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Near-IR absorption and photocurrent generation using a first-of-its-kind boron difluoride formazanate non-fullerene acceptor†

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Herein, we report the synthesis and characterization of the first non-fullerene acceptor (NFA) containing a boron difluoride formazanate (**BF₂fz**) core end-capped with N-annulated perylene diimides (PDIs). Electronic coupling between the **BF₂fz** core and the PDI endcaps enabled tuning of the lowest unoccupied molecular orbital, leading to near-panchromatic optical absorption. Post-deposition solvent vapor annealing of the new NFA resulted in a significant red-shift in the optical spectra, which stretched into the near-IR. Proof-of-concept organic photovoltaic (OPV) devices were constructed to demonstrate the potential of this new material as an NFA. SVA treatment of the active layer resulted in a 2-fold increase in power conversion efficiency (PCE), due mainly to increases in the **BF₂PDI₂** generated photocurrent that extended into the near-IR.

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Introduction

For applications in organic photovoltaics (OPVs), π -conjugated materials are perfectly suited for use as non-fullerene acceptors (NFAs) because both physical and optoelectronic properties may be optimized to match the electron-donor material with which they are paired in the active layer.^{1,2} One class of non-fullerene acceptors (NFAs) recognized for high redox and thermal stability, as well as high molar absorptivity, are perylene diimides (PDIs).^{3,4} Despite such favorable qualities, the efficiency of charge-extraction for PDI-based NFA materials is often hindered by the formation of large π - π stacking domains throughout the BHJ.¹ To promote more favorable phase separation in the BHJ, PDI self-assembly may be disrupted through either direct dimerization of PDIs⁵⁻⁸ or insertion of a core between the PDI-moieties.⁹⁻²⁰

The Welch research group has previously explored the optoelectronic influence of thienoisindigo, thienyl- and pyridyl-diketopyrrolopyrrole cores that were acetylene-linked to N-annulated PDI (Fig. 1).²¹ Strong electronic communication between the cores and PDI endcaps adjusted the highest occupied molecular orbital (HOMO) energy level of these molecules, affording near-panchromatic absorptions ideally suited for OPV. In search of a core that could achieve similar absorptivity, while instead

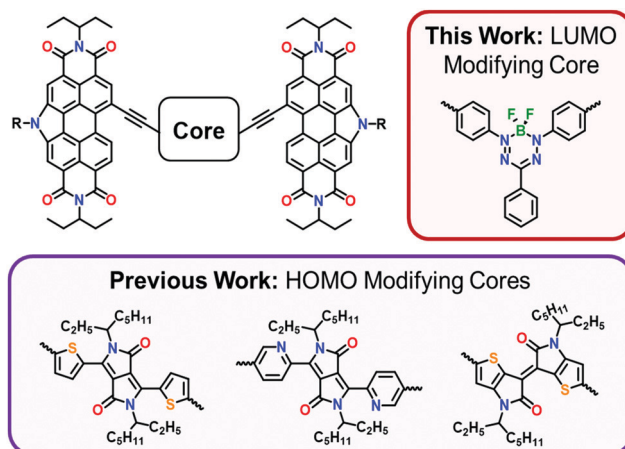


Fig. 1 Depicting previously investigated HOMO-modifying and newly synthesized LUMO-modifying N-annulated PDI-core-PDI materials. R = hexyl (HOMO modifying cores) or 2-ethylhexyl (LUMO modifying core).

influencing the lowest unoccupied molecular (LUMO) energy level, we targeted an acetylene-terminated boron difluoride formazanate (**BF₂fz**), a chromophore popularized by the Gilroy research group.²²⁻²⁴ The properties of **BF₂fz** materials are highly sensitive to structural variation at the *N*-aryl substituents,²⁵⁻²⁷ meaning the optoelectronic properties can be tuned by the choice of endcap material. In this contribution, we report the synthesis, characterization, and NFA capability of a new π -conjugated material comprised of a **BF₂fz** core acetylene-linked to N-annulated PDI endcaps (**BF₂PDI₂**).

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Characterization

The **BF₂fz** core²² and N-annulated PDI (Br-PDIN-EH)⁸ end caps were connected *via* a Sonogashira cross-coupling reaction to generate **BF₂PDI₂** (see ESI† for full experimental details). The identity of **BF₂PDI₂** was confirmed by ¹H, ¹¹B, ¹³C, and ¹⁹F NMR spectroscopy, as well as MALDI TOF mass spectrometry and CHN elemental analysis (Fig. S1–S7, ESI†). The ¹¹B and ¹⁹F NMR spectra exhibited diagnostic 1:2:1 triplet and 1:1:1:1 quartet coupling patterns, respectively.²⁵ Moreover, the ¹H NMR spectrum showed no evidence of a formazan related N-H peak (at ~15 ppm),²² strongly suggesting the **BF₂fz** core remained intact throughout synthesis and purification.

The thermal properties of **BF₂PDI₂** were measured using a combination of differential scanning calorimetry and thermal gravimetric analysis (Fig. S8 and S9, ESI†). No obvious glass transitions or melting points were observed between 100–300 °C, while the onset of molecular decomposition was not observed until >300 °C. The high thermal stability observed in **BF₂PDI₂** may be attributed to significant π -conjugation between the **BF₂fz** core and the N-annulated PDI endcaps. This notion was supported by the density functional theory (DFT) optimized structure of **BF₂PDI₂** at the B3LYP-6-31G(d,p) level of theory (Fig. S14, ESI†). The PDI units were nearly co-planar with each other, with only a small degree of bending caused by the **BF₂fz** core. This DFT optimized ‘dragonfly’ structure corresponded well with previously determined X-ray crystallography structures for compounds using the same **BF₂fz** core.^{23,24}

Next, the electronic properties of **BF₂PDI₂** were probed using cyclic voltammetry (CV), with additional information provided by DFT calculations. The CV of **BF₂PDI₂** was comprised of three irreversible oxidation events, as well as four fully reversible reduction events (Fig. 2). While the number oxidation events could be determined by differential pulse voltammetry (Fig. S13, ESI†), the precise electrochemical origin may not be readily

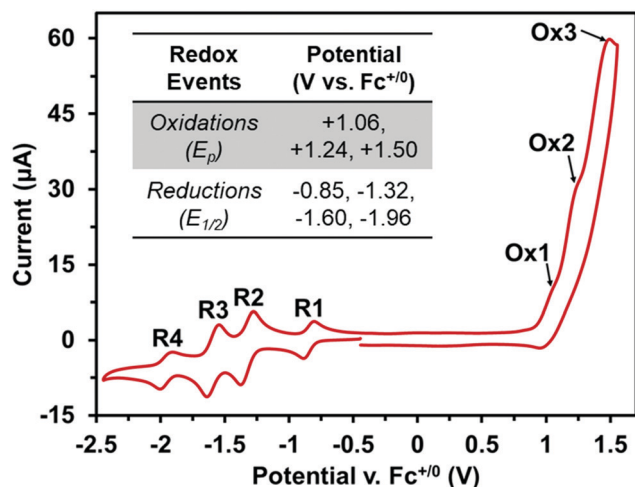


Fig. 2 Cyclic voltammogram of **BF₂PDI₂**, measured at 100 mV s⁻¹ in CH₂Cl₂ under argon with 0.1 M TBAPF₆ supporting electrolyte (WE = glassy carbon, CE = Pt-wire, *pseudo*-RE = Ag/AgCl). Inset are all measured oxidation (Ox) and reduction (R) events, referenced to Fc⁺⁰.

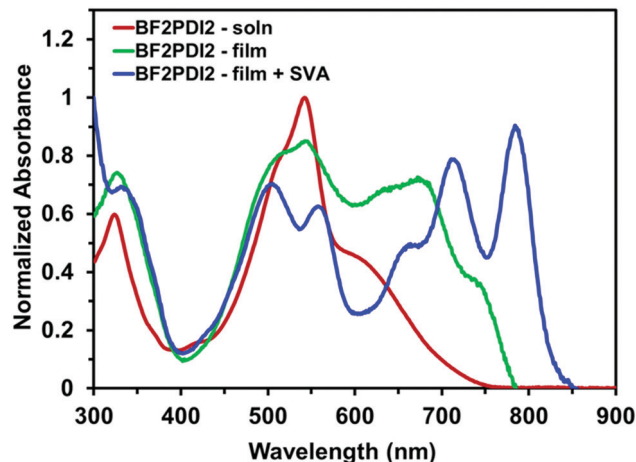


Fig. 3 UV-vis-nIR absorption profile of **BF₂PDI₂** in CHCl₃ solution (red), thin-film spin-cast from *o*-dichlorobenzene (green), and the same thin-film solvent vapor annealed from CHCl₃ (blue).

assigned. On the other hand, the first and fourth reductions ($E_{1/2} = -0.85$ and -1.96 V vs. Fc⁺⁰) may be attributed to **BF₂fz** core, while the second and third reduction events ($E_{1/2} = -1.32$ and -1.60 V vs. Fc⁺⁰) may be attributed to N-annulated PDI as the current passed during these redox processes was 2× larger. By DFT calculations, the first oxidation event appeared to be delocalized across the entire molecule, while the first reduction event was largely centered on the **BF₂fz** core (Fig. S15, ESI†). The predicted HOMO–LUMO energy levels correlate well with the observed CV data. Together, these data strongly suggest that the **BF₂fz** core has a higher electron affinity than the N-annulated PDI endcaps, which served to lower the LUMO energy level of **BF₂PDI₂**, when compared to related compounds with different cores.²¹

The optical properties of **BF₂PDI₂** were measured by UV-visible-nearIR absorption spectroscopy (UV-vis-nIR). The UV-vis-nIR profile of **BF₂PDI₂** in solution exhibited a broad absorbance between 450–750 nm, with an absorption maximum (λ_{max}) at 543 nm attributable to the PDI endcaps and a low energy shoulder just beyond 600 nm attributed to the **BF₂fz** core (Fig. 3). By overlaying the optical spectra of **BF₂PDI₂** with its constituent fragments (BF₂Ace₂ and PDIN-EH, Fig. S11, ESI†), it was revealed that the low energy shoulder attributed to **BF₂fz** core was red-shifted in **BF₂PDI₂**, emphasizing the extension of π -conjugation induced by the PDI endcaps. When spin-cast into a thin-film, the optical profile of **BF₂PDI₂** underwent several notable changes. Beyond the slightly red-shifted onset of absorption (λ_{onset}), the broadening of λ_{max} was also accompanied by an appreciable increase in the intensity of the low-energy shoulder, consistent with enhanced electron delocalization along the π -conjugated backbone.²¹

In the past, we have shown that post-deposition solvent vapor annealing (SVA) can induce structural order within the solid-state morphology of similar PDI-core–PDI materials.^{11,28–31} Exposure of the **BF₂PDI₂** thin-film to CHCl₃ solvent vapors caused the once broad solid-state optical profile to resolve into two distinct absorption regions. The PDI-based λ_{max} region was split into two peaks ($\lambda = 508$ and 560 nm), while the low-energy shoulder

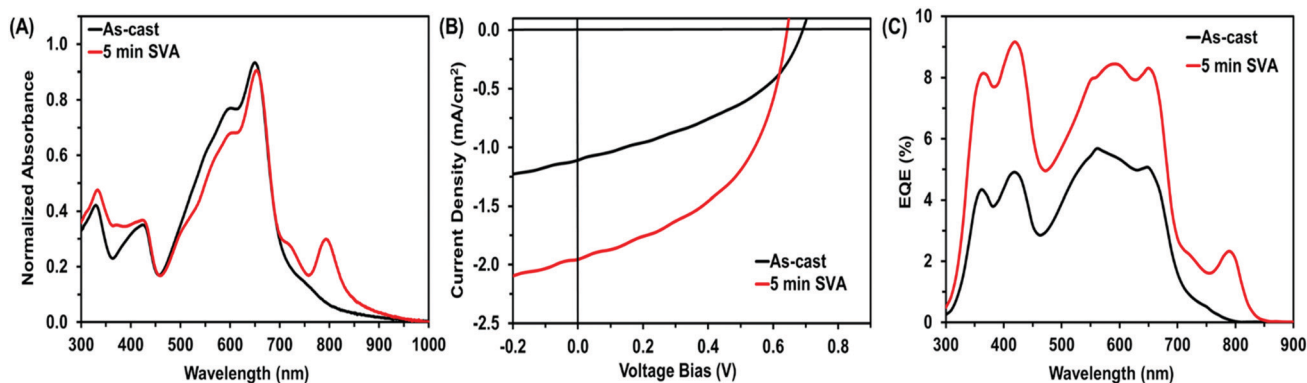


Fig. 4 Optical absorption profile (A), J - V curves (B), an external quantum efficiency plots (C) comparing the effects of solvent vapor annealing with CHCl_3 on ternary blend OPV devices with a FBT: BF_2PDI_2 : PC_{61}BM (1:1:0.5) active layer at 10 mg mL^{-1} total concentration.

developed fine structure ($\lambda_{\text{max}} = 790 \text{ nm}$) that extended well into the near-IR ($\lambda_{\text{onset}} = 850 \text{ nm}$). This behaviour is strongly indicative of molecular reorganization and/or aggregation of BF_2PDI_2 into ordered domains with strong intermolecular electronic-coupling in the solid-state.^{32–34}

OPV devices

The NFA capabilities of BF_2PDI_2 were assessed by constructing some proof-of-concept OPV devices with the following inverted architecture: ITO/ZnO/ternary active layer/MoOx/Ag (full experimental details in ESI†). A ternary active layer comprised of electron-donor polymer PPDT2FBT (FBT), PC_{61}BM , and BF_2PDI_2 was employed for OPV devices. FBT was selected because of its complementary absorption with the solvent vapor annealed film of BF_2PDI_2 (Fig. S16, ESI†). PC_{61}BM was added to this ternary blend to assist with charge mobility.³⁵ Using a FBT: BF_2PDI_2 : PC_{61}BM blend ratio of (1:1:0.5) at 10 mg mL^{-1} total concentration, the best OPV devices achieved an open circuit voltage (V_{oc}) of 0.69 V, a short circuit current (J_{sc}) of 1.1 mA cm^{-2} , and a fill factor (FF) of 41%, leading to a power conversion efficiency (PCE) of 0.3% (Table S1, ESI†).

Post-deposition treatment of these films with CHCl_3 SVA resulted in the desired optical profile shift of BF_2PDI_2 , giving the OPV devices a near-panchromatic absorbance (Fig. 4A). Device performance was maximized after 5 min of CHCl_3 SVA, where both the J_{sc} and FF increased to 1.9 mA cm^{-2} and 49%, respectively, leading to a 2-fold increase in PCE to 0.6% (Fig. 4B). Longer SVA treatments led to OPV performances similar to as-cast devices (Fig. S17 and Table S2, ESI†). This phenomena has previously been observed with our N-annulated PDI-core-PDI materials and was attributed to over-annealing of the active layer.^{11,28}

To better understand the observed enhancement in OPV performance for FBT: BF_2PDI_2 : PC_{61}BM (1:1:0.5) ternary blends that were SVA using CHCl_3 for 5 min, photoluminescence (PL) and external quantum efficiency (EQE) experiments were performed. PL measurements of the ternary blend showed efficient quenching of the FBT polymer before and after SVA treatment (Fig. S18, ESI†). Analysis of the EQE spectra, the

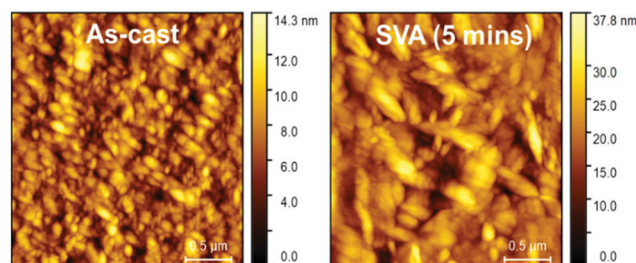


Fig. 5 Atomic force microscopy height images of ternary blend OPV devices with an FBT: BF_2PDI_2 : PC_{61}BM (1:1:0.5) active layer at 10 mg mL^{-1} total concentration.

measured photocurrent clearly displays contributions from all components of the ternary blend (Fig. 4C). Following SVA treatment, photocurrent generation was extended well into the near-IR ($\lambda_{\text{max}} = 790 \text{ nm}$), clearly emphasizing the increased contribution from the new NFA material, BF_2PDI_2 .

Surface morphology differences between the as-cast and SVA treated devices were also analyzed by atomic force microscopy (AFM). AFM height images showed significant differences between the as-cast and SVA treated devices (Fig. 5), as the root-mean square surface roughness of the films increased from 1.9 nm to 4.8 nm. X-ray diffraction (XRD) measurements of ternary blend films before and after CHCl_3 SVA failed to show any distinguishing features that could be attributed to BF_2PDI_2 (Fig. S19, ESI†).³⁶ Together, these data suggest that SVA enhanced OPV performance by inducing BF_2PDI_2 aggregation into phase separated domains, rather than crystallization.

Conclusions

In conclusion, we have synthesized and fully characterized a first-of-its-kind NFA containing a BF_2fz core. The use of acetylene-linkers enabled through-conjugation between the BF_2fz core and the PDI endcaps, leading to an altered LUMO energy level that resulted in near-panchromatic absorption for BF_2PDI_2 . The new compound is a rare example of an acceptor-acceptor type π -conjugated architecture. Treatment of solid-state BF_2PDI_2 with CHCl_3 SVA resulted in a significant

bathochromic shift of the optical spectra, leading to near-IR absorption. The overall performance in a series of proof-of-concept OPV devices, where **BF₂PDI₂** was used as an NFA in a ternary blend system, was improved 2-fold by SVA treatment of the active layer. The increase in PCE could be mainly attributed to favorable aggregation of **BF₂PDI₂** in the active layer which increased the generated photocurrent. This notion was supported by EQE and AFM measurements. This work demonstrates the utility of the **BF₂fz** organic dye to construct narrow bandgap π -conjugated materials for use in organic electronics and provides the groundwork for further development.

Conflicts of interest

There are no conflicts to declare.

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