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We report the synthesis of two barbiturate end-capped non-fullerene acceptors and demonstrate their efficient function in high voltage output organic solar cells. The acceptor with the lower LUMO level is shown to exhibit suppressed geminate recombination losses, resulting in enhanced photocurrent generation and higher overall device efficiency.

Non-fullerene acceptors (NFAs) are attracting increasing interest for organic solar cell (OSC) applications due to their low synthesis costs, chemical tunability, high power conversion efficiencies and stabilities. In particular, the higher LUMO levels of some NFAs relative to more widely used fullerene acceptors have been shown to yield OSCs with higher output voltages. However, the efficiency of organic solar cells employing NFAs have typically been limited by relatively modest external quantum efficiencies (EQEs) for photocurrent generation—with peak EQEs typically in the range 50-65%. Very recently, a few studies have reported higher EQEs, but have not explored fully the origin of the enhanced EQEs they reported. In this study, we address the role that geminate recombination of photogenerated charges play in limiting the EQE of NFA-based OSCs, and show that these losses can be suppressed by judicious tuning of acceptor LUMO level.

Of the non-fullerene acceptor motifs developed recently, calamitic acceptor-donor-acceptor (A-D-A) type structures have shown particular promise as a molecular design template for low band gap, highly modular materials that deliver high efficiencies. Extended, fused ring core systems such as indacenodithienothiophene (IDTIDT) and indacenodithienophenoindacenodithiophene (IDTI-DT) have been shown to be particularly effective as the electron-rich core moiety. Despite the high efficiency of these NFA materials, they often lack the synthetic simplicity that is advantageous for commercial scale-up. By contrast, cross-coupled, fluorene-cored materials provide particularly promising scope for structural and optoelectronic diversification via relatively simple, low cost synthetic routes. Coupling units such as benzothiadiazoles and thiophenes onto this core provides a modular approach to acceptor design, as incorporating different units can effectively tune optical and electronic character. Moreover by end-capping with rhodanine, barbiturate, malononitrile, indenemalononitrile and indandione derivatives, the molecular optoelectronic and morphological properties can be modified further. Here we compare two fluorene based non-fullerene acceptors that are synthesised in two steps from commercially available precursors. Both acceptors comprise a thiophene-fluorene-thiophene triad, end-capped with either the barbiturate derivative 1,3-dimethylbarbituric acid (FTB) or 1,3-diethyl-2-thiobarbituric acid (FTTB) (Figure 2). Thio carbonyl substitution has emerged as a promising means of controlling the optoelectronic properties in

![Figure 1](image1.png)

Figure 1: a) Synthetic scheme of FTB and FTTB, b) UV-vis absorption spectra of FTB and FTTB solutions and films, c) First heating and cooling differential scanning calorimetry (DSC) cycle of FTB and FTTB films at a scan rate of 5 °C min⁻¹.
organismic semiconducting materials. However, the effect of this functional group remains poorly understood, and currently there are no studies regarding thiocarbonyl substitution in the context of small molecule acceptors. In this work, two NFAs with carbonyl and thiocarbonyl functionalised barbiturate derivatives are compared directly in order to investigate the effect of this group on the optoelectronic and device properties. Both acceptors were blended with a medium-band gap donor polymer PSEHTT, which has successfully been utilised in non-fullerene OSCs.

The synthetic schemes for FTB and FTTB are shown in Figure 1a, and described in greater detail in the SI. In brief, Suzuki coupling of 9,9-dioctylfluorene-2,7-diboronic acid pinacol ester with 2-bromo-5-formylthiophene yields the aryl diaidehyde intermediate. Knoevenagel condensation of this intermediate with 1,3-dimethylbarbituric acid yields the final product FTB, whilst condensation with 1,3-diethyl-2-thiobarbituric acid yields FTTB. Due to commercial availability of the barbiturate precursors, methyl groups were incorporated for FTB while ethyl groups were used in the case of FTTB. Studies are underway to explore the influence of alkyl groups and thiocarbonyl substitution independently on the materials properties. As demonstrated by the DFT (B3LYP/6-31G*) structural optimizations shown in Figure S5, both acceptors exhibit a similar, slightly twisted molecular structure due to torsion between the fluorene and thiophene units, but with slightly bulkier ethyl groups in the case of FTTB.

Figure 1b shows the UV-vis absorption spectra of the FTB and FTTB solutions and neat films. The solutions yield a pronounced absorption band 400-600 nm with maximum extinction coefficients of 7.7 x 10^4 M^-1 cm^-1 and 8.9 x 10^4 M^-1 cm^-1 for FTB and FTTB respectively (Table S1), both higher than for PCEBM within the visible region (0.5 x 10^4 M^-1 cm^-1)\(^\text{18}\), making them suitable for photon harvesting applications such as OSCs. The FTTB spectrum is red-shifted by about 30 nm compared to FTB, signifying a lower optical band gap. Both materials show a ~20-30 nm absorption red shift from solution to film.

Figure 2: a) A graphic representation of the LUMO and HOMO levels calculated by cyclic voltammetry (CV) and optical band gap (refer ESI) and b) chemical structures of PSEHTT, FTB and FTTB, c) Device J-V characteristics and d) External quantum efficiency (EQE) of FTTB:PSEHTT (red) and FTB:PSEHTT (blue) systems.

Differential scanning calorimetry (DSC) was carried out on FTB and FTTB films (Figure 1c). FTB shows a higher melting transition with a peak at around 230°C compared to FTTB (180°C), consistent with FTB’s higher planarity and the increased intermolecular interactions that are expected from its less bulky methyl groups. In addition, the DSC scan for FTB shows a small exothermic crystallization transition at 140°C which is not observed in FTTB above glass transition temperatures (120°C and 130°C for FTB and FTTB respectively), consistent with the XRD data before and after annealing (refer to SI). We note that ordering of FTB molecules is almost entirely repressed in blend after annealing as confirmed by XRD and UV-vis absorption data (Figure S10).

The thin film electrochemical characteristics of the two acceptors and PSEHTT donor polymer were investigated by cyclic voltammetry (CV) combined with \(E_{\text{onset}}\), derived from the UV-vis absorption spectra of neat films, to estimate their HOMO and LUMO energy levels, as illustrated in Figure 2a (refer to Table S1, Figure S6-8 for details). FTB has a deeper HOMO (-5.8 eV) and LUMO (-3.7 eV) levels than FTTB (-5.7 eV and -3.5 eV respectively), which can be attributed to the more polarizable nature of the C=S bond compared to C=O, making the thioketone a stronger acceptor group. Consistent with previous studies, thioketone substitution is observed to have a more significant effect on the LUMO energy, resulting in a slightly reduced optical bandgap. This stronger acceptor group creates larger LUMO-LUMO and HOMO-HOMO offsets between PSEHTT and FTTB (0.4 eV and 0.6 eV respectively) compared to FTB in blends (0.2 eV and 0.5 eV respectively), corresponding to higher driving forces for charge separation in devices employing FTTB.

OSCs were fabricated in an ITO/ZnO/PSEHTT: Acceptor /MoO\(_3\)/Ag inverted architecture and their J-V curves were measured under 100 mWcm\(^{-2}\) simulated AM1.5G illumination (Figure 2b). Device performance was optimised by varying the blend ratios, concentrations, solvent and annealing temperatures (refer to Table S2 and S3). For PSEHTT:FTTB devices, optimised conditions (1:2 blend ratio in 10 gL\(^{-1}\) CB solvent without annealing), yielded a PCE of up to 7.2%. Similar optimised conditions were found for PSEHTT:FTB leading to a PCE of up to 5.4%. The higher efficiency of the FTTB devices results from higher photocurrent generation (13.5 mAcm\(^{-2}\) compared to FTB 8.9 mAcm\(^{-2}\)), offset in part by a lower open circuit voltage (0.98 V vs 1.13 V). We note that both processing additives and thermal annealing lowered the device efficiency, due mainly to the reduced \(J_{SC}\). The higher \(V_{OC}\) of the FTTB devices is consistent with its higher LUMO level. We focus herein rather on the cause of the difference in photocurrent density which results in the higher PCE for FTTB devices.

The higher photocurrent obtained for FTTB devices compared to FTB was confirmed by external quantum efficiency (EQE) as shown in Figure 2c. Whilst FTB devices exhibited a modest maximum EQE (54%), a maximum EQE of 84% was attained for FTTB devices, comparable to some of the highest values reported for polymer:fullerene systems (we note drop off in EQE for \(\lambda > 550\) nm is due to lower sample absorption). Both blends showed similar absorption maxima, indicating that this difference in EQE values does not arise from differences in light harvesting.
Photoluminescence quenching (PLQ) was employed to investigate whether the higher EQE values for the PSEHTT:FTB devices could result from more efficient exciton separation. For a selective excitation of PSEHTT (Figure S11), PSEHTT:FTB blends showed modestly higher PLQ than PSEHTT:FTB relative to neat PSEHTT films (96% vs 85%). Analogous data were collected for acceptor PLQ employing acceptor excitation, showing 95% and 89% PLQs for FTB and FTTB blends respectively (Figure S12). These data are consistent with the higher energy offsets between PSEHTT and FTTB increasing the efficiency of exciton separation. However, the difference in PLQ between the two blends (6%) is too small to explain the 30% difference in maximal EQEs between FTTB and FTB devices.

Blend mobilities were measured using the space-charge limiting current (SCLC) method (Figure S13 and S14). Electron and hole mobilities for PSEHTT:FTB and PSEHTT:FTTB blends were both found to be similar. The electron mobility ranged from 3 - 6x10⁻⁵ cm²V⁻¹s⁻¹ while the hole mobility ranged from 7 - 8x10⁻⁵ cm²V⁻¹s⁻¹ for both systems. It thus appears unlikely that the difference in EQE values derives from differences in charge transport between the two blends.

Ultrafast transient absorption data were employed to investigate further the charge generation process in the two blends, adopting a selective PSEHTT excitation at 650 nm, as shown in Figure 4. Both blends show an initial photoinduced absorption maximum at ~1300 nm, assigned by comparison to neat film data (Figure S15) to PSEHTT exciton absorption. At longer time delays this exciton absorption is replaced by a narrower absorption band peaking at 1050 nm, assigned to PSEHTT polaron absorption. Figure 4c shows the kinetics of PSEHTT exciton signal decay in neat PSEHTT (assigned primarily to non-radiative decay to ground) and both the FTB and FTTB blend films, determined following by deconvolution of the exciton and polaron spectra (see SI for details). The PSEHTT exciton decay time accelerates from ~35 ps in the neat polymer film to 5.2 and 1.3 ps in the blends with FTB and FTTB respectively. These data are in reasonable agreement the PLQ data, confirming efficient exciton separation in both blends, with this PSEHTT exciton separation being modestly more efficient in blends with FTTB.

Figure 4d shows kinetics of PSEHTT polaron generation and decay, again determined by deconvolution of the transient spectra shown in Figures 4a and 4b. The rise of the polaron absorption is in reasonable agreement with the exciton decay kinetics plotted in Figure 4c. We also note the appearance of significant polaron absorption within our instrument response (~300 fs), also apparent as a reduction in the initial exciton absorption intensity in both blend films relative to neat PSEHTT. It is striking that this PSEHTT polaron absorption is longer lived for the FTTB blend than for FTB blend. For the FTTB blend, a modest (20%) decay of polaron absorption within the timescale of our measurement (6 ns) is observed with a decay half-life of 1.5 ns. By contrast, in the FTB blend, this decay is both larger in amplitude (40%) and faster (~650 ps). Further TAS data were collected as a function of excitation intensity to determine whether these decays resulted from geminate or non-geminate recombination processes (Figure S16). For the FTB blend the decay was observed to be intensity independent, indicating that the decay originates from a geminate recombination process. By contrast, some intensity dependence was observed for the FTTB blend, indicating that the (in any case more modest) decay in this blend originates in part from non-geminate losses. It can thus be concluded that the PSEHTT:FTB blend shows substantially higher geminate recombination losses than the PSEHTT:FTTB (~20% vs 40%). Such geminate recombination losses, assigned to recombination to ground of interfacial, bound electron-hole pairs, primarily impact on the efficiency of photocurrent generation in organic solar cells. It is apparent that this difference in geminate recombination losses between the two blends is sufficient to be the largest cause of the higher EQE values, and therefore higher PCEs obtained for PSEHTT:FTTB devices relative to PSEHTT:FTB devices. Based on the bulkier Et group in FTB that inhibits crystallization, as well as the absence of any crystalline diffraction peaks in the unannealed films of either acceptor, it is unlikely that higher geminate recombination losses for PSEHTT:FTB result from differences in film morphology (increased crystallinity can reduce exciton separation efficiency but typically suppresses geminate recombination losses). Instead, the suppression of geminate recombination losses for PSEHTT:FTTB can be more reasonably assigned to the ~0.2 eV larger energetic offset driving charge separation in this blend compared to PSEHTT:FTB, consistent with several studies reporting that larger energy offsets can suppress the geminate recombination of bound charge pairs at organic donor/acceptor interfaces.

In summary, two simple non-fullerene acceptors FTB and FTTB were synthesised with different barbituric acid functionalised end groups to explore the potential of the carbonyl and thiocarbonyl derivatives in the context of small molecule acceptors. While the higher-lying LUMO of the barbituric acid analogue FTB benefited the open circuit voltage, yielding an impressive VOC of 1.13 V in blends with
PSEHTT, photocurrent generation was only modestly efficient in these devices (maximal EQE of 54%), leading to PCE of up to 5.4%. Substitution of the 1,3-dimethyl barbiturate derivative in FTB for the more electron withdrawing thiocarbonyl derivative N-ethyl thiobarbiturate, in FTBb resulted in a 0.2 eV deeper LUMO and red-shifted absorption. This lower LUMO resulted in a slightly reduced device Voc of 0.98 V, which was more than compensated by an increase in maximal EQE to 84%, leading to an increase in overall device efficiency to up to 7.2%, comparable to the highest reported to date for binary PSEHTT based NFA systems. The increase in EQE is shown to result primarily from a suppression of geminate recombination losses in PSEHTT:FTTB blends relative to PSEHTT:FTB, attributed to the lower FTTB LUMO and HOMO levels which increase the energy offsets, and in turn drive more efficient dissociated charge generation in these devices. Detailed morphological studies would be needed to fully characterise the effect of differences in phase separation on device performance with these materials. In addition, future studies should explore the use of other donor polymers that can further reduce the geminate recombination losses. The results shown herein demonstrate that tuning the optoelectronic properties of calamitic non-fullerene acceptors utilising carbonyl and thiocarbonyl functionalised barbituric acid based end groups is simple and effective strategy to optimise the performance of organic solar cells employing such non-fullerene acceptors.

Notes and references

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