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*Chem. Mater.,* **Just Accepted Manuscript** • DOI: 10.1021/acs.chemmater.6b00131 • Publication Date (Web): 25 Feb 2016

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\(\pi\)-Bridge-Independent 2-(Benzo[c][1,2,5]thiadiazol-4-ylmethylene)malononitrile-Substituted Nonfullerene Acceptors for Efficient Solar Cells

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Supporting Information Placeholder

ABSTRACT: Molecular acceptors are promising alternatives to fullerenes (e.g. PC\(_{60}\)...BM) in the fabrication of high-efficiency bulk-heterojunction (BHJ) solar cells. While solution-processed polymer-fullerene BHJ devices have recently met the 10% efficiency threshold, molecular acceptors have yet to prove comparably efficient with polymer donors. At this point in time, it is important to forge a better understanding of the design parameters that directly impact small-molecule (SM) acceptor performance in BHJ solar cells. In this report, we show that 2-(benzo[c][1,2,5]thiadiazol-4-ylmethylene)malononitrile (BM)-terminated SM acceptors can achieve efficiencies as high as 5.3% in BHJ solar cells with the polymer donor PCE0. Through systematic device optimization and characterization studies, we find that the nonfullerene analogues (FBM, CBM and CDTBM) all perform comparably well, independent of the molecular structure and electronics of the \(\pi\)-bridge that links the two electron-deficient BM end groups. With estimated electron affinities within range of those of common fullerenes (4.0-4.3 eV), and a wider range of ionization potentials (6.2-5.6 eV), the SM acceptors absorb in the visible spectrum and effectively contribute to the BHJ device photocurrent. BM-substituted SM acceptors are promising alternatives to fullerenes in solution-processed BHJ solar cells.

Introduction

Fullerene acceptors, such as phenyl-C\(_{61}\)-butyric acid methyl ester or its C\(_{n}\) analogue (PC\(_{60}\)...BM, PC\(_{70}\)...BM), have long represented the most effective electron-transport material in solution-processed bulk-heterojunction (BHJ) solar cells with \(\pi\)-conjugated polymer and small-molecule (SM) donors.\(^5\)\(^-\)\(^7\) Fullerenes have large electron affinity (EA) and ionization potential (IP) values of ca. 4.1-4.3 eV and 5.9 eV, respectively, favorable electron mobilities on the order of 10\(^{-3}\) cm\(^2\)/Vs\(^-\) in diode configurations, and isotropic carrier transport characteristics. In addition, they tend to develop intimately mixed percolation networks with polymer and SM donors, with domain sizes on the order of exciton diffusion lengths common to organic electronics (5-20 nm). Achieving comparable characteristics with alternative, planar \(\pi\)-conjugated molecular systems has shown to be a remarkably challenging exercise over the years,\(^6\)\(^-\)\(^{10}\) and fullerenes remain the best-performing electron acceptors to date, yielding power conversion efficiencies (PCEs) of over 10% in BHJ solar cells with various polymer and SM donors.\(^11\)\(^-\)\(^{14}\) It is worth noting that planar SM acceptors can combine tunable EA and IP values, visible spectral absorption and charge transport characteristics by design.\(^5\) In principle, these fullerene alternatives should rival PCBM acceptors, whose absorption is mostly confined to the short-wavelength range of the UV-visible spectrum (ca. 300-500 nm). Despite compelling potential benefits over PCBM acceptors, including synthetic accessibility and modularity, the reasons why planar SM acceptors are not currently outperforming their fullerene counterparts remain a matter of some debate.\(^16\)\(^-\)\(^{19}\) In turn, at this point in time, it is important to forge a better understanding of the design parameters that directly impact nonfullerene acceptor performance in BHJ solar cells.

Given the outstanding headway made in the past recent years in optimizing polymer and SM donor performance using fullerenes as model systems,\(^5\)\(^-\)\(^{20}\)\(^-\)\(^{22}\) a case could be made that further BHJ solar cell efficiency improvements...
should come from the optimization of the acceptor component. Several approaches are currently being explored in the design of nonfullerene acceptors, generally using some of the following motifs to promote the electron-transport properties of polymer and/or SM systems: perylene diimide (PDI), naphthalene diimides (NDI), diketopyrrolopyrrole (DPP), benzothiadiazole and analogues, and more recently rhodamines. In the design of efficient SM acceptors, the use of motifs that can induce “out-of-plane” molecular geometries and limit excess SM crystallization in BHJ thin films has been described as an important parameter in several studies. However, it is worth noting that (i) published polymer and SM acceptor systems do not currently outperform PCBM acceptors, and (ii) more planar and efficiently. At present, several SM systems can achieve PCE >6% in BHJ solar cells with specific polymer donors, but most reported systems have met with PCE limits of 5% or less, and it remains critically important to continue examining the key design principles that will help identify SM acceptors outperforming their fullerene counterparts. For practical reasons, the most synthetically accessible systems will likely become the most relevant.

Another promising electron-accepting motif for the design of SM acceptors may be 2-(benzo[c][1,2,5]thiadiazol-4-ylmethylene)malononitrile (BM). Used in earlier work on SM donors for vacuum-deposited SM solar cells, BM end groups induce high EAs (i.e. low-lying LUMOs), efficient intramolecular charge transfer characteristics with electron-rich motifs, and promote rigid-planar structures that favors the development of specific intermolecular interactions (e.g. π-π stacking) which, in turn, tend to improve carrier mobilities. While BM-substituted SM donors have led to high-efficiency (vacuum-deposited) triple-junction solar cells of PCEs >1%, this motif has rarely been used in the design of nonfullerene acceptors. Recent work has, however, shown that BM-substituted SM acceptors can yield PCEs >4% in BHJ solar cells with the polymer donor PBDTTT-C-T. In this contribution, we report on a set of three solution-processable SM acceptors composed of BM end groups linked via distinct π-bridges: fluorene (FBM), carbazole (CBM) and cyclopenta[2,1-b]dithiophene (CDTBDM) (Chart 1). The π-bridges are shown to fine-tune the electronics and the molecular conformation of the SM acceptors, imparting estimated EAs within range of those of common fullerene acceptors (4.0-4.3 eV) and a wider range of IPs (6.2-5.6 eV). The nonfullerene analogues absorb in the visible spectrum (FBM, CBM: 400-600 nm; CDTBDM: 500-850 nm), and we show that BHJ solar cells efficiencies >5% can be achieved with the polymer donor PCE10 (Chart 1).

Importantly, we demonstrate that the SM analogues all perform comparably well in BHJ solar cells, independent of the molecular structure and electronics of the π-bridge that links the two electron-deficient BM end groups, suggesting that BM-substituted SMs are a very promising class of nonfullerene acceptors.

**Chart 1.** 2-(Benzo[c][1,2,5]thiadiazol-4-ylmethylene)-malononitrile-substituted SM Acceptors: FBM, CBM and CDTBDM.

### Results and Discussion

#### Design, Synthesis and Material Properties

The design of molecular acceptors with finite, relatively short conjugation lengths, as alternatives to fullerenes, has practical implications that span synthetic accessibility and potentially low synthetic costs compared to those associated with the synthesis of PCBM analogues (subject to extensive purification protocols). The ability to tune the optoelectronic properties (i.e. EAs, IPs, spectral absorption, etc.) of SM acceptors by design is another clear benefit given that fullerene derivatizations have either modest effects on their optoelectronics or tend to lead to lower material performance in BHJ solar cells with polymer donors. A few recently published studies point to the relevance of small-size, “linear”, solution-processable molecular acceptors as PCBM replacements, some with promising BHJ solar cell efficiencies >2%. Following these considerations, the synthetic route to FBM and CBM involve the two key steps depicted in Scheme 1: (i) Pd-mediated Suzuki cross-coupling between the diboronic acid bis(pinacol) esters of fluorene or carbazole and 7-bromobenzo[c][1,2,5]thiadiazole-4-carbaldehyde, and (ii) Knoevenagel condensation of intermediates 1 and 2 with malononitrile; see details in the Supporting Information, SI. The synthetic route to CDTBDM (Scheme 1) involves a microwave-assisted direct Pd-mediated Stille cross-coupling between 4,4-diioctyl-2,6-bis(trimethylstannylyl)-4H-cyclopenta[2,1-b][3,4-b']dithiophene and 2-(7-bromobenzo[c][1,2,5]thiadiazol-4-yl)methylene)malononitrile. After sequential purifications
via column chromatography and recycling SEC (see details in SI), the SM acceptors FBM and CBM were collected as dark red solids in overall 45-55% yields, and CDTBM was obtained as a dark blue-green solid in a yield of ca. 65%. All three SM systems were found to be soluble in common organic solvents such as dichloromethane, chloroform, 1-chlorobenzene and 1,2-dichlorobenzene (appropriate solvents in the making of BHJ solar cells with established polymer donors, such as PC60M). Further synthetic details and structural analyses including 1H NMR, 13C NMR, and high-resolution mass spectrometry (HRMS) for all intermediates and products are provided in the SI.

First-level density functional theory (DFT) calculations (Fig. S2) show that the BM end groups tend to localize electron density on the periphery of the LUMOs in FBM and CBM SM acceptors, while the π-electron system is more delocalized and quinoidal in character in CDTBM; DFT at the B3LYP/6-31G(d,p) level with Gaussian 09 (Revision C.01) (cf. details in SI). These effects correlate with the “out-of-plane” geometry of FBM and CBM (Fig. S1), for which dihedral angles of ca. 34° and 32°, respectively, exist between the fluorene/carbazole motifs and the BM end groups; results consistent with prior calculations. In contrast, the SM acceptor CDTBM is expected to be relatively planar and its π-system more delocalized in the ground state (see HOMO of CDTBM in Fig. S2). Although side chains play an important role in molecular self-assembly, it is commonly assumed that the electronic properties and backbone geometry of single isolated π-conjugated systems are well represented in gas phase calculations where side chains are swapped for methyl groups (to optimize computational time).

Figure 1 shows the thin-film UV-Vis optical absorption spectra of FBM, CBM and CDTBM in terms of absorption coefficients (in the range 2.6-2.9 x 10^4 cm^-1 at the longer-wavelength peak maxima). While FBM and CBM are found to have comparable onsets of absorption (ca. 590 and 610 nm, respectively) and, in turn, equivalent optical bandgap ($E_{opt}$) values of ca. 2 eV, CDTBM shows a significantly more red-shifted onset of absorption (ca. 850 nm) and a narrower $E_{opt}$ of ca. 1.5 eV. These differences can, in part, be explained by the larger extent of planarity expected in CDTBM compared to the “out-of-plane” conformations seen in FBM and CBM (Fig. S1). The solution and thin-film UV-Vis absorption spectra of the three SM acceptors FBM, CBM and CDTBM are overlaid in Figure S2. A comparison of the spectral absorption in solution and in the neat films shows that CDTBM undergoes a substantially more pronounced red-shift of ca. 100 nm (compared to ca. 40 nm for FBM and CBM; referenced to the onset), suggesting a relatively strong propensity to form ordered aggregates in thin films. In solution, however, the absence of long-wavelength absorption shoulders in the spectra of all SM acceptors indicate that the molecules are not prone to π-aggregate formation and can be well dispersed.

![Figure 1](image-url)
CBM, and ca. 5.7 eV for CDTBM; expectedly large IP values within range of those commonly inferred for fullerene acceptors, and only slightly larger than the HOMO energy levels of ca. 6.2 eV, 6.1 eV and 5.8 eV (respectively) inferred from our DFT calculations. Table 1 provides further details, including electrochemically-estimated IPs and EAs (cf. details in SI), and bandgap estimations obtained from the DFT calculations (H\textsubscript{L}agap). Figure S5 shows the reduction scans from which the electrochemically-estimated EAs were inferred: ca. 4.1 eV for FBM, ca. 4.1 eV for CBM, and ca. 4.3 eV for CDTBM; values within range of those of common fullerene acceptors such as PC\textsubscript{60}BM and PC\textsubscript{71}BM (4.1-4.3 eV).

The thermogravimetric analyses (TGA) given in Figure S6 show that the SM acceptors FBM, CBM and CDTBM are thermally stable in nitrogen atmosphere until ca. 350°C (ca. 5% weight loss observed at 373°C; 361°C and 432°C, respectively). The differential scanning calorimetry (DSC) analyses shown in Figure S7 for FBM and CBM do not show any specific characteristic phase transitions, but the DSC traces of CDTBM indicate that a phase transition occurs in the range 80-100 °C, tentatively assigned to a melt in light of the apparent first order solidification peak on the reverse (cooling) scan (cf. details in SI).

The grazing incidence wide-angle X-ray scattering plots (GIWAXS; cf. details in SI) for neat films of FBM, CBM and CDTBM in Figure S8 indicate that the SM acceptors form relatively disordered films, without long-range ordering characteristics. In particular, the absence of scattering reflections in the 2D patterns of FBM and CBM (Fig. S8a and S8b) supports the idea that amorphous morphologies prevail in thin films made with these two SM analogues. Meanwhile, the scattering peak intensity seen in the 2D pattern of CDTBM along q\textsubscript{||} (0.2-0.5 Å\textsuperscript{-1}) and the weak π-stacking reflection centered along q\textsubscript{∥} (ca. 1.75 Å\textsuperscript{-1}) suggest the presence of edge-on-oriented aggregates in thin films (Fig. S8c). We note, however, that the absence of any pronounced scattering intensity at high q values (1.5-2 Å\textsuperscript{-1}) in neat films of FBM, CBM and CDTBM implies that the SM aggregates are not correlated along the π-stacking direction.

### Table 1. Summary of Optoelectronic Parameters for the SM Acceptors: FBM, CBM and CDTBM.

<table>
<thead>
<tr>
<th>SM Acceptor</th>
<th>λ\textsubscript{abs/sol} (nm)</th>
<th>λ\textsubscript{abs/film} (nm)</th>
<th>IP\textsuperscript{a} (eV)</th>
<th>EA\textsuperscript{b} (eV)</th>
<th>E\textsubscript{Lagap} (eV)</th>
<th>IP\textsuperscript{c} (eV)</th>
<th>EA\textsuperscript{d} (eV)</th>
<th>E\textsubscript{chem} (eV)</th>
<th>HOMO\textsuperscript{c} (eV)</th>
<th>LUMO\textsuperscript{c} (eV)</th>
<th>H\textsubscript{L}agap\textsuperscript{e} (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FBM</td>
<td>486 (5.18)</td>
<td>501 (4.46)</td>
<td>6.14</td>
<td>4.03</td>
<td>2.11</td>
<td>6.25</td>
<td>4.14</td>
<td>1.02</td>
<td>6.18</td>
<td>3.67</td>
<td>2.51</td>
</tr>
<tr>
<td>CBM</td>
<td>497 (5.20)</td>
<td>517 (4.43)</td>
<td>5.97</td>
<td>4.04</td>
<td>2.02</td>
<td>6.05</td>
<td>4.13</td>
<td>1.92</td>
<td>6.10</td>
<td>3.64</td>
<td>2.46</td>
</tr>
<tr>
<td>CDTBM</td>
<td>681 (5.34)</td>
<td>701 (4.47)</td>
<td>5.72</td>
<td>4.27</td>
<td>1.45</td>
<td>5.69</td>
<td>4.28</td>
<td>1.41</td>
<td>5.79</td>
<td>3.90</td>
<td>1.89</td>
</tr>
</tbody>
</table>

\textsuperscript{a}Estimated by photoelectron spectroscopy (PESA). \textsuperscript{b}Inferred from PESA-estimated IPs and E\textsubscript{opt} values. \textsuperscript{c}Optical bandgaps estimated from the onset of the UV-Vis absorption spectra (films). \textsuperscript{d}Estimated from cyclic voltammetry (CV) measurements; IP=I\textsubscript{opt,ox}+5.1 eV and EA=I\textsubscript{opt,red}+5.1 eV (absolute values), E\textsubscript{chem}=IP-EA. \textsuperscript{e}DFT-calculated HOMO and LUMO energy levels (absolute values), and HOMO→LUMO gaps (H\textsubscript{L}agap); obtained at the B3LYP/6-31G(d,p) level.

### Device Testing and Characterizations

Thin-film BHJ solar cells with the inverted device structure ITO/α-ZnO\textsuperscript{6}/PCEio:SM/MoO\textsubscript{3}/Ag (device area: 0.1 cm\textsuperscript{2}) were fabricated and tested under AM1.5G solar illumination (100 mW/cm\textsuperscript{2}). The cells with optimized PCEio:SM blend ratios (PCEio:FBM, 4.6 wt/wt; PCEio:CDTBM, 4.6 wt/wt; PCEio:CBM, 3.7 wt/wt) were cast from chlorobenzene (CB) (cf. details in SI, active layer thicknesses: Avg. 65 nm); the control PCEio:PC\textsubscript{71}BM (4.6 wt/wt) devices were cast from chlorobenzene (CB) according to established optimized protocols (cf. details in SI).\textsuperscript{63} Figure 2a depicts the current-voltage (J-V) characteristics of optimized FBM, CBM and CDTBM-based BHJ solar cells with the polymer donor PCEio. As shown in Table 2 (device statistics provided in the SI, Tables S1 and S2), "as-cast" BHJ devices made from the SM acceptors FBM, CBM and CDTBM all achieved substantial average PCE values of ca. 4% (Max. 4.6% obtained for CDTBM), with high short-circuit currents (I\textsubscript{SC}) >9 mA/cm\textsuperscript{2}, but relatively modest fill-factor (FF) values in the range 44-53%. Optimized BHJ devices made from blends containing 0.8-2% (v/v) of the processing additive 1-chloronaphthalene (CN) or 1,8-diiodooctane (DIO) showed improved I\textsubscript{SC} (10-12 mA/cm\textsuperscript{2}) and FF (50-60%) values, and reached higher PCEs of ca. 5% (Max. 5.3% obtained with CBM). Small-molecule additives, such as CN and DIO, are now commonly used in the optimization of BHJ solar cells,\textsuperscript{64} inducing changes in the blend morphologies and/or its structural ordering pattern, and \textit{in the favorable instances} – resulting in improved device PCEs. It should be noted that the large open-circuit voltage (V\textsubscript{OC}) values of ca. 0.9 V obtained in BHJ solar cells with FBM and CBM (vs. ca. 0.8 V for the reference PCEio:PC\textsubscript{71}BM solar cells, cf. details in SI) are consistent with the shallower electrochemically-estimated EAs of these two SM acceptors (ca. 4.1 eV) compared to that of PC\textsubscript{71}BM (4.1-4.3 eV); the lower V\textsubscript{OC} of ca. 0.65-0.7 V obtained with CDTBM is in agreement with the larger electrochemically-estimated EAs of this system (ca. 4.3 eV) compared to those of FBM and CBM. Interestingly, the lower V\textsubscript{OC} of the CDTBM-based BHJ devices is outweighed by the higher J\textsubscript{SC} and FF values, and overall, all SM acceptors perform comparably well.

The comparable J\textsubscript{SC} values achieved in optimized FBM-, CBM- and CDTBM-based BHJ solar cells (Fig. 2a) are consistent with the external quantum efficiency (EQE) spectra (Fig. 2b); integrated EQEs vs. J\textsubscript{SC} ± 0.6 mA/cm\textsuperscript{2}; ± 5%. Figure 2b emphasizes the significant contributions of FBM and CBM to the EQE in the range 400-600 nm (region complementary to the spectral absorption of PCEio), reaching ca. 70% at the SM acceptors' maximum absorp-
tion peak. In contrast, the spectral absorption of CDTBM reinforces that of PCEio in the range 550-850 nm.

**Figure 2.** (a) Characteristic J-V curves of optimized BHJ solar cells fabricated from FBM (cast from CB, 1% CN v/v), CBM (cast from CB, 2% DIO v/v), and CDTBM (cast from CB, 0.8% CN v/v), with PCEio as the polymer donor; AM1.5G solar illumination (100 mW/cm²). (b) EQE spectra of the devices fabricated from the SM acceptors and PCEio under optimized conditions. Integrated EQEs are in agreement (± 0.6 mA/cm²; ± 5%) with the Jsc values reported in Table 2.

Table 2. PV Performance of the SM Acceptors FBM, CBM and CDTBM in Inverted BHJ Devices with PCEio as the Polymer Donor.

<table>
<thead>
<tr>
<th>SM</th>
<th>additive (%)</th>
<th>Jsc [mA/cm²]</th>
<th>Voc [V]</th>
<th>FF [%]</th>
<th>Avg. PCE [%]</th>
<th>Max. PCE [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>FBM</td>
<td>0</td>
<td>10.8</td>
<td>0.88</td>
<td>44</td>
<td>4.2</td>
<td>4.4</td>
</tr>
<tr>
<td></td>
<td>1.0&lt;sup&gt;e&lt;/sup&gt;</td>
<td>11.2</td>
<td>0.88</td>
<td>51</td>
<td>5.0</td>
<td>5.1</td>
</tr>
<tr>
<td>CBM</td>
<td>0</td>
<td>9.4</td>
<td>0.89</td>
<td>48</td>
<td>4.0</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>2.0&lt;sup&gt;e&lt;/sup&gt;</td>
<td>10.6</td>
<td>0.88</td>
<td>53</td>
<td>5.0</td>
<td>5.3</td>
</tr>
<tr>
<td>CDTBM</td>
<td>0</td>
<td>11.7</td>
<td>0.68</td>
<td>53</td>
<td>4.2</td>
<td>4.6</td>
</tr>
<tr>
<td></td>
<td>0.8&lt;sup&gt;e&lt;/sup&gt;</td>
<td>11.9</td>
<td>0.66</td>
<td>60</td>
<td>4.8</td>
<td>5.0</td>
</tr>
</tbody>
</table>

<sup>6</sup>Device with optimized PCEio:SM ratio of 4:6 (wt/wt) solution-cast from chlorobenzene (CB) with CN as processing additive. <sup>7</sup>Device with optimized PCEio:SM ratio of 3:7 (wt/wt) solution-cast from chlorobenzene (CB) with DIO as processing additive. <sup>8</sup>Average values across ≥20 devices (device area: 0.1 cm²). <sup>d</sup>Additional device statistics, including standard deviations, are provided in the SI (Table S1–S2). 

Contributing to the pronounced EQE response in the long-wavelength region of the visible spectrum (where high photon flux densities occur), and peaking to ca. 60% at the SM acceptors’ absorption maximum. The onset of EQE for CDTBM-based BHJ solar cells is also red-shifted compared to that for FBM and CBM-based devices; observation in agreement with the absorption pattern of CDTBM (Fig. 1a) extending to longer wavelengths than the thin-film absorption onset of PCEio. Our transfer matrix simulations<sup>65</sup> shown in Figure 1b (max. theoretical Jsc vs. active layer thickness, assuming 100% IQE; cf. details in SI) are consistent with the observation that the Jsc values achieved in FBM-, CBM- and CDTBM-based devices with ca. 65 nm active layers fall within the same range. From these simulations, it can also be inferred that higher Jsc values may be achievable for active layers of ca. 65 nm if recombination loss pathways could be suppressed (max. theoretical Jsc at 65 nm: 17-18.5 mA/cm²; estimated Jsc losses from experimental values: 35-40%). Despite expectations of higher Jsc values from the model, thicker active layers (e.g. 90 nm) cast from optimized BHJ device processing conditions did not yield higher experimental PCEs, as incremental FF reductions prevail in increasingly thick devices. The BHJ morphologies of “as-cast” and optimized FBM, CBM and CDTBM-based BHJ devices were examined by bright-field electron transmission microscopy (TEM; cf. details in SI). The TEM images shown in Figure 3 emphasize the development of relatively fine-scale morphologies for all nonfullerene-based active layers, consistent with the promising figures of merit discussed earlier (Table 2), including PCEs >4% both for “as-cast” and optimized BHJ solar cells. We note that significant differences in phase separation patterns are known to impact BHJ solar cell performance.<sup>63-64</sup>

Here, the BHJ morphologies of the optimized nonfullerene-based devices appear comparably well mixed, and no clear difference in phase separation patterns can be observed at the scale of those analyses. Concurrent imaging of the topography and phase of the BHJ thin films via atomic force microscopy (AFM; cf. details in SI, Fig. S1-S3) is consistent with the expectation of homogeneous, non-aggregated active layer morphologies (root-mean-square (RMS) roughness <4 nm). These observations are
in agreement with (i) the high $J_{SC}$ values (>9 mA/cm$^2$) achieved across the set of nonfullerene acceptors in “as-cast” and optimized devices (Table 2 and Fig. 2a), and (ii) the near-complete photoluminescence (PL) quenching of PCE10 in the presence of FBM, CBM and CDTBM as illustrated in Figures 4 and S4 (quenching efficiencies >96% in all cases, at optimized donor-acceptor ratios). Since the

Figure 4. Photoluminescence (PL) quenching of PCE10 and the SM acceptor analogues FBM and CBM in neat films without additive (solid lines), and in the presence of the donor/acceptor counterpart (dashed lines) as in optimized BHJ thin films with additive: (a) PCE10:FBM, excitation at 500 nm, (b) PCE10:FBM, excitation at 650 nm, (c) PCE10:CBM, excitation at 500 nm, (d) PCE10:CBM, excitation at 650 nm.

spectral absorptions and PL patterns of PCE10 and the SM acceptors FBM and CBM lie in regions of distinct wavelengths, the donor and acceptor components can be individually excited at different wavelengths (Fig. 4: 650 nm and 500 nm, respectively), emphasizing that both electron and hole transfers are occurring quantitatively in the BHJ active layers. Quantitative electron and hole transfers at the donor-acceptor interfaces is reflected in the EQE spectra (Fig. 2b), where both PCE10 and the SM acceptors contribute significantly to photoinduced charge generation at short-circuit. These results further indicate that morphological aspects are not limiting the diffusion of photogenerated excitons to the PCE10-rich and SM acceptor-rich domain interfaces.

In parallel, we note that our GIWAXS analyses of the optimized PCE10:SM blend films (cf. details in SI, Fig. S15) confirm the lack of SM aggregates with pronounced π-stacking correlations and long-range ordering characteristics in thin films.

While not always apparent, subtle morphological differences between BHJ thin films can sometimes translate into distinct charge transport patterns. Turning to carrier effects, we measured the hole mobilities of PCE10 and the electron mobilities of FBM, CBM and CDTBM in optimized BHJ thin films; values inferred from the space charge limited current (SCLC) model (cf. details in SI).

Blends of PCE10:PC$_7$BM were also examined for comparison. Hole-only diodes with the configuration ITO/PEDOT/PCE10:SM/MoO$_3$/Ag, and electron-only diodes with the configuration ITO/a-ZnO/PFN-Ox/PCE10:SM/Ca/Al (device area: 0.1 cm$^2$) were fabricated for these measurements and analyzed in the dark. Figure 5 shows the dark current densities of the optimized BHJ thin films in the carrier-selective diodes as a function of applied effective field (various BHJ thicknesses were examined for more accuracy in those estimations, see Fig. S6). Our analyses indicate that the zero-field hole mobilities of the PCE10:SM blends fall within the same range, with average estimated values of 1.4×10$^{-5}$, 1.0×10$^{-4}$ and 3.4×10$^{-5}$ cm$^2$ V$^{-1}$ s$^{-1}$ with FBM, CBM and CDTBM, respectively (see Table S3). The electron mobility curves for the PCE10:SM blends followed Poole-Frenkel-type mobility fits (electric-field activated) of the form $\mu(F) = \mu_0 \exp(yF^{1/2})$, where $\mu_0$ is the zero field mobility, $y$ is the Poole-Frenkel slope and $F$ is the electric field. In turn, the zero-field electron mobilities of the PCE10:SM blends were estimated to be 1.0×10$^{-6}$, 1.9×10$^{-6}$

Figure 5. Experimental dark current densities as a function of effective electric field for (a) hole-only diodes (ITO/PEDOT/PCE10:SM/MoO$_3$/Ag); here, $V_{bi} = 0$ (flat band pattern formed by PEDOT-MoO$_3$) and (b) electron-only diodes (ITO/a-ZnO/PFN-Ox/PCE10:SM/Ca/Al) made with optimized BHJ thin films ($V_{bi} = 0.4$ V), with FBM, CBM and CDTBM as SM acceptors (film thicknesses: 140-150 nm). Data obtained for different thin thicknesses are given in SI (Fig. S6). The experimental data is fitted using the single-carrier SCLC model (solid lines; cf. details in SI).
and $1.8 \times 10^{-6}$ cm$^2$/V·s, with FBM, CBM and CDTBHM, respectively (see Table S3); results indicating that the three SM acceptors transport electrons with comparable efficiency. We note, however, that the imbalance between hole and electron mobilities in the PCEio:SM blend thin films is likely to be at the origin of significant charge build-up in the optimized BHJ solar cells, limiting the FF and $J_{sc}$. In comparison, estimated (average) hole and electron mobilities for PCEio:PC$_2$BM blends were measured to be $7.3 \times 10^{-4}$ cm$^2$/V·s and $1.5 \times 10^{-4}$ cm$^2$/V·s, respectively; results in agreement with the higher FF (ca. 70%) and $J_{sc}$ (ca. 17 mA/cm$^2$) values obtained with the reference PCEio:PC$_2$BM devices (cf. details in SI). In developing new SM acceptors, it will be critically important to identify systems with higher electron mobilities in BHJ thin films that can concurrently achieve more balanced carrier mobilities comparable to those of polymer donors (here, ca. $10^{-4}$ cm$^2$/V·s$^2$ in BHJ thin films).

Conclusions
In summary, we showed that 2-(benzo[c][1,2,5]-thiadiazol-4-yl)methylene)malononitrile (BM)-substituted SMs can be used as efficient nonfullerene acceptors in BHJ solar cells – with PCEs ≥5% achievable – independent of the π-bridge that links the two electron-deficient BM termini. Estimated EAs within range of those of common fullerene acceptors (4.0-4.3 eV) and a wider range of IPs (6.2-5.6 eV) impart the nonfullerene analogues with absorption spectra that fall within the visible range: 400-600 nm for FBM and CBM; 500-850 nm for CDTBHM. While fullerene derivatizations and purifications can be tedious and tend to have modest effects on their optoelectronics, the ability to tune the optoelectronic properties of SM acceptors by design and the absence of isomeric byproducts produced at the synthetic stage are clear benefits. In BM-terminated SM acceptors, the modularity of the π-bridge may be amenable to higher-efficiency systems and we note that further solar cell PCE improvements may also come from the selection of alternative polymer donors. Overall, this concise study shows that BM-substituted SMs are a promising class of nonfullerene acceptors for solution-processable BHJ solar cells.

Experimental Section
Material Characterizations. All compounds were characterized by NMR spectroscopy on Bruker Avance III Ultrasound Plus instruments using a 400 or 700 MHz proton frequency. High-resolution mass spectrometry (HRMS) analyses were performed on a Thermo Scientific - LTQ Velos Orbitrap MS. Synthetic methods and procedures for the syntheses of the SM acceptors are detailed in the Supporting Information (SI). Further details on UV-vis, PESA, CV, TGA, DSC, GIWAXS (neat films) and corresponding experimental conditions are developed in the SI.

Computational Analyses. All density functional theory (DFT) calculations were performed at the B3LYP/6-31G(d,p) level of theory with the Gaussian 09 (Revision C.01) software. Additional details and references can be found in the SI.

Device Testing Protocols. The BHJ solar cells were prepared on glass substrates with tin-doped indium oxide (ITO, 15 Ω sq$^{-1}$) patterned on the surface (device area: 0.1 cm$^2$). Details on substrate preparation, active layer and contact depositions are provided in the SI. J-V measurements were performed in the glovebox with a Keithley 2400 source meter and an Oriel Sol3A Class AAA solar simulator calibrated to 1 sun, AM1.5 G, with a KG-5 silicon reference cell certified by Newport. The external quantum efficiency (EQE) measurements were performed at zero bias by illuminating the device with monochromatic light supplied from a Xenon arc lamp in combination with a dual-grating monochromator. The number of photons incident on the sample was calculated for each wavelength by using a silicon photodiode calibrated by NIST. Additional details on various active layer deposition conditions, $J_{sc}$ modeling, BHJ thin-film UV-vis, TEM, AFM, PL instrumentation, GIWAXS (BHJ films), and carrier mobility measurements are developed in the SI.

ASSOCIATED CONTENT
Experimental methods, characterization, and additional figures and tables. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes
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ACKNOWLEDGMENT
This publication is based upon work supported by the King Abdullah University of Science and Technology (KAUST) Office of Sponsored Research (OSR) under Award No. CRG_R2 13_BEAU_KAUST 1. The authors acknowledge concurrent support under Baseline Research Funding from KAUST. The authors thank KAUST ACL for technical support in the mass spectrometry analyses. W.P. and T.M. gratefully acknowledge the staff of beamline 9 at the DELTA electron storage ring in Dortmund for providing beamtime and technical support for the GIWAXS measurements. W.P. and T.M. thank Marcelina Rojek for technical support in the GIWAXS measurements.

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