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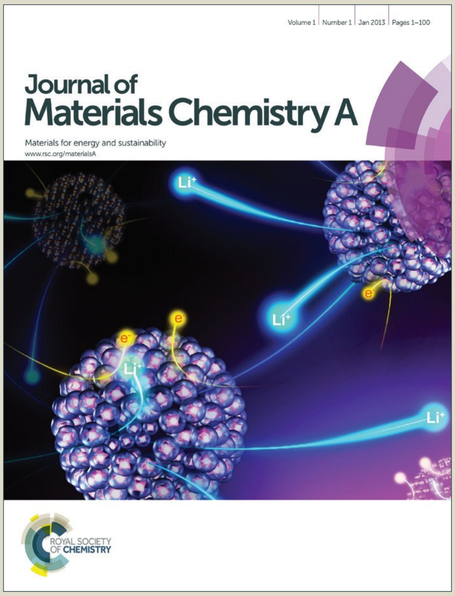

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Phthalimide end-capped thienoisoindigo and diketopyrrolopyrrole as non-fullerene molecular acceptors for organic solar cells

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Abstract: Two acetylene-bridged molecules, built by grafting phthalimides on thienoisoindigo (**TII**) and diketopyrrolopyrrole (**DPP**) blocks have been synthesized, characterized and evaluated as electron acceptor material in air-processed inverted organic solar cells. Once blended with the poly(3-hexylthiophene), power conversion efficiencies (PCEs) of *ca* 0.4% and 3.3% were achieved for **TII** and **DPP** based devices respectively. To the best of our knowledge these PCEs (*i*) rank amongst the highest reported so far for diketopyrrolopyrrole based acceptors and (*ii*) make this contribution the very first example of thienoisoidingo based material used as non-fullerene electron acceptor.

1. Introduction

The synthesis of active materials for organic solar cells (OSCs) is a focus of considerable attention.[1-3] Multi-disciplinary research effort in device fabrication and design of donor materials has led to rapid progress.[4-7] Actually, power conversion efficiencies (PCEs) exceeding 10.0% have been recently reported for cells based either on low band gap polymers or on molecular donors.[8-10]

On the other hand, fullerene derivatives have served as the standard electron-acceptor materials for almost two decades.[11-14] However, despite of large electron affinity, high electron-mobility and isotropic charge-transport, owing to their 3-dimensional structures,[15-17] fullerenes derivatives present several drawbacks such as low absorption in the visible spectrum, limited structural tunability of energy levels and relatively high cost and environmental impact of their soluble derivatives $PC_{61}BM$ and $PC_{71}BM$.

In this context, polymeric and molecular non-fullerene acceptors have received increasing attention in recent years.[18-21] In particular, it has been a surge in the development of well-defined small molecules due to their inherent advantages in terms of synthesis, purification and analysis of structure-properties relationships. Various classes of molecular systems have been synthesized and evaluated as acceptors including vinazene,[22-24] 9,9′-bifluorenylidene,[25, 26] diketopyrrolopyrrole derivatives,[27-30] dicyan-substituted quinacridone,[31] functionalized isoindigo,[32] BODIPYs,[33] electron-deficient pentacenes,[34] fluoranthene-fused imide,[35, 36] spiro-annulated derivatives,[37, 38] naphthalene-diimides[39, 40] or perylene-diimides.[41-44] Rapid improvement of *PCE*s have been reported for OSCs combining extended molecular architectures,[45-47] mainly based on PDIs,[48-52] with high performance low band gap polymers. For instance, Nuckolls et al. recently achieved an impressive 8.3% power conversion efficiency by blending helical perylene diimide oligomers with the well-known **PTB7-Th**, thus competing with the best fullerene based OSCs.[53] On the other hand, few examples of *PCEs* exceeding 2.5% have been recorded so far with the standard poly(3-hexylthiophene) (**P3HT**) donor material.[22, 54]

In our continuing commitment towards simplified chemical structures of active OPV materials,[55-58] we report here on the synthesis and preliminary evaluation of two electron-acceptors built, in few steps, by attaching electron-withdrawing phthalimide groups on two central chromophore blocks namely the thienoisoindigo (**TII**) and diketopyrrolopyrrole (**DPP**) (Scheme 1) through the use of acetylenic linkages. Such connectors indeed permit to extend the effective conjugation while lowering the energy level of the frontier orbitals and reducing the steric interactions between thiophene units and phenyl rings.[59, 60]

2. Experimental section

Materials

All reagents and chemicals from commercial sources were used without further purification. Reactions were carried out under neutral atmosphere unless otherwise stated. Solvents were dried and purified using standard techniques.

Measurements and characterization

Flash chromatography was performed with analytical-grade solvents using Aldrich silica gel (technical grade, pore size 60 Å, 230-400 mesh particle size). Flexible plates ALUGRAM® Xtra SIL G UV_{254} from MACHEREY-NAGEL were used for TLC. Compounds were detected by UV irradiation (Bioblock Scientific) or staining with I_2, unless stated otherwise. Melting point measurements were performed using a Reichert Jung THERMOVAR (ranging from room temperature to 250°C). NMR spectra were recorded with a Bruker AVANCE III 300 (^1H, 300 MHz and ^{13}C, 75 MHz). Chemical shifts are given in ppm relative to TMS and coupling constants *J* in Hz. UV-Vis spectra were recorded with a Perkin Elmer 950 spectrometer. Mass spectrometry was performed with a **JEOL JMS-700 B/E.** Cyclic voltammetry was performed in 1.0 M Bu_4NPF_6/CH_2Cl_2 (HPLC grade). Solutions were degassed by argon bubbling prior to each experiment. Experiments were carried out in a one-compartment cell equipped with platinum electrodes and a saturated calomel reference electrode (SCE) using a Biologic SP-150 potentiostat with positive feedback compensation. FTIR measurements were performed using a Bruker Vertex 70 instrument.

Synthetic procedures

(E)-2,2'-dibromo-4,4'-bis(2-ethylhexyl)-[6,6'-bithieno[3,2-b]pyrrolylidene]-5,5'(4H,4'H)-dione **TII-Br$_2$**,[61] 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-ethylhexyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione **DPP-Br$_2$**[62] and 5-ethynyl-2-hexylisoindoline-1,3-dione **Pht**[63] were synthesized according to previously reported methods.

General procedure for the synthesis of ***TII-Pht$_2$*** *and* ***DPP-Pht$_2$****:*

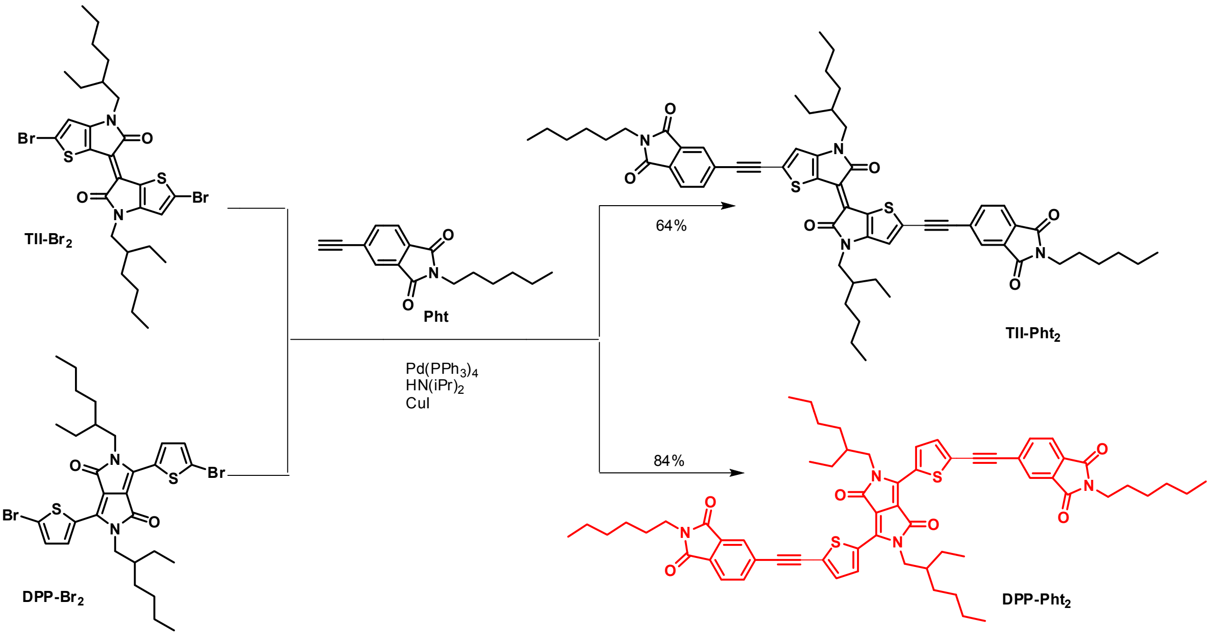
TII-Br$_2$ or **DPP-Br$_2$** (100 mg ; 1 eq), **Pht** (2 eq), copper(I) iodide (0.07 eq) and tetrakis-(triphenylphosphine) palladium(0) (0.06 eq) were combined into a dry Schlenk tube equipped with a stir bar and degassed under vacuum. A solution of toluene (20 mL, HPLC grade) and diisopropylamine (2 eq) was degassed separately by freeze-pump-thaw cycles (3 x 30 min). The later was then added to the powders and reaction mixture was heated overnight at 50°C under Ar atmosphere. After cooling down to room temperature, the organic layer was washed with water (3 x 100 mL) and dried over $MgSO_4$. After removal of the solvent, crude product were subjected to silica column chromatography using chloroform as eluent to provide the desired compounds.

TII-Pht$_2$: (99 mg, 64% yield) **^{1}H NMR** (300 MHz, CDCl$_3$, ppm) δ: 7.90 (s, 2H), 7.82 (d, J = 7.8 Hz, 2H), 7.76 (dd, ^{3}J = 6.6 Hz, ^{4}J = 1.2 Hz, 2H), 6.96 (s, 2H), 3.73-3.65 (m, 8H), 1.89-1.81 (m, 2H), 1.72-1.63 (m, 4H), 1.44-1.25 (m, 28H), 0.97-0.86 (m, 18H). **^{13}C NMR** (75 MHz, CDCl$_3$, ppm) δ: 170.68, 167.80, 167.70, 151.26, 136.47, 132.71, 131.27, 130.26, 128.66, 125.71, 123.41, 120.97, 117.37, 115.83, 96.90, 88.63, 46.05, 38.64, 38.44, 31.50, 28.79, 28.66, 26.68, 24.07, 23.20, 22.65, 14.21, 14.15, 10.75. **FAB+ HRMS**: calculated for $C_{60}H_{68}N_4O_6S_2$ 1004.4580, found 1004.4574. **FTIR** (cm^{-1}): 2169 ($\nu_{st(C\equiv C)}$); 1711 ($\nu_{st(C=O)}$). **MP**: >250°C.

DPP-Pht$_2$: (128 mg, 84% yield) **^{1}H NMR** (300 MHz, CDCl$_3$, ppm) δ: 8.91 (d, J = 4.2 Hz, 2H), 7.96 (s, 2H), 7.84 (s, 4H), 7.45 (d, J = 4.2 Hz, 2H), 4.02 (d, J = 7.8 Hz, 4H), 3.68 (t, J = 7.2 Hz, 4H), 1.90 (m, 2H), 1.68 (m, 4H), 1.44-1.25 (m, 28H), 0.94-0.86 (m, 18H). **^{13}C NMR** (75 MHz, CDCl$_3$, ppm) δ: 167.80, 167.68, 161.61, 139.69, 136.70, 135.72, 134.22, 132.72, 131.82, 131.58, 129.18, 128.37, 127.28, 125.44, 123.44, 109.42, 95.96, 86.49, 46.31, 39.31, 38.47, 31.49, 30.27, 28.66, 28.44, 26.68, 23.70, 23.19, 22.65, 14.19, 14.14, 10.61. **FAB+ HRMS**: calculated for $C_{62}H_{70}N_4O_6S_2$ 1030.4737, found 1030.4754. **FTIR** (cm^{-1}): 2192 ($\nu_{st(C\equiv C)}$); 1770 ($\nu_{st(C=O)}$). **MP**: 219°C.

3. Results and discussion

TII-Pht$_2$ and **DPP-Pht$_2$** were obtained in 64 and 84% yields respectively by Sonogashira cross-coupling reaction between the di-brominated dyes **TII-Br$_2$** or **DPP-Br$_2$** and the 5-ethynyl-2-hexylisoindoline-1,3-dione (**Pht**) (Scheme 1).



Scheme 1. Synthetic route to **TII-Pht$_2$** (black) and **DPP-Pht$_2$** (red)

The targeted compounds were worked-up using conventional methods and purified by simple column chromatography (see SI).

Figure 1 shows the UV-Vis absorption spectra of the two acceptors in chloroform solutions and as spin-cast films while the corresponding data are listed in Table 1.

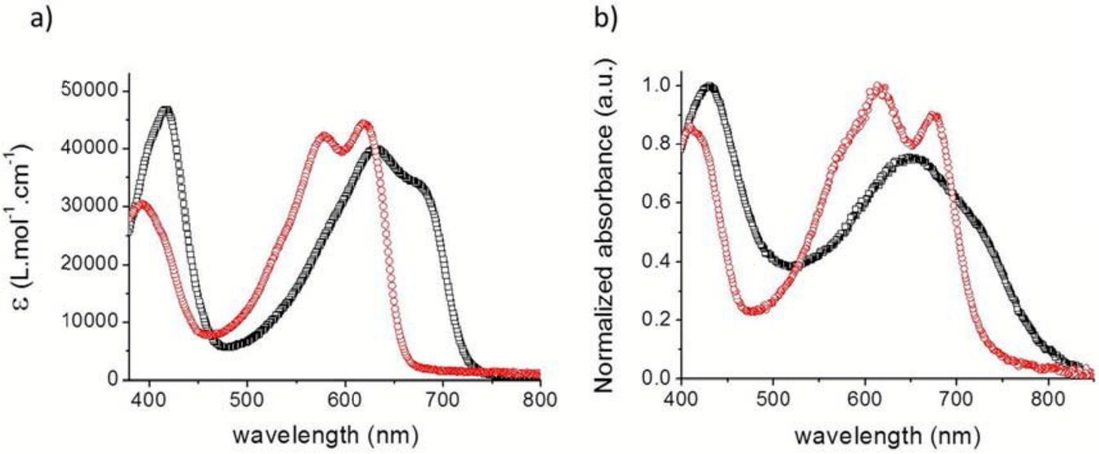


Figure 1. UV-Vis absorption spectra of **TII-Pht$_2$** (black squares) and **DPP-Pht$_2$** (red circles) in $CHCl_3$ solutions (a) and as thin film on glass (b)

The spectrum of both materials displays two absorption bands attributed to π–π* (350-450 nm) and intramolecular charge transfer (ICT) transitions (500-750 nm) respectively. Although comparable extinction coefficients (*ε*) were estimated, **TII-Pht$_2$** is characterized by a broader and significantly red-shifted (of *ca* 50 nm) absorption band compared to **DPP-Pht$_2$**. As expected, the spectra of the films show broader absorption bands and red-shifted long wavelength absorption onsets at 751 and 800 nm corresponding to optical energy gaps (E_g^{opt}) of 1.65 and 1.55 eV for **DPP-Pht$_2$** and **TII-Pht$_2$** respectively.

Table 1. UV-vis absorption data for **TII-Pht$_2$** and **DPP-Pht$_2$**

Compound	λ_{max} (nm) in $CHCl_3$	ε (M^{-1} cm^{-1})	λ_{max} (nm) Film	λ_{onset} (nm) Film	E_g^{opt} (eV)
TII-Pht$_2$	417	47000	432	800	1.55
	631	40000	652		
DPP-Pht$_2$	579	42000	614	751	1.65
	620	44000	677		

Cyclic voltammetry was performed in dichloromethane with Bu_4NPF_6 as the supporting electrolyte. The cyclic voltammogram (CV) shows a reversible oxidation wave with anodic peak potential (E_{pa}) at *ca* 1.0 V for both compounds (Figure 2 and Table 2).

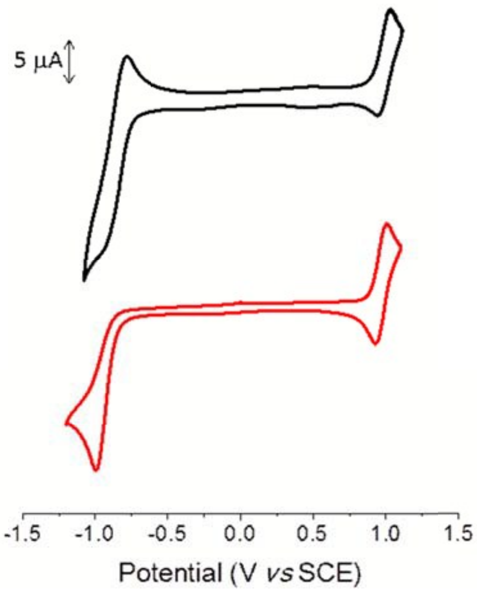


Figure 2. Cyclic voltammograms of **TII-Pht$_2$** (black) and **DPP-Pht$_2$** (red) 1 mM in 0.1 M Bu_4NPF_6/CH_2Cl_2, 100 mV s^{-1}, Pt working electrode

Table 2. Cyclic voltammetric data for **TII-Pht$_2$** and **DPP-Pht$_2$** (1 mM) in 0.1 M Bu_4NPF_6/CH_2Cl_2, scan rate 100 mV s^{-1}, Pt working electrode, ref. SCE

Compound	E_{pa}^{1} (V)	E_{pc}^{1} (V)	HOMO[a] (eV)	LUMO[b] (eV)
TII-Pht$_2$	1.03	-0.95	-5.89	-4.24
DPP-Pht$_2$	1.01	-0.99	-5.88	-4.13

$^{a}HOMO = -(E_{ox(onset)}+4.99)$ (eV), $^{b}E_{LUMO} = -(E_{red(onset)}+4.99)$[64]

The CV of the **DPP** derivative exhibits an irreversible reduction wave with a cathodic peak potential (E_{pc}) of -0.99 V, whereas a quasi-reversible reduction process is observed for **TII-Pht$_2$** with E_{pc} = -0.95 V. The potentials of the onsets of oxidation and reduction processes lead to estimated HOMO/LUMO levels of -5.89/-4.24 eV and -5.88/-4.13 eV for **TII-Pht$_2$** and **DPP-Pht$_2$** respectively (Table 2).

Density functional theory (DFT) calculations using Gaussian 9 program based on PBE1PBE 6-311++G(2df,2pd) were carried out in parallel. The branched alkyl chains of the phthalimide moieties were replaced by simple methyl groups in order to reduce computation time. Figure 3 shows the optimized geometries and distribution of the frontier orbitals for the two compounds.

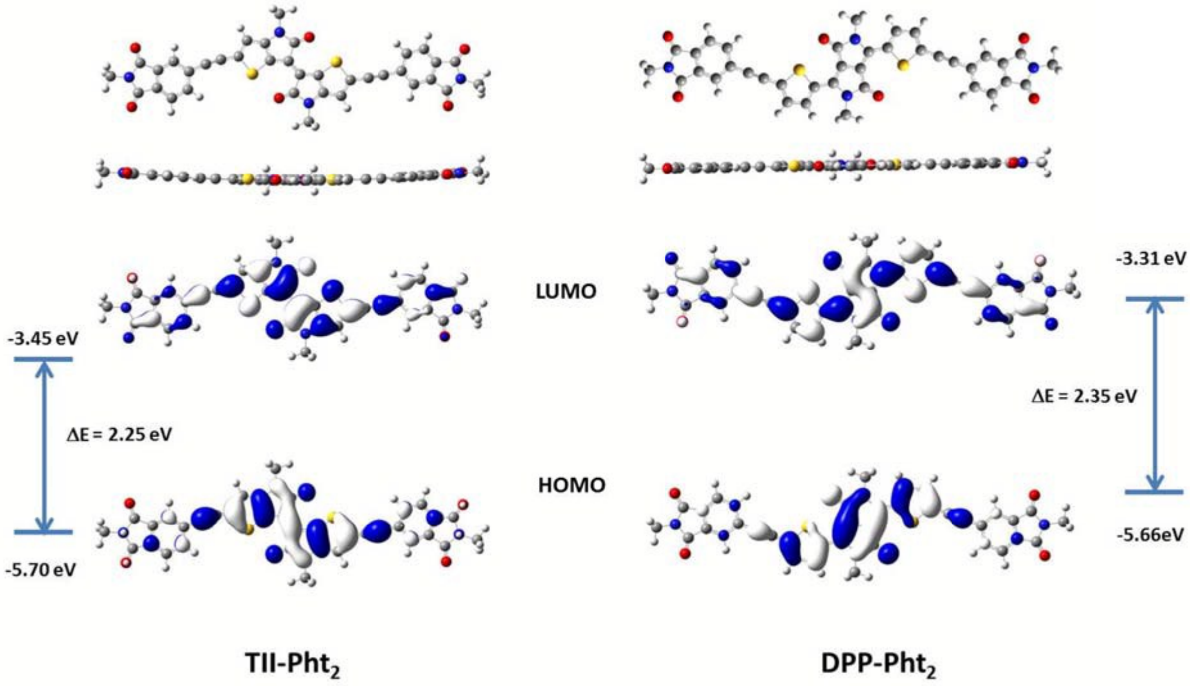


Figure 3. Optimized geometries and molecular orbital distributions for **TII-Pht$_2$** and **DPP-Pht$_2$**

Both molecules exhibit a quasi-planar structure with a torsion angle between the phthalimide block and the central core of *ca* 1.0 and 0.04° for **TII-Pht$_2$** and **DPP-Pht$_2$** respectively. For both compounds the HOMO is essentially localized on the central dye while the LUMO is more evenly distributed along the whole backbone. The calculated energy levels and energy gaps are in satisfying agreement with the values estimated from UV-vis absorption and cyclic voltammetric data.

A preliminary evaluation of the potential of the two compounds as electron acceptor materials for OSCs has been carried out on solution-processed bulk heterojunction (BHJ) solar cells. Although higher *PCE* could probably be obtained with high performance low band gap polymers, the use of P3HT as donor material allows a direct comparison with the large body of results published for the P3HT/PCBM standard system.[65] To this end, inverted solar cells of configuration: ITO/ZnO/Active layer/MoO_3/Ag were fabricated (see SI). Devices characteristics are summarized in Table 3 and the best current density-voltage (*J-V*) curves measured under AM. 1.5 simulated solar illumination (80 mW cm^{-2}) are plotted in Figure 4.

Table 3. Photovoltaic characteristics of BHJ cells based on P3HT and **TII-Pht$_2$** or **DPP-Pht$_2$**. [a](average value of 12 cells)

Acceptor	DIO	V_{oc} (V)	J_{sc} (mA cm^{-2})	*FF* (%)	*PCE* (%) **Max**, (average)[a]
TII-Pht$_2$	w/o	0.59	1.05	31	**0.24** (0.21)
	2 %	0.66	1.62	27	**0.36** (0.34)
DPP-Pht$_2$	w/o	0.73	2.29	29	**0.60** (0.58)
	2 %	0.89	5.91	50	**3.28** (3.00)

The best results were obtained with active layers spun-cast at 1000 rpm from chloroform solutions containing 20 mg/mL of donor and acceptor materials and annealed at 110°C for 5 min. Optimal weight to weight **P3HT**/acceptor ratios were 1:1.5 and 1:2 for **TII-Pht$_2$** and **DPP-Pht$_2$** respectively. In addition, the impact of diiodooctane (DIO) as additive for the processing of the active film was investigated.[66, 67]

Comparison of the results clearly shows that **DPP-Pht$_2$** leads to better open-circuit voltage, (V_{oc}), short-circuit current density (J_{sc}) and *PCE* than **TII-Pht$_2$**. Moreover, for both acceptors, DIO significantly improves efficiencies through a simultaneous increase of V_{oc}, J_{sc} and fill factor (*FF*). These effects are particularly spectacular for the **DPP-Pht$_2$** cells for which a five-fold increase of *PCE* is observed.[68, 69] Thus, a promising *PCE* of 3.28 % with a V_{oc} of 0.89 V, a J_{sc} of 5.91 mA cm^{-2} and *FF* of 50% were obtained. This results ranks among the highest reported so far for DPP-based acceptors.[18] On the other hand, despite a moderate efficiency of *ca* 0.36%, it is noteworthy that we report herein the very first example of OSCs incorporating thienoisoindigo-based molecular acceptor.

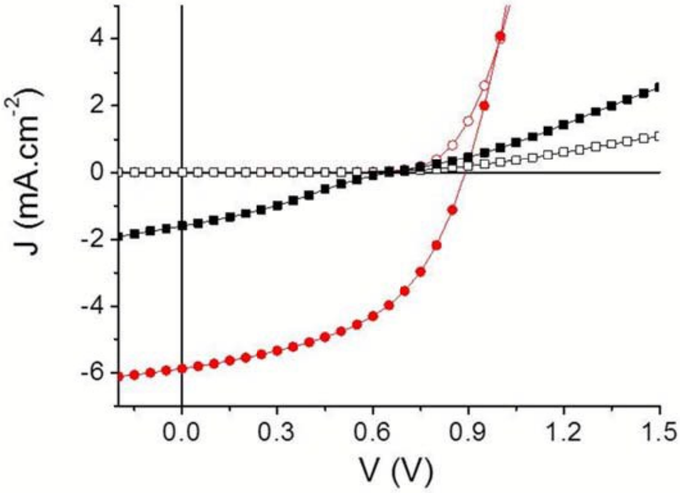


Figure 4. Current density-voltage characteristics of the best inverted cells. **TII-Pht$_2$** (black squares) and **DPP-Pht$_2$** (red circles) based devices in the dark (open) and under illumination (full)

In order to assess the respective contribution of each component of the cells on the overall *PCE*, the external quantum efficiencies (*EQE*) of the best performing inverted solar cells have been recorded.

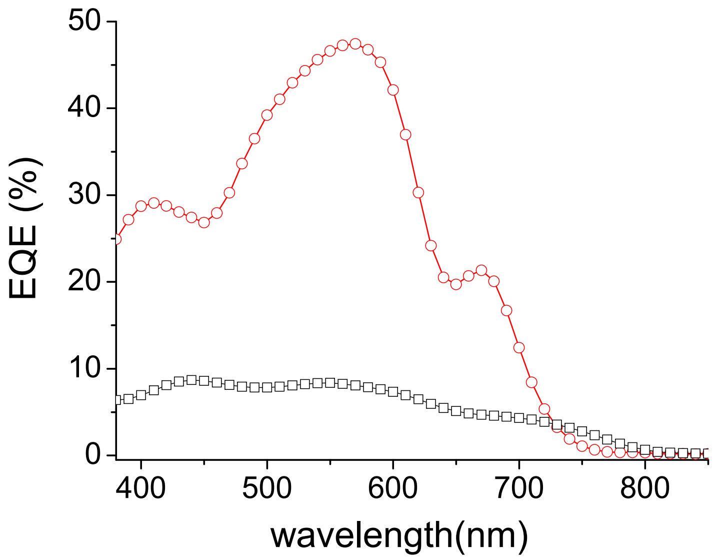


Figure 5. EQE curves of **DPP-Pht$_2$** (red circles) and **TII-Pht$_2$** (black squares) based OSCs

The spectra in Figure 5 reveal a common peak around 560 nm attributed to the absorption of the P3HT donor material and broad shoulders in the 650-730 nm and 650-800 nm regions attributed to the contribution of **DPP-Pht$_2$** and **TII-Pht$_2$** respectively to the photo-current. The large difference in intensity between the two *EQE* curves is in good agreement with the higher J_{sc} values obtained for the **DPP** based-devices. Finally, it is noteworthy that the current density integrated from the EQE of the best **DPP-Pht$_2$** and **TII-Pht$_2$** based devices are close to their corresponding J_{sc} values (5.85 and 1.42 mA.cm^{-2} *vs* 5.91 and 1.62 mA.cm^{-2}).

In order to complete these results, the electron mobilities (μ_e) of both acceptors were investigated using the space-charge limited current (SCLC) method with devices of structure ITO/ **DPP-Pht$_2$** or **TII-Pht$_2$**/LiF/Al (see SI).[70] μ_e values of 2.3×10^{-5} and 1.5×10^{-4} cm^2 V^{-1} s^{-1} were obtained for **TII-Pht$_2$** and **DPP-Pht$_2$** respectively. This *ca* one order of magnitude higher electron mobility of **DPP-Pht$_2$** probably contributes to the better J_{sc}, *FF* and consequently *PCE* of OSCs based on this acceptor.

The nano-scale morphology of the optimized active layers has been investigated using atomic force microscopy (AFM). As shown in Figure 6, the **P3HT**:**TII-Pht$_2$** blend exhibits smaller and more homogenous domains than those observed on the surface of **DPP-Pht$_2$**-based cells with an average root mean square (RMS) roughness value of *ca* 6 nm *vs ca* 32 nm for **DPP-Pht$_2$** based cells.

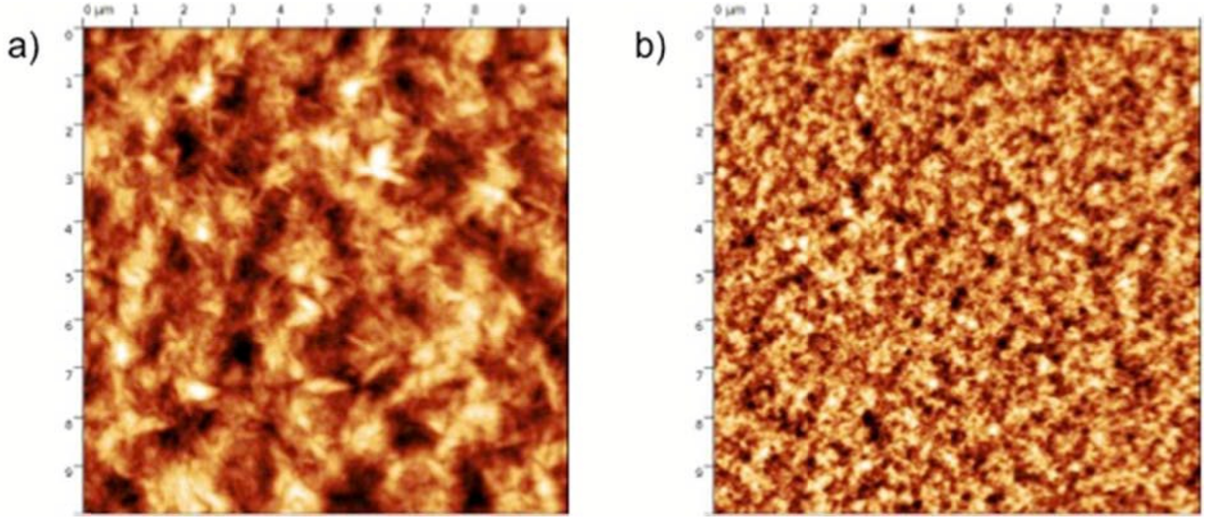


Figure 6. AFM phase images (10 x 10 µm) of optimized **DPP-Pht$_2$** (a) and **TII-Pht$_2$** (b) based active layers

Furthermore, this imaging technique also revealed the presence of fibrillar microcrystalline domains in the **P3HT:DPP-Pht$_2$** blend that can be associated to a better self-organization of the donor which is expected to be beneficial for effective charge transport.[71]

4. Conclusion

In summary, two simple acetylene-bridged n-type small molecules based on diketopyrrolopyrrole or thienoisoindigo core end-capped with phthalimide electron-accepting moieties have been synthesized. Their potential as electron-acceptor material for OSCs was estimated in inverted BHJ solar cells. Once blended with **P3HT**, promising PCEs of *ca* 0.36% and 3.28% for **TII-Pht$_2$** and **DPP-Pht$_2$** based devices respectively were reached. It is worth noting that it is, to the best of our knowledge, (*i*) the first example of thienoisoidingo based material used as a non-fullerene electron acceptor and (*ii*) the highest efficiency reported so far for a diketopyrrolopyrrole based molecular acceptor material in BHJ solar cells. Further device optimizations and side chain engineering are ongoing to improve these performances.

5. Acknowledgments

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