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Effects of heteroatom substitution in conjugated heterocyclic compounds on photovoltaic performance: from sulfur to tellurium†

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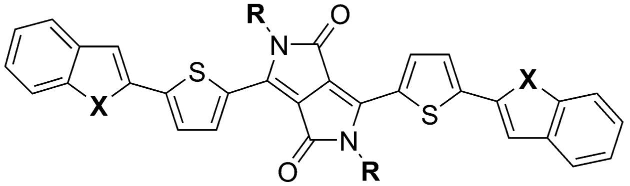
We report a general strategy for fine-tuning the bandgap of donor–acceptor–donor based organic molecules by modulating the electron-donating ability of the donor moiety by changing the benzochalcogenophene donor groups from benzothiophenes to benzoselenophenes to benzotellurophenes. These molecules show red-shifts in absorption and external quantum efficiency maxima from sulfur to selenium to tellurium. In bulk heterojunction solar cell devices, the benzoselenophene derivative shows a power conversion efficiency as high as 5.8% with $PC_{61}BM$ as the electron acceptor.

Understanding structure–property relationships in conjugated organic materials is essential for improving the characteristics of optoelectronic devices.[1,2] The rational design of organic semiconducting materials has led to notable improvements in the efficiencies of organic photovoltaic (OPV) devices. Bandgap engineering strategies, in which the frontier molecular orbital energy levels of both the electron donor and electron acceptor components of bulk heterojunction OPV cells are adjusted to optimize performance, have proven effective in enabling improvements in efficiency. Here, we describe systematic studies on benzochalcogenophene-containing donor–acceptor–donor type molecules by changing the donor moieties from benzothiophene to benzoselenophene and benzotellurophene, and demonstrate their performance as efficient electron donors in OPV cells.

Conjugated organic light-absorbing molecules or macromolecules with alternating electron-rich and electron-deficient moieties have narrower bandgaps, which enhances light harvesting and results in higher short circuit current densities (J_{sc}).[3] However, open circuit voltage (V_{oc}), which is related to the energy offset between the highest occupied molecular orbital (HOMO) of the donor and the lowest unoccupied molecular orbital (LUMO) of the acceptor, is often lowered in these molecules due to elevation of the HOMO energy level of the donor. In order to obtain simultaneous enhancements in V_{oc} and J_{sc}, designing organic electron donors and fine-tuning their energy levels is a useful approach towards maximizing OPV efficiency.[4,5] Seferos and coworkers have demonstrated that energy levels can be controlled through atomistic bandgap engineering in conjugated donor–acceptor polymer backbones by changing the heteroatom in the acceptor benzochalcogenodiazole unit from sulfur to selenium to tellurium.[6,7] In comparisons with analogous thiophene-containing polymers, smaller bandgaps have been observed in the tellurophene-based polymers.[8,9]

From this perspective, isoelectronic substitution,[10] or systematic replacement of heteroatoms in aromatic heterocycles of electron donors would modulate electron-donating ability and potentially enhance properties such as optical absorption and carrier mobility that positively affect OPV device power conversion efficiency.[11]

To this end, we have chosen the benzofuran end-capped diketopyrrolopyrrole (DPP) derivative, **DPP(TBFu)₂** (**1**, Fig. 1) developed by Nguyen and co-workers, which is a high efficiency molecular system boasting a power conversion efficiency (PCE) of 4.4% with $PC_{71}BM$,[12,13] as a parent structure and investigated the effect of changing the benzochalcogenophene heteroatom from sulfur to selenium to tellurium on optoelectronic and



DPP(TBFu)$_2$ (1)
X = O
R = 2-ethylhexyl

⟹

DPP2T(BTh)$_2$ (2): X = S
DPP2T(BSe)$_2$ (3): X = Se
DPP2T(BTe)$_2$ (4): X = Te
R = 2-butyloctyl

Fig. 1 Structures of **DPP(TBFu)$_2$**, **DPP2T(BTh)$_2$**, **DPP2T(BSe)$_2$**, and **DPP2T(BTe)$_2$**.

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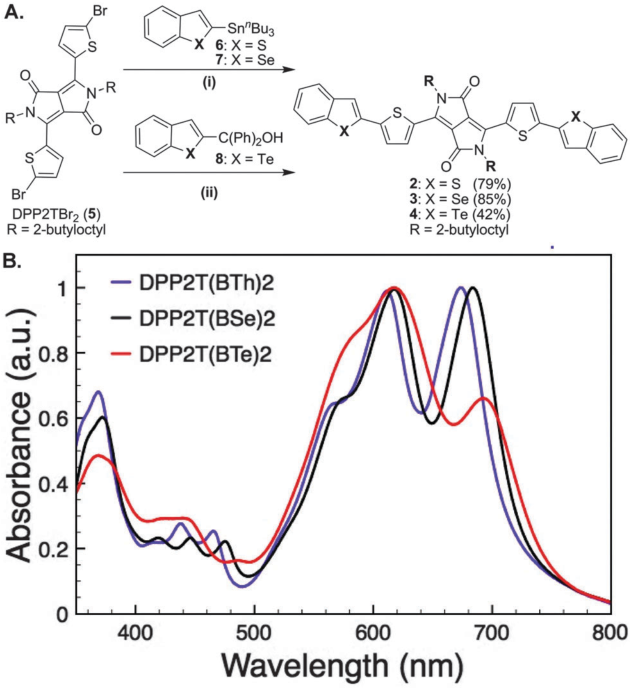

Fig. 2 (A) Synthesis of **2**, **3**, and **4**. (i) Pd(PPh$_3$)$_4$/toluene (110 °C); (ii) Pd(OAc)$_2$, PCy$_3$, Cs$_2$CO$_3$/*o*-xylene (140 °C). (B) Optical absorption spectra in thin films cast from chloroform.

device properties. Because solubility of this series of molecules in common solvents decreases as furan groups are replaced with other heterocycles, the use of longer 2-butyloctyl solubilizing chains was necessary.[14,15]

Compounds **DPP2T(BTh)$_2$** (**2**) and **DPP2T(BSe)$_2$** (**3**) containing benzothiophene and benzoselenophene units were synthesized efficiently (isolated yields of 79% for **2** and 85% for **3**) using a Stille coupling methodology with 3,6-bis(5-bromo-2-thienyl)-2,5-dihydro-2,5-di(2-butyloctyl)pyrrolo[3,4-*c*]pyrrolo-1,4-dione **DPP2TBr$_2$** (**5**)[16] and 2-tributylstannylbenzothiophene (**6**) or 2-tributylstannylbenzo-selenophene (**7**) (Fig. 2A). For the benzotellurophene-containing compound **DPP2T(BTe)$_2$** (**8**), the Stille coupling route offered low yields, as have previously been observed with other tellurophene derivatives.[6] Because the *ipso*-arylative coupling of diphenylcarbinol-substituted heterocycles has previously been reported,[17] it was examined as an alternative strategy. Benzo[*b*]tellurophene[18] was lithiated in the 2-position followed by addition of benzophenone to afford (2-benzotellurophenyl)diphenylmethanol (**8**). The palladium-catalyzed *ipso*-arylation reaction between benzotellurophene derivative **8** and DPP core **5** allowed us to obtain compound **DPP2T(BTe)$_2$** (**4**) in a moderate yield (42% isolated yield).

In ^{1}H-NMR spectra of these compounds, singlets arising from the 2-benzochalcogenophene protons (H$_a$) shifted downfield from **DPP2T(BTh)$_2$** (δ 7.59 ppm) to **DPP2T(BSe)$_2$** (δ 7.74 ppm) to **DPP2T(BTe)$_2$** (δ 8.01 ppm), whereas thienyl doublets (H$_b$) shifted upfield from **DPP2T(BTh)$_2$** (δ 7.48 ppm) to **DPP2T(BSe)$_2$** (δ 7.38 ppm) to **DPP2T(BTe)$_2$** (δ 7.24 ppm) (Fig. S1, ESI†). These shifts are indicative of changes in heterocycle electron density as the electronegativity of the heteroatom decreases down the period.

UV-Vis absorption spectra in solution and in film show slight but consistent red-shifts in absorption maxima from **DPP2T(BTh)$_2$** ($\lambda_{\max}$ = 584 and 624 nm) to **DPP2T(BSe)$_2$** ($\lambda_{\max}$ = 588 and 629 nm) to **DPP2T(BTe)$_2$** ($\lambda_{\max}$ = 596 and 633 nm) (Fig. S2, ESI†). These strong absorption bands from 480 to 680 nm can be attributed to the intramolecular charge transfer between electron acceptor (DPP) and electron donor (thienyl and benzochalcogenophene) moiety, where atomic changes in the remote benzochalcogen units affect optical properties.

Compared to optical spectra in solution, absorption bands of all three compounds in thin films (Fig. 2B) become broad and further red-shifted as a result of intermolecular interactions. While **DPP2T(BTh)$_2$** and **DPP2T(BSe)$_2$** show similar intensities for the two absorption maxima in films, **DPP2T(BTe)$_2$** shows a weaker relative absorbance at the longer wavelength maximum (694 nm), suggesting that tellurium substitution has significant effects on molecular packing. In film, similar red-shifts on absorption maxima are observed from **DPP2T(BTh)$_2$** ($\lambda_{\max}$ = 611 and 673 nm) to **DPP2T(BSe)$_2$** ($\lambda_{\max}$ = 618 and 683 nm) to **DPP2T(BTe)$_2$** ($\lambda_{\max}$ = 618 and 694 nm). From onsets of absorption in films, optical bandgaps are estimated as 1.74 eV for **DPP2T(BTh)$_2$**, 1.71 eV for **DPP2T(BSe)$_2$**, and 1.66 eV for **DPP2T(BTe)$_2$**, confirming that the bandgap can be fine-tuned by varying the heteroatom within the same group of the periodic table.

Electrochemical bandgaps were calculated by cyclic voltammetry (Fig. S3, ESI†) as 1.83 eV for **DPP2T(BTh)$_2$**, and 1.80 eV for **DPP2T(BSe)$_2$**, which are in good agreement with the optical bandgaps. However, a smaller relative electrochemical bandgap for **DPP2T(BTe)$_2$** (1.60 eV) was calculated due to the elevated HOMO energy level of **DPP2T(BTe)$_2$** (−5.55 eV), as has been observed in benzoditellurophene due to the lower ionization energy of tellurium.[19]

Solution-processed bulk heterojunction solar cell devices were fabricated in air with **DPP2T(BTh)$_2$**, **DPP2T(BSe)$_2$**, and **DPP2T(BTe)$_2$** as the electron donor. Current–voltage (*J*–*V*) curves and incident photon conversion efficiency (IPCE) measurements for the best performing devices are shown in Fig. 3 and all device parameters are summarized in Table 1. The superior performance for devices prepared from **DPP2T(BSe)$_2$** resulted mainly from a higher J_{sc}, which originates from a higher external quantum efficiency across the absorption spectrum, with a peak of 61% around 600 nm (Fig. 3B). As we observed in film absorption spectra of the donor molecules, the IPCE curves show red-shifted absorption from **DPP2T(BTh)$_2$** to **DPP2T(BTe)$_2$**, which contributes to photocurrent generation. Optimized devices prepared from compound **DPP2T(BSe)$_2$** show power conversion efficiencies (PCE) as high as 5.8%. Devices prepared from **DPP2T(BTe)$_2$** showed lower V_{oc} values than devices prepared from the other molecules. This can be explained by the higher HOMO level of **DPP2T(BTe)$_2$** since V_{oc} is correlated to energy offset between HOMO of the donor and the LUMO of PC$_{61}$BM.

In order to further investigate the better device performance from **DPP2T(BSe)$_2$**, carrier mobilities for each compound were measured by analyzing *J*–*V* characteristics of hole-only ohmic devices with the space-charge-limited current (SCLC) model,[20,21] which is relevant to OPV devices with an out-of-plane charge

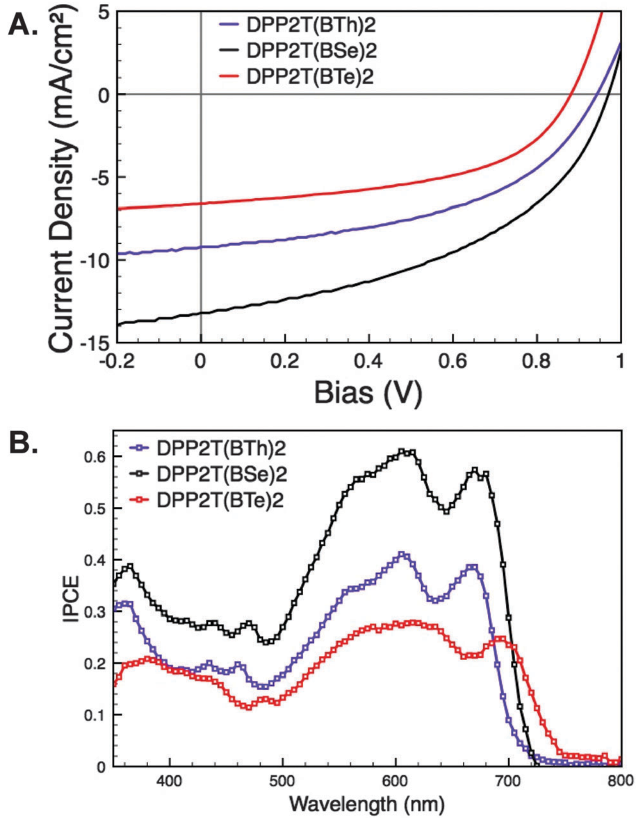

Fig. 3 (A) *J*–*V* curves and (B) IPCE measurements for solar cells prepared from compounds **2–4** (device structure: indium tin oxide (ITO)/MoO$_x$/Donor:PC$_{61}$BM/Al).

Table 1 Solar cell device parameters

Donor	V_{oc} (V)	J_{sc} (mA cm^{-2})	FF	PCE (%) Max	PCE (%) Avg
DPP2T(BTh)$_2$	0.94	9.2	0.49	4.2	3.9[a]
DPP2T(BSe)$_2$	0.98	13.2	0.45	5.8	5.1[a]
DPP2T(BTe)$_2$	0.88	6.6	0.52	3.0	2.8[b]

[a] Averaged over 25 devices. [b] Averaged over 5 devices.

transport orientation. Molecule **DPP2T(BSe)$_2$** displays a hole mobility of $\sim 5 \times 10^{-5}$ cm^2 V^{-1} s^{-1}, comparable to that of **DPP(TBFu)$_2$** ($\sim 1 \times 10^{-5}$ cm^2 V^{-1} s^{-1}),[12] an order of magnitude higher than that of **DPP2T(BTh)$_2$** ($\sim 7 \times 10^{-6}$ cm^2 V^{-1} s^{-1}) and ~60% higher than **DPP2T(BTe)$_2$** ($\sim 3 \times 10^{-5}$ cm^2 V^{-1} s^{-1}) (Fig. S4 and S5, ESI†). This is consistent with the overall superior IPCE and J_{sc} observed in **DPP2T(BSe)$_2$**.

In conclusion, we have prepared a series of benzochalcogenophene–DPP–benzochalcogenophene-based molecules with the benzochalcogenophene heteroatom changed from sulfur to selenium to tellurium and evaluated each molecule as the electron donating material in bulk heterojunction solar cell devices. **DPP(TBTh)$_2$**, the 2-ethylhexyl analogue of **DPP2T(BTh)$_2$**, has been reported to show a power conversion efficiency of 1.4% (1 : 1 blend with PC$_{71}$BM),[15] so the use of 2-butyloctyl side chains to improve solution processability of these molecules was also a key step in obtaining high efficiency devices.[22,23] The optical bandgap was observed to narrow down the period from **DPP2T(BTh)$_2$** to **DPP2T(BSe)$_2$** to **DPP2T(BTe)$_2$**, and the highest efficiency was observed for **DPP2T(BSe)$_2$** devices. These results confirm that an atomistic bandgap engineering approach can be adopted as rational molecular design strategy for OPV devices since solar cell parameters, such as V_{oc} and J_{sc}, are correlated, however, control of other properties such as morphology[24] and mobility[25] are crucial for obtaining high efficiency devices. Even though **DPP2T(BTe)$_2$** devices did not show the highest J_{sc} in the series, they are a rare example of tellurium containing organic solar cells and the red-shifted light absorption when compared to compounds **DPP2T(BTh)$_2$** and **DPP2T(BSe)$_2$** suggests that in depth studies of morphology and charge separation in these systems could lead to further increases in efficiency. We are working to improve the efficiency of these compounds, especially **DPP2T(BTe)$_2$**, through further structural variation, using PC$_{71}$BM[26] as an electron acceptor, and by optimizing the cathode interlayer.[27]

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