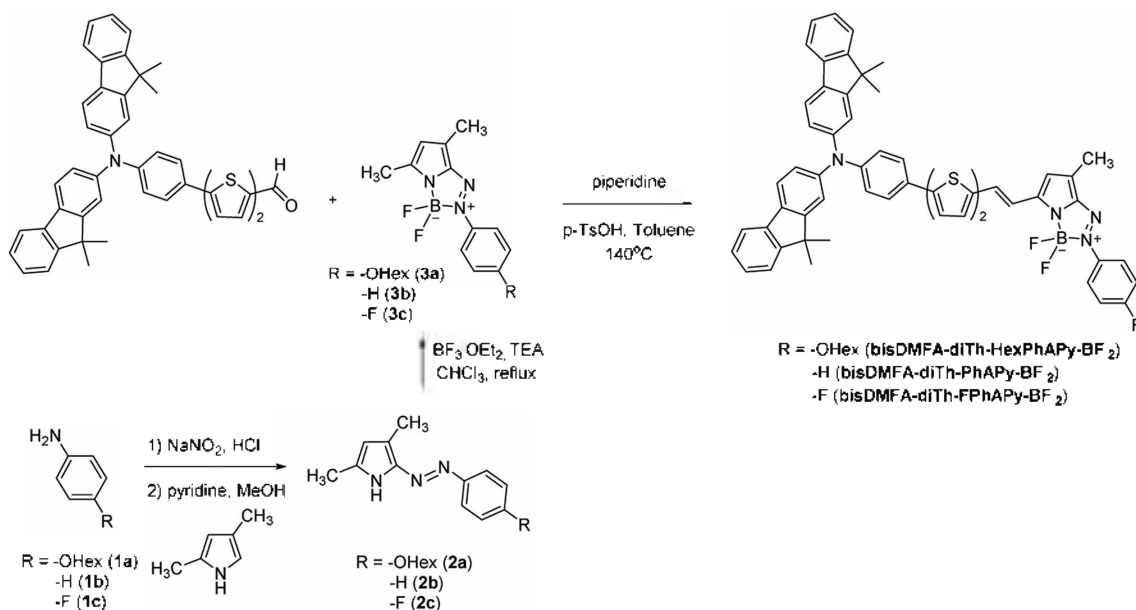
**Scheme 1.** Synthetic routes of three push-pull chromophores.

4-fluorophenylazo-methylpyrrolyl-boron difluoride (**bisDMFA-diTh-FPhAPy-BF₂**), that have more electron withdrawing moieties than the previous cases.[11]

Herein, we report the synthesis and optoelectronic characteristics of these push-pull chromophores (**bisDMFA-diTh-HexPhAPy-BF₂, bisDMFA-diTh-PhAPy-BF₂, and bisDMFA-diTh-FPhAPy-BF₂**) and their performance in solution processed BHJ solar cells.

## EXPERIMENTAL

### General methods

$^1$H- and $^{13}$C-NMR spectra were obtained on a Varian Mercury 300 spectrometer, a Varian/Oxford As-500 (500 MHz) spectrophotometer. Chemical shift values were recorded as parts per million relative to tetramethylsilane as an internal standard unless otherwise indicated, and coupling constants in Hertz. Optimized structures calculated by TD-DFT using the B3LYP functional and the 3-21G* basis set. The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) energies were determined using minimized singlet geometries to approximate the ground state. UV-vis data was measured with a Perkin-Elmer Lambda 2S UV-vis spectrometer. Photoluminescence spectra were recorded on a Perkin LS fluorescence Spectrometer. Cyclic voltammetry (CV) was performed using VersaSTAT 3 (Princeton Applied Research). Methylene chloride was used as the solvent and 0.1 M of tetrabutyl ammonium hexafluorophosphate was used as

the supporting electrolyte. A platinum rod electrode coated with the donor compounds, a platinum wire and an Ag/AgNO₃ (0.10 M) electrode were used as the working electrode, as the counter electrode and as the reference electrode, respectively. The measurements were done using a scan rate of 100 mV/s and ferrocenium/ferrocene redox couple was used as an internal reference. AFM measurements were performed with a Digital Instruments NanoScope IV in the tapping mode.

### Fabrication and characterization of solar cell devices

The BHJ films were prepared under optimized conditions according to the following procedure reported previously:[11] The indium tin oxide (ITO)-coated glass substrate was first cleaned with detergent, ultrasonicated in acetone and isopropyl alcohol, and subsequently dried overnight in an oven. Poly(3,4-ethylenedioxythiophene) : poly(styrene-sulfonate) (PEDOT : PSS) in aqueous solution was spun-cast to form a film with thickness of approximately 40 nm. The substrate was dried for 10 min at 140 °C in air, then transferred into a glove-box to spin-cast the photoactive layer. The donor/PCBM BHJ blend solutions (weight ratio, 1:2 or 1:3) were prepared in chlorobenzene at a concentration of 30 mg/mL, and then spun-cast on top of the PEDOT layer. Then, the device was pumped down to lower than 10$^{-7}$ torr and a ~100 nm thick Al electrode was deposited on top. Solar cell's efficiencies were characterized under simulated 100 mW/cm² AM 1.5G irradiation from a 1000 W Xe arc lamp (Oriel 91193). The light intensity was adjusted

with a Si solar cell that was double-checked with an NREL-calibrated Si solar cell (PV Measurement Inc.). The applied potential and measured cell current were measured using a Keithley model 2400 digital source meter. The current-voltage characteristics of the cell under these conditions were determined by biasing the cell externally and measuring the generated photocurrent. This process was fully automated using Wavemetrics software. The incident photon-to-current conversion efficiency (IPCE) spectra for the cells were measured on an IPCE measuring system (PV measurements).

**4-Hexyloxyphenylazo-dimethyl-1$H$-pyrrole (2a).** NaNO$_2$ (74 mg, 1.03 mmol) in water (1 mL) was added to a solution of 4-(hexyloxy)benzamine (200 mg, 1.03 mmol) in water (1 mL) and hydrochloric acid (0.4 mL) at 0 °C. The reaction mixture was stirred for 0.5 h at 0-5 °C. The solution of the diazonium salt thus prepared was immediately used for the next coupling reaction. 2,4-dimethyl-1$H$-pyrrole (0.11 mL, 1.03 mmol) and pyridine (0.4 mL) in methanol (6 mL) were added to a solution of diazonium salt at 0-5 °C. The reaction mixture was stirred for 10 h at room temperature. The precipitate was filtered and washed repeatedly with water and dried to afford 4-hexyloxyphenylazo-dimethyl-1$H$-pyrrole. $^1$H-NMR (300 MHz, CDCl$_3$): δ 7.72 (d, 2H, $J$ = 9.0 Hz), 6.94 (d, 2H, $J$ = 9.0 Hz), 5.90 (s, 1H), 4.00 (t, 2H, $J$ =6.6 Hz), 2.39 (s, 3H), 2.28 (s, 3H), 1.83-1.78 (m, 2H), 1.47-1.33 (m, 6H), 0.91 (t, 3H, $J$ = 6.9 Hz) $^{13}$C-NMR (125 MHz, CDCl$_3$): δ 159.6, 147.4, 142.0, 132.6, 127.5, 123.0, 114.8, 111.4, 68.4, 31.8, 29.4, 25.9, 22.8, 14.3, 13.7, 10.7.

**Phenylazo-dimethyl-1$H$-pyrrole (2b).** This compound was synthesized by a method similar to that used for 4-hexyloxyphenylazo-dimethyl-1$H$-pyrrole. $^1$H-NMR (300 MHz, CDCl$_3$): δ 7.75 (d, 2H, $J$ = 8.4 Hz), 7.43 (t, 2H, $J$ = 7.7 Hz), 7.32-7.26 (m, 1H), 5.94 (s, 1H), 2.42 (s, 3H), 2.27 (s, 3H), $^{13}$C-NMR (125 MHz, CDCl$_3$): δ 129.2, 128.4, 121.7, 112.2, 13.8, 10.8.

**4-Fluorophenylazo-dimethyl-1$H$-pyrrole (2c).** This compound was synthesized by a method similar to that used for 4-hexyloxyphenylazo-dimethyl-1$H$-pyrrole. $^1$H-NMR (300 MHz, CDCl$_3$): δ 7.76-7.71 (m, 2H), 7.13-7.08 (m, 2H), 5.93 (s, 1H), 2.40 (s, 3H), 2.28 (s, 3H), $^{13}$C-NMR (125 MHz, CDCl$_3$): δ 123.2, 116.1, 115.9, 112.1, 13.8, 10.8.

**4-Hexyloxyphenylazo-dimethylpyrrolyl-boron difluoride (3a).** To a solution of 4-hexyloxyphenylazo-dimethyl-1$H$-pyrrole (250 mg, 0.83 mmol) and triethylamine (3.9 mL, 27.4 mmol) in chloroform (40 mL) was slowly added boron trifluoride diethyl etherate (2.2 mL, 17.9 mmol) under N$_2$. The reaction mixture was heated under reflux for 36 h.

Concentration and purification of the residue by flash column chromatography (Hex-DCM, 3:1) gave 4-hexyloxyphenylazo-dimethylpyrrolyl-boron difluoride (203 mg, 70%). R$_f$ 0.43 (Hex-DCM, 3:1). $^1$H-NMR (300 MHz, CDCl$_3$): δ 7.71 (d, 2H, $J$ = 8.1 Hz), 6.93 (d, 2H, $J$ = 9.0 Hz), 6.08 (s, 1H), 3.99 (t, 2H, $J$ = 6.6 Hz), 2.41 (s, 3H), 2.34 (s, 3H), 1.82-1.77 (m, 2H), 1.47-1.34 (m, 6H), 0.93-0.91 (m, 3H) $^{13}$C-NMR (125 MHz, CDCl$_3$): δ 158.9, 152.7, 137.5, 135.9, 120.5, 120.3, 116.1, 114.6, 68.5, 31.7, 29.3, 25.9, 22.8, 13.9, 11.6, 10.8.

**Phenylazo-dimethylpyrrolyl-boron difluoride (3b).** Using a method similar to 4-hexyloxyphenylazo-dimethylpyrrolyl-boron difluoride, this compound was obtained (68%). R$_f$ 0.43 (Hex-DCM, 3:1). $^1$H-NMR (300 MHz, CDCl$_3$): δ 7.74 (d, 2H, $J$ = 9.0 Hz), 7.42 (t, 2H, $J$ = 7.9 Hz), 7.22-7.28 (m, 1H), 6.16 (s, 1H), 2.45 (s, 3H), 2.37 (s, 3H) $^{13}$C-NMR (75 MHz, CDCl$_3$): δ 129.4, 127.1, 122.0, 118.5, 14.6, 11.1.

**4-Fluorophenylazo-dimethylpyrrolyl-boron difluoride (3c).** Using a method similar to 4-hexyloxyphenylazo-dimethylpyrrolyl-boron difluoride, this compound was obtained (50%). R$_f$ 0.36 (Hex-DCM, 3:1). $^1$H-NMR (300 MHz, CDCl$_3$): δ 7.74-7.69 (m, 2H), 7.10 (t, 2H, $J$ = 8.4 Hz), 6.14 (s, 1H), 2.43 (s, 3H), 2.34 (s, 3H) $^{13}$C-NMR (125 MHz, CDCl$_3$): δ 122.4, 120.4, 120.3, 116.7, 116.5, 14.8, 11.3.

**2-((5'-(4-(Bis(9,9-dimethyl-9$H$-fluoren-2-yl)amino)phenyl)-2,2'-bithiophen-5-yl)ethylene)-4-hexyloxyphenylazo-methylpyrrolyl-boron difluoride (bisDMFA-diTh-HexP-hAPy-BF$_2$).** $p$-TsOH (catalytic amount) and piperidine (3~5 drops) were added to a solution of 5'-(4-(bis(9,9-dimethyl-9$H$-fluoren-2-yl)amino)phenyl)-2,2'-bithophene-5-carbaldehyde (50 mg, 0.075 mmol) and 4-hexyloxyphenylazo-dimethylpyrrolyl-boron difluoride (26 mg, 0.075 mmol) in Toluene (20 mL) at room temperature. The reaction mixture was heated under reflux for 36 h. Concentration and purification of the residue by flash column chromatography (Hex-EtOAc, 5:1) gave 2-((5'-(4-(bis(9,9-dimethyl-9$H$-fluoren-2-yl)amino)-phenyl)-2,2'-bithiophen-5-yl)ethylene)-4-hexyloxyphenylazo-methylpyrrolyl-boron difluoride (60 mg, 78%). R$_f$ 0.5 (Hex-EtOAc, 5:1). $^1$H-NMR (300 MHz, CDCl$_3$): δ 7.78 (d, 2H, $J$ = 9.0 Hz), 7.64 (dd, 4H, $J$ = 13.8, 7.8 Hz), 7.50 (d, 2H, $J$ = 8.4 Hz), 7.41-7.27 (m, 7H), 7.25-7.09 (m, 9H), 6.98-6.95 (m, 3H), 6.65 (d, 1H, $J$ = 16.2 Hz), 6.33 (s, 1H), 4.02 (t, 2H, $J$ = 6.6 Hz), 2.43 (s, 3H), 1.84-1.79 (m, 2H), 1.54-1.35 (m, 18H), 0.92 (t, 3H, $J$ = 6.7 Hz) $^{13}$C-NMR (125 MHz, CDCl$_3$): δ 160.3, 155.4, 153.8, 147.8, 147.7, 147.2, 143.8, 143.6, 141.5, 139.1, 136.9, 135.9, 134.7, 133.3, 127.8, 127.3, 126.8, 126.6, 125.0, 124.5, 123.9, 123.6, 123.2, 122.8, 121.1, 120.9, 119.7, 119.1, 117.4, 115.0, 113.7, 68.5, 47.1, 31.8, 29.5, 27.3, 25.9, 22.9, 14.3, 10.7.

**2-((5'-(4-(Bis(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-2,2'-bithiophen-5-yl)ethylene)-phenylazo-methylpyrrolyl-boron difluoride (bisDMFA-diTh-PhAPy-BF₂).** This compound was synthesized by a method similar to that used for 2-((5'-(4-(bis(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-2,2'-bithiophen-5-yl)ethylene)-4-hexyloxyphenylazo-methylpyrrolyl-boron difluoride (70%). R$_f$ 0.54 (Hex-EtOAc, 5:1). ¹H-NMR (300 MHz, CDCl₃): δ 7.80 (d, 2H, J = 7.8 Hz), 7.64 (dd, 4H, J = 13.4, 7.3 Hz), 7.52–7.30 (m, 11H), 7.21–7.10 (m, 9H), 7.08–6.98 (m, 2H), 6.66 (d, 1H, J = 15.9 Hz), 6.37 (s, 1H), 2.46 (s, 3H), 1.43 (s, 12H) ¹³C-NMR (75 MHz, CDCl₃): δ 155.1, 153.5, 146.9, 138.9, 134.5, 129.0, 127.8, 127.0, 126.6, 126.4, 124.9, 123.9, 123.7, 123.4, 122.9, 122.5, 121.6, 120.7, 119.5, 118.8, 46.9, 27.0.

**2-((5'-(4-(bis(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-2,2'-bithiophen-5-yl)ethylene)-4-fluorophenylazo-methylpyrrolyl-boron difluoride (bisDMFA-diTh-FPhAPy-BF₂).** This compound was synthesized by a method similar to that used for 2-((5'-(4-(bis(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-2,2'-bithiophen-5-yl)ethylene)-4-hexyloxyphenylazo-methylpyrrolyl-boron difluoride (55%). R$_f$ 0.4 (Hex-EtOAc, 5:1). ¹H-NMR (300 MHz, CDCl₃): δ 7.82–7.77 (m, 2H), 7.68–7.61 (m, 5H), 7.50 (d, 3H, J = 8.6 Hz), 7.42–7.27 (m, 7H), 7.23–6.99 (m, 10H), 6.66 (d, 1H, J = 16 Hz), 6.36 (s, 1H), 2.44 (s, 3H), 1.43 (s, 12H) ¹³C-NMR (75 MHz, CDCl₃): δ 155.1, 153.5, 147.6, 146.9, 138.9, 134.5, 127.8, 127.0, 126.6, 126.4, 124.9, 124.0, 123.6, 123.4, 123.3, 122.9, 122.5, 120.6, 119.4, 118.8, 116.9, 116.0, 115.7, 113.5, 46.8, 27.0.

## RESULTS AND DISCUSSION

The synthetic routes of **bisDMFA-diTh-HexPhAPy-BF₂, bisDMFA-diTh-PhAPy-BF₂,** and **bisDMFA-diTh-FPhAPy-BF₂** are outlined in Scheme 1. 5'-(4-(bis(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-2,2'-bithiophene-5-carbaldehyde[12,13] and 4-(hexyloxy)benzamine[7] were prepared according to the procedure reported previously. Phenylazo-dimethyl-1H-pyrrole derivatives (**2a, 2b, 2c**) were synthesized from benzamines (**1a, 1b, 1c**) through treatment with NaNO₂/aqueous HCl and subsequent neutralization with pyridine and 2,4-dimethyl-1H-pyrrole in methanol.

The use of 2, 4-dimethyl-1H-pyrrole was important in the synthesis of asymmetric phenylazo-dimethyl-1H-pyrrole to afford new BF₂-azopyrrole complexes. Phenylazo-dimethyl-1H-pyrroles (**2a, 2b, 2c**) were converted into the corresponding phenylazo-dimethylpyrrolyl-boron difluorides (**3a, 3b, 3c**) through treatment with boron trifluoride

diethyl etherate in the presence of triethylamine. Finally, **bisDMFA-diTh-HexPhAPy-BF₂, bisDMFA-diTh-PhAPy-BF₂,** and **bisDMFA-diTh-FPhAPy-BF₂** were obtained from the corresponding phenylazo-dimethylpyrrolyl-boron difluorides (**3a, 3b, 3c**) and 5'-(4-(bis(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-2,2'-bithiophene-5-carbaldehyde through a Knoevenagel condensation reaction in the presence of p-TsOH and piperidine.[14,15]

*Figure* 1 displays the UV-vis absorption spectra of **bisDMFA-diTh-HexPhAPy-BF₂, bisDMFA-diTh-PhAPy-BF₂,** and **bisDMFA-diTh-FPhAPy-BF₂** in chlorobenzene solution and thin films, as well as the emission spectra in solution. The corresponding optical properties are summarized in *Table* 1. As shown in *Figure* 1(a), the absorption spectra of **bisDMFA-diTh-HexPhAPy-BF₂, bisDMFA-diTh-PhAPy-BF₂,** and **bisDMFA-diTh-FPhAPy-BF₂** in solution show two absorption bands at ~370 nm and ~520 nm. The molar absorption coefficients were 60,936 M⁻¹ cm⁻¹ at 524 nm, 48,549 M⁻¹ cm⁻¹ at 521 nm, and 55,957 M⁻¹ cm⁻¹ at 521 nm,
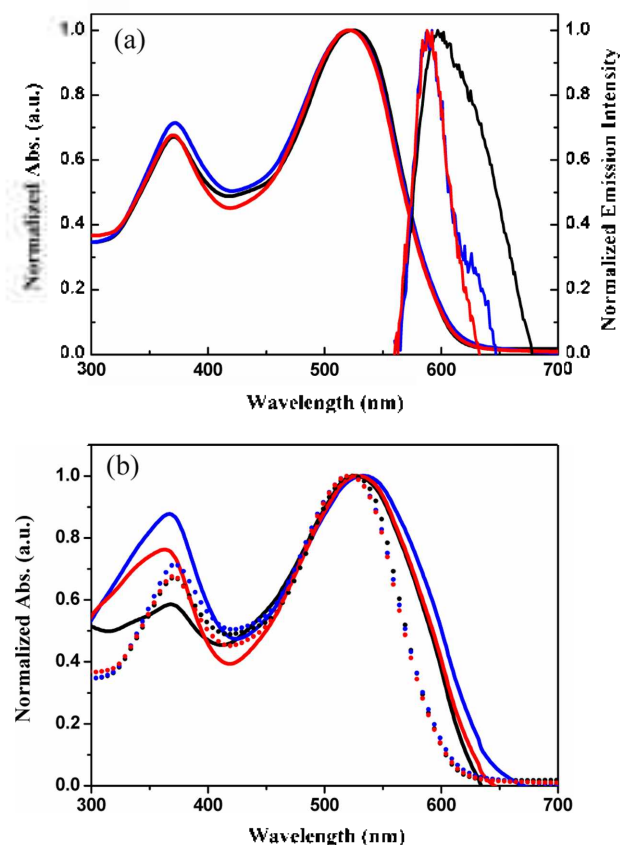


*Figure* 1.(a) UV-vis absorption and emission spectra in chlorobenzene and (b) UV-vis absorption spectra in chlorobenzene (dot line) and thin films (solid line) of **bisDMFA-diTh-HexPhAPy-BF₂** (black line), **bisDMFA-diTh-PhAPy-BF₂** (blue line), and **bisDMFA-diTh-FPhAPy-BF₂** (red line).

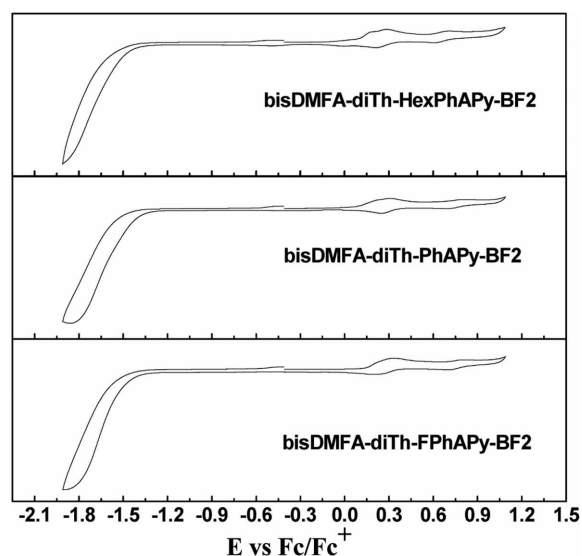*Table* **1.** Optical and redox parameters of the compounds

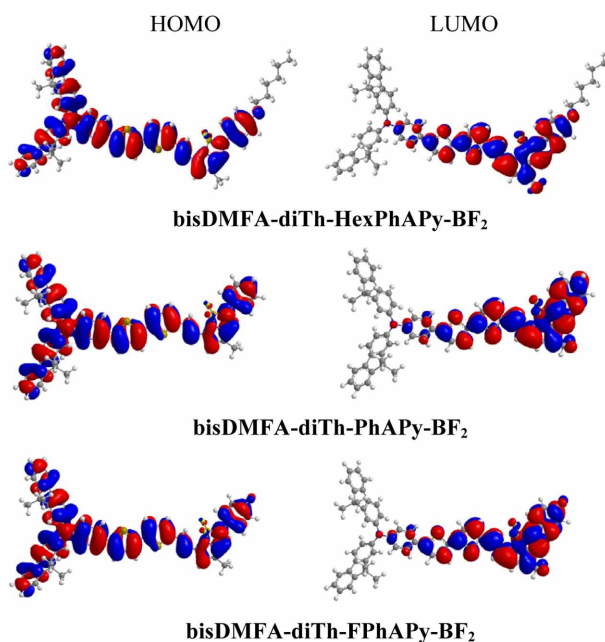| Compounds | $\lambda_{abs}$[a]/nm ($\epsilon$/M⁻¹ cm⁻¹) | $\lambda_{Pt}$[a]/nm | HOMO (eV)[b] | LUMO (eV) | Egopt (eV)[c] |
|---|---|---|---|---|---|
| **bisDMFA-diTh-HexPhAPy-BF2** | 524(60,936) | 596 | -4.871 | -3.398 | 1.947 |
| **bisDMFA-diTh-PhAPy-BF2** | 521(48,549) | 592 | -4.866 | -3.421 | 1.905 |
| **bisDMFA-diTh-FPhAPy-BF2** | 521(55,957) | 587 | -4.944 | -3.383 | 1.934 |

[a]Absorption spectra were measured in ClBz solution. [b]Redox potentials of the compounds were measured in CH₂Cl₂ with 0.1 M ($n$-C₄H₉)₄NPF₆, at a scan rate of 100 mV s⁻¹ ($vs$. Fc/Fc⁺). [c]E$_g$$^{opt}$ was calculated from the absorption thresholds obtained from the absorption spectra of films that were spin-coated onto a PEDOT/PSS layer on the TCO substrate.

respectively. These absorption trends fit with the standard dual absorption profiles characteristic of intramolecular charge transfer (ICT) and are very similar to previously reported cases.[11]Although **bisDMFA-diTh-FPhAPy-BF₂** has an additional electron withdrawing fluoro group, the absorption spectra of these **bisDMFA-diTh-PhAPy** series compounds were not very different. In solid-state thin film, (*Figure* 1(b)) the absorption spectra of **bisDMFA-diTh-PhAPy** series compounds showed a small (~10 nm) red-shift and broad bands compared to the spectra in solution.

In order to investigate the electrochemical properties of these three small molecules, cyclic voltammetry (CV) measurements were conducted on a Pt electrode at a scan rate of 100 mV s⁻¹. The CV curves of these molecules are shown in *Figure* 2, and the corresponding electrochemical data are summarized in *Table* 1. The HOMO and LUMO levels can be deduced from the oxidation and reduction onsets with the assumption that the energy level of ferrocene (Fc) is 4.8 eV below the vacuum level. The CV of these materials in solid-state thin film could not be mea-
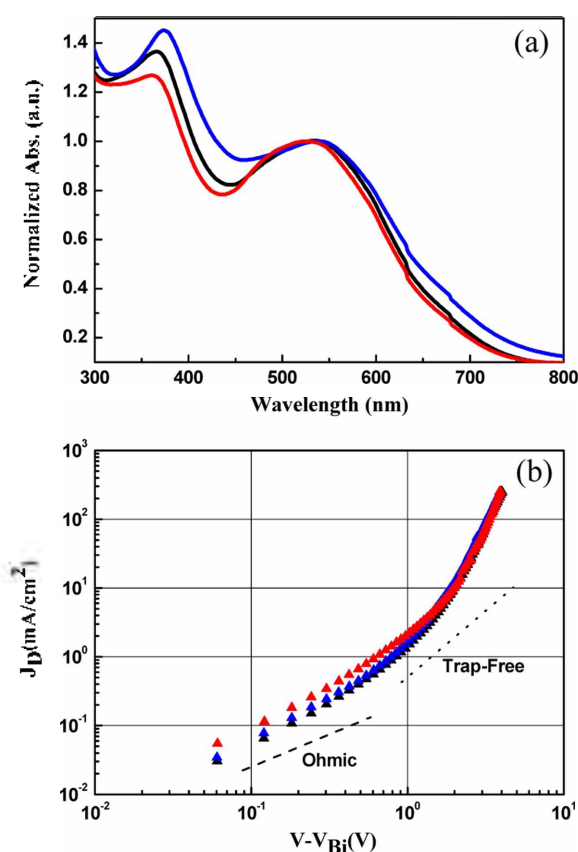


HOMO     LUMO

**bisDMFA-diTh-HexPhAPy-BF₂**

**bisDMFA-diTh-PhAPy-BF₂**

**bisDMFA-diTh-FPhAPy-BF₂**

***Figure* 3.** Isodensity surface plots of the **bisDMFA-diTh- PhAPy** series.



***Figure* 2.** Electrochemical characterization of the **bisDMFA-diTh-PhAPy** series in dichloromethane/TBAHFP (0.1 M); scan speed 100 mV/s, potentials vs Fc/Fc⁺.

sured due to stripping of the film on the electrode. Therefore, we determined the optical band gap of these materials from their respective absorption thresholds calculated from the absorption spectra of spin-coated films on quartz substrates. The values of the HOMO and LUMO energy levels of these molecules were calculated as ~4.9 eV and ~3.4 eV respectively.

To estimate the oxidative and reductive properties of these three small molecules, their geometries and electronic structures were calculated by time dependent-density functional theory (TD-DFT) calculations using the B3LYP functional / 3-21G* basis set. The geometries and the HOMO /LUMO surface plots of the ground-state optimized structures are shown in *Figure* 3. The orbital density of the HOMO is distributed evenly over the small molecules, whereas the orbital density of the LUMO is localized on the acceptor units such as HexPhAPy-BF₂, PhAPy-BF₂, and FPhAPy-BF₂. These calculations demonstrate that a light-triggered ICT

*Figure* 4. (a) UV-vis absorption spectra of **bisDMFA-diTh-Hex-PhAPy-BF₂** (black solid line) or **bisDMFA-diTh-PhAPy-BF₂** (blue solid line) or **bisDMFA-diTh-FPhAPy-BF₂** (red solid line)/C₇₁-PCBM films (b) Hole-only devices (ITO/PEDOT:PSS/**bisDMFA-diTh-PhAPy** series:PCBM /Au) with a thickness L = 90 ± 5 nm.

can occur effectively from the electron-donating amine units (**bisDMFA**) to the acceptor groups in these molecules.

To investigate space-charge effects in these cases, we examined the hole mobility from the space-charge limitation of current (SCLC) $J$–$V$ characteristics obtained in the dark for hole-only devices. *Figure* 4(b) shows the dark-current characteristics of ITO/PEDOT:PSS/donor:C₇₁-PCBM/Au devices as a function of the bias corrected by the built-in voltage determined from the difference in work function between Au and the HOMO level of the donor. Ohm's law can be observed at low voltages because of thermal free carriers. For the presence of carrier traps in the active layer, there is a trap-filled-limit (TFL) region between the ohmic and trap-free SCLC regions. The SCLC behavior in the trap-free region can be characterized using the Mott Gurney square law,[16,17] where ε is the static dielectric constant of the medium and μ is carrier mobility.

$$J = (9/8)\,\varepsilon\,\mu(V^2/L^3)$$

The hole mobilities of **bisDMFA-diTh-HexPhAPy-BF₂**, **bisDMFA-diTh-PhAPy-BF₂**, and **bisDMFA-diTh-FPhAPy-BF₂** evaluated using the above Mott-Gurney law (ε = 3ε₀) were $6.69 \times 10^{-7}\,cm^2/V\cdot s$, $7.79 \times 10^{-7}\,cm^2/V\cdot s$, and $8.04 \times 10^{-7}\,cm^2/V\cdot s$, respectively.

As a result, the hole mobilities of **bisDMFA-diTh-Hex-PhAPy-BF₂**, **bisDMFA-diTh-PhAPy-BF₂**, and **bisDMFA-diTh-FPhAPy-BF₂** were two orders lower than those of the push-pull chromophores that we had reported previously.[11]

BHJ solar cells were fabricated with **bisDMFA-diTh-HexPhAPy-BF₂**, **bisDMFA-diTh-PhAPy-BF₂**, and **bisDMFA-diTh-FPhAPy-BF₂** as the donor materials and C₇₁-PCBM as the acceptor material using a conventional solution spin-coating process. The device prepared by **bisDMFA-diTh-FPhAPy-BF₂**/C₇₁-PCBM has a PCE of ~0.34%, with short-circuit current ($J_{sc}$) − 2.34 mA/cm², fill factor ($FF$) − 0.33, and open-circuit voltage ($V_{oc}$) = 0.45 V without post-annealing at 100 °C for 10 min. The PCEs of the other devices using **bisDMFA-diTh-HexPhAPy-BF₂** and **bisDMFA-diTh-PhAPy-BF₂** are very similar to that of **bisDMFA-diTh-FPhAPy-BF₂**, and the corresponding UV-vis absorption spectra of these BHJ films are shown in *Figure* 4(a). These results were probably caused by the lower hole-mobility of the **bisDMFA-diTh-HexPhAPy-BF₂**/C₇₁-PCBM film (or the **bisDMFA-diTh-PhAPy-BF₂**/C₇₁-PCBM and **bisDMFA-diTh-FPhAPy-BF₂**/C₇₁-PCBM films). The thickness of **bisDMFA-diTh-HexPhAPy-BF₂**/C₇₁-PCBM, **bisDMFA-diTh-PhAPy-BF₂**/C₇₁-PCBM, and **bisDMFA-diTh-FPhAPy-BF₂**/C₇₁-PCBM BHJ films obtained under these conditions were approximately 46.1 nm, 46.1 nm, and 44 nm, respectively.

## CONCLUSION

In summary, we have designed and synthesized new push-pull small molecules that comprise BF₂-azopyrrole derivatives as acceptors. Their properties were characterized by UV-vis spectroscopy, cyclic voltammetry measurements, and TD-DFT calculations. Preliminary investigations on photovoltaic behavior were also conducted. Our results indicate that the absorption spectra of these push-pull small molecules in thin films were broader than those in the solution phase, and these molecules were structurally well suited for intramolecular charge transfer. Based on the above observations, these novel push-pull molecules are promising candidates for electron donor materials in organic solar cells. Further studies have to focus on fabricating PV

devices using different solvents/blending techniques before spin-coating or by using an additive for controlling thin film morphology. Efforts are currently on in our laboratory to discover more efficient photovoltaic systems using these new push-pull small molecules and to further extend the scope of various acceptors for intramolecular charge transfer.

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