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Naphthyl derivatives functionalised with electron acceptor units: Synthesis, electronic characterization and DFT calculations**

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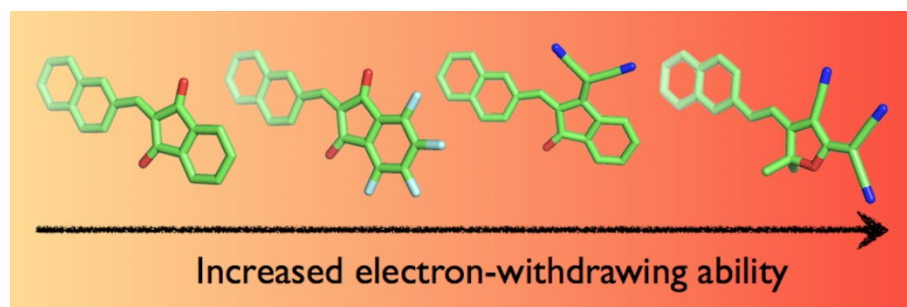
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Abstract

A series of unsymmetrical dyes containing a naphthyl unit connected to an electron acceptor moiety has been designed and synthesized. By modifying the electron acceptor unit a shift of the LUMO energy level as well as its distribution through the molecule have been achieved. These dyes have been fully characterized by optical, computational and electrochemical techniques. In addition, crystal structures reveal different packing depending upon the nature of the acceptor. Their potential use as electron-acceptor materials for organic photovoltaics has also been investigated by photoluminescence studies of blends with the common OPV polymers P3HT and PCDTBT.

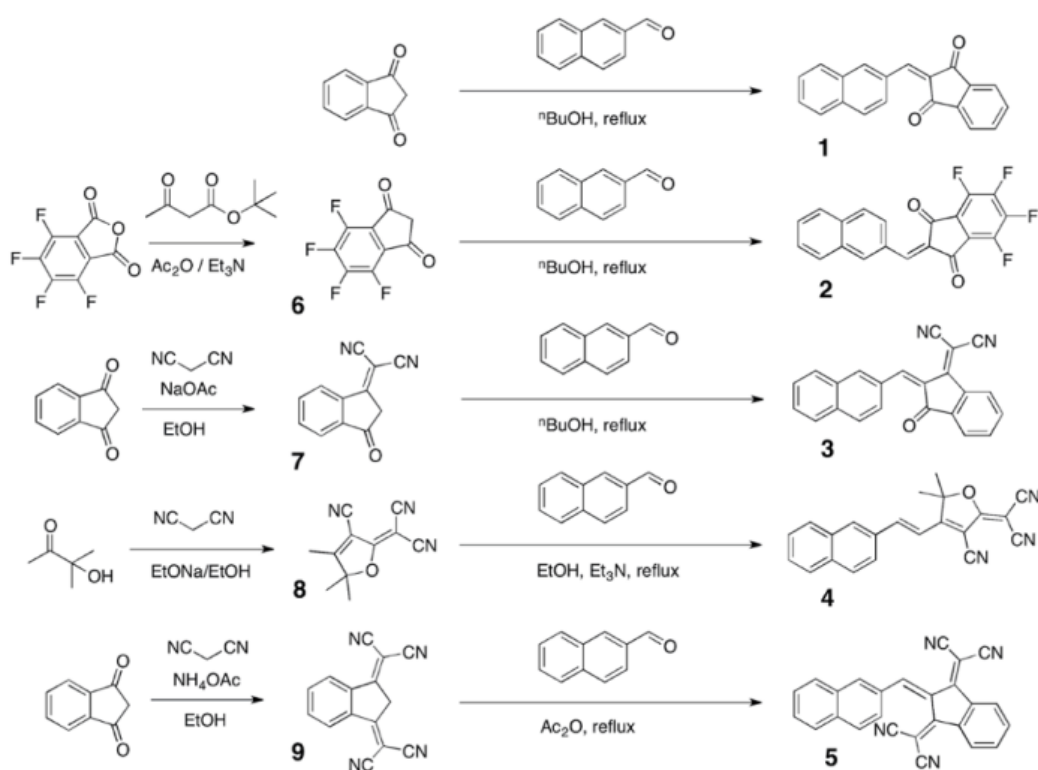
Introduction

Organic semiconductor materials have attracted the attention of both the academic and the industrial community due to their potential use in low-cost and lightweight organic electronic devices, such as organic photovoltaics (OPV). The most widely used active layer for these OPVs, the so-called Bulk-heterojunction OPV, is based on a blend of P3HT (electron-donor) and PCBM (electron-acceptor).^[1-6] This has been widely developed and studied during the last decade. Although extensive research has been done to obtain better electron-donor materials with improved efficiencies, less success has been achieved in the development of alternative electron acceptor materials.^[7] This is due to the unique properties of fullerene and its derivatives such as good charge transport and the formation of a favourable morphology when blended with an acceptor polymer.^[8-9] Due to their high cost and limited light harvesting however, replacing the fullerene derivative in OPV is an important target and a significant current challenge. In this context, an interesting approach consists of developing new molecules containing electron-withdrawing groups. Following this approach, several materials have been synthesized, such as modified pentacene,^[10-11] perylene,^[12] benzothiazoles,^[13] vinazene,^[14] phthalocyanines,^[15] thiophene-S,S-oxide^[16] and bifluorenylidene compounds.^[17]

A straightforward and attractive approach to new acceptor molecules comprises the combination of a simple, common core aromatic unit with electron-withdrawing substituent moieties. This offers a modular synthetic approach from common building blocks, however the suitability of differing acceptor units, in terms of both electronic and structural properties, requires further study. Accordingly in this paper, we will address the synthesis, optical and electrochemical characterization and DFT calculations of a series of dyes containing the naphthyl π system as a core unit, and modifying the acceptor by attaching different electron withdrawing groups. This provides a series of fundamental model compounds to explore the effect of the different acceptor units. The attachment of cyano and fluorinated groups on the acceptor moiety allows fine-tuning of the molecular electronic properties. We also evaluate the solid-state packing properties of compounds **1**, **3** and **4** as well as the photoluminescence quenching with common electron donor polymers.

Results and Discussion

Electron acceptor units were synthesized as shown in Scheme 1. Indane derivatives **7** and **9** were prepared by condensation of malononitrile (2 or 3 equivalents for **7** and **9**, respectively) to commercially-available 1,3-indanedione.^[18-19] Tetrafluoroindane derivative **6** was obtained by reacting tetrafluorophthalic anhydride with *tert*-butyl acetoacetate,^[20] and tricyanofurane **8** (TCF) by a two-step condensation of malononitrile in basic media.^[21-22] Chromophores **1** – **5** were prepared by a condensation of 2-naphthaldehyde with acceptors **6** – **9** following different synthetic procedure, depending on the nature of the acceptor, and collected by filtration.



Scheme 1. Synthesis of acceptors **1** – **5**.

The stability of these new compounds was tested by leaving the dyes for a few days in CDCl_3 or $\text{DMSO}-d_6$ solutions and monitoring by ^1H NMR. All the chromophores showed a good stability, except for molecule **5**. In this case, a peak at 10 ppm arose after 1 day, which indicated that **5** had decomposed into starting 2-naphthaldehyde and acceptor **9**. This result is not unexpected since chromophore **5** exhibits a significant strain between the naphthyl and tetracyanoindane unit and therefore, a high tendency to dissociate (Figure 1). We

believe that traces of water in the solvent drive the system back to starting materials and therefore molecule **5** can only be obtained and treated in an anhydrous environment, such as acetic anhydride.^[23]

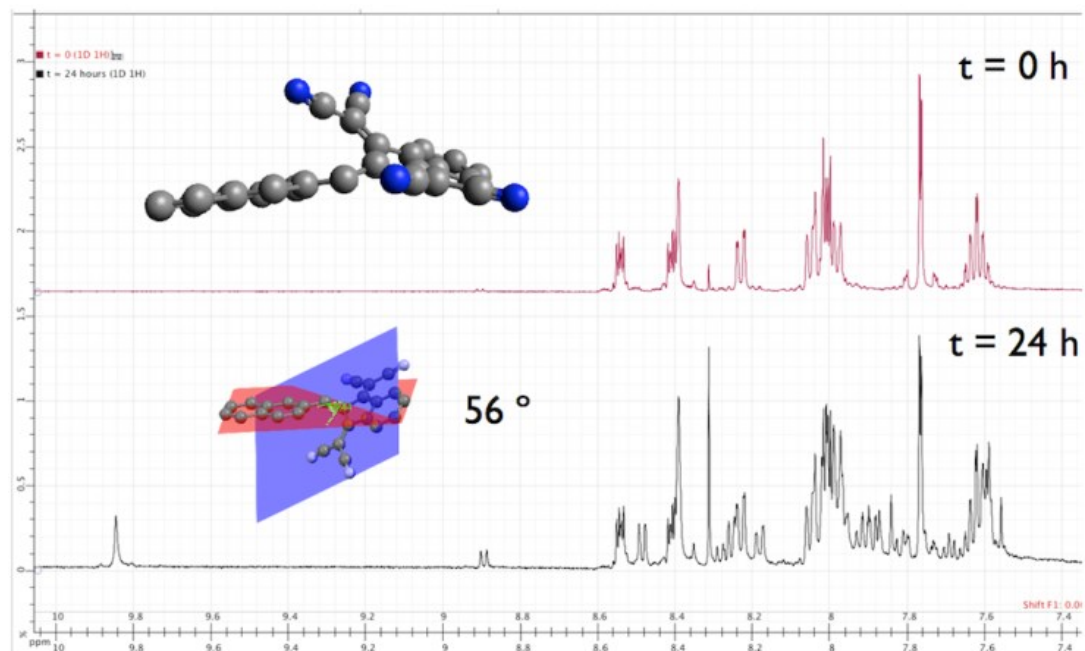


Figure 1. ¹H NMR spectra of pristine **5** (top) and after 24 hours (bottom) in DMSO-*d*₆. DFT calculations show a large ring twist of 56 degrees.

Optical properties were measured by UV-Visible absorption and photoluminescence techniques in dichloromethane solution. All dyes showed a strong absorption peak centred between 360 and 500 nm and most of them showed fluorescence emission. Spectroscopic data are shown in Figure 2 and summarised in Table 1 together with the electrochemical properties. The intense absorption in the visible region is assigned to an intramolecular charge transfer (ICT) from the naphthyl π system to the electron acceptor unit and accordingly, the shift of the ICT band is related to the electron acceptor strength. Therefore, molecule **1** (with a weaker electron-withdrawing unit) showed a maximum at 360 nm, whereas a red shift is observed when fluorine atoms (molecule **2**) or cyano groups (molecules **3** and **4**) are introduced. This red shift can be up to 80 nm as we increase the electron acceptor ability. Additionally, these dyes also show a solvatochromic effect, which is expected for such donor-acceptor molecules and indicates a significant difference in charge distribution between the ground and excited states (Figures S1 and S2 – supporting information).^[24] In this case, an increase in solvent polarity leads to a blue-shifted absorption maximum, indicating a reduction in dipole moment of the excited state compared with the ground state of the dye.

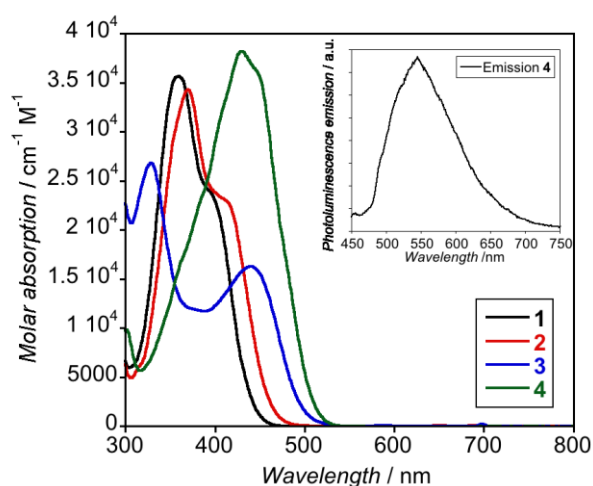


Figure 2. Absorption of **1** (black line), **2** (red line), **3** (blue line) and **4** (green line) recorded in CH₂Cl₂ at room temperature. Inset: Emission spectrum of **4** in CH₂Cl₂ at room temperature after excitation at 430 nm.

Table 1. Electrochemical and optical data for **1** – **4**.

	λ_{\max} (nm) ^[a]	ϵ (cm ⁻¹ M ⁻¹)	λ_{em} (nm) ^[b]	λ_{onset} (nm)	$E_{\text{gap}}^{\text{opt}}$ (eV)	E_{OX} (V) ^[c]	E_{RED} (V) ^[c]	$E_{\text{gap}}^{\text{CV}}$ (eV) ^[d]
1	360	35000	450 ^[e]	440	2.82	+1.36	-1.41	2.77
2	370	34000	n.o. ^[f]	460	2.69	+1.38	-1.20	2.58
3	440	16000	n.o. ^[f]	500	2.48	+1.47	-1.04	2.51
4	430	38000	545	505	2.45	+1.38	-1.11	2.49

[a] Measured at $5 \cdot 10^{-5}$ M in CH₂Cl₂. [b] Measured at $5 \cdot 10^{-6}$ M in CH₂Cl₂ and excited at λ_{\max} . [c] DPV measured from 0.1 M [TBA][PF₆] in CH₂Cl₂ and referenced to ferrocene. [d] $E_{\text{gap}}^{\text{CV}} (\text{eV}) = E_{\text{OX}} - E_{\text{RED}}$. [e] Low intensity. [f] n.o. = non observed.

Electrochemical behaviour was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in a CH₂Cl₂ solution containing 0.1 M [TBA][PF₆] as supporting electrolyte. All values are reported in Table 1. As expected, oxidation potentials remain similar for all samples, consistent with a HOMO based on the naphthyl unit in each case. These potentials are on the edge of the solvent window and can only be observed by the DPV technique (Figure S3 and S4 – supporting information). On the other hand, reduction potentials shifted to more positive potentials upon increase of the electron-withdrawing ability of the molecule, i.e. when the number of cyano/fluorinated units increases. All the first reduction processes can be observed by both CV and DPV, and showed an irreversible wave (Figure 3). Although electrochemically irreversible waves indicate that the radical anions are not stable on the electrochemical timescale, the molecule is reduced only transiently in the solid state solar cell and can still possess sufficient stability for model studies.

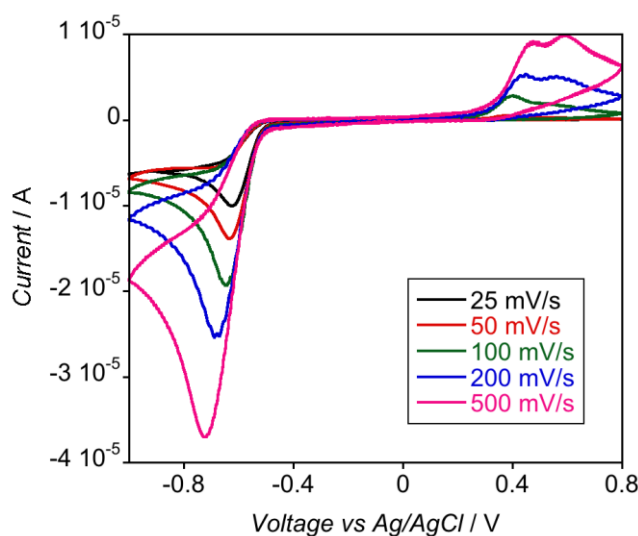


Figure 3. Cyclic voltammetry of **4** performed at different scan rates (CH_2Cl_2 , 0.1 M [TBA][PF₆], V vs. Ag/AgCl).

DFT calculations were performed with Gaussian 03, B3LYP 6-31G(d,p) level of theory. Computational details can be found in the supplementary information. Figure 2 shows representations of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals. It can be observed that the HOMO is localised over the naphthyl unit and the ethylene bridge. The orbital energies calculated are similar (ca. - 6.0 eV) for all the molecules. In contrast, localisation of the LUMO varies depending on the nature of the acceptor. In general, the LUMO is delocalised on either the indane or TCF unit, together with the ethylene bridge. The fluorinated analogue **2** shows a lower LUMO energy compared to non-fluorinated analogue **1** (0.2 eV), although the LUMO is slightly distributed on the fluorine atoms. On the other hand, the addition of cyano groups (molecules **3** and **4**) leads to a strong downward shift of the LUMO energy by 0.5 eV, compared to **1**. In this case, the molecular orbital distribution is localised on the cyano groups together with the ethylene moieties.

Although the absolute values do not agree with the experimental values obtained by CV and DPV, the trend and shift in energy between molecules is consistent.

Single crystals suitable for X-Ray diffraction were obtained by slow recrystallization in hot 1-butanol for **1** and chlorobenzene for **2** and **4**. Multiple attempts have been carried out to obtain crystals from solution processing for molecule **3**, with no success. However, suitable crystals were obtained after sublimation..

As can be seen in Figure 5, the packing follows a head-to-tail motif for all samples, characteristic of non-symmetrical donor-acceptor molecules, in order to cancel the dipole moment.^[25-26] Acceptors **1**, **2** and **3** pack as a dimer, with alternating (overlapping) naphthyl units over indanedione moieties. In contrast, acceptor **4**

packs by overlapping two naphthyl units, without involving the TCF moiety. This could be due to the steric hindrance of the methyl groups of TCF unit, which are out of plane.

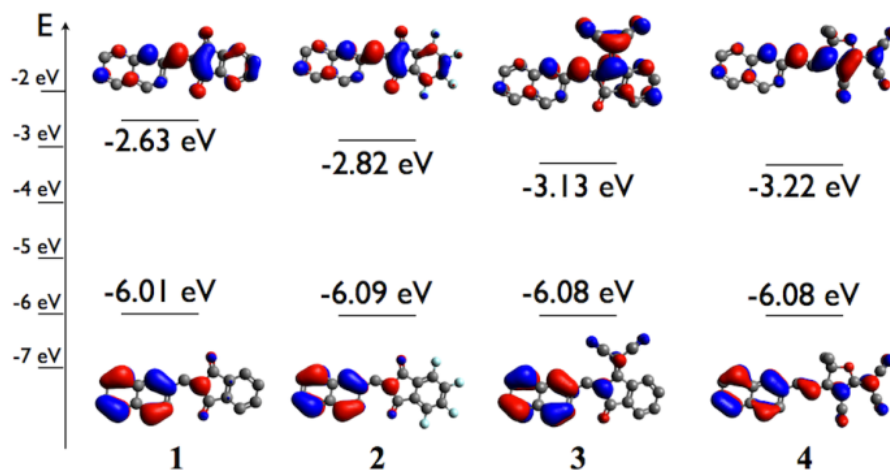


Figure 4. Molecular orbital distribution (isodensity = 0.03) and orbital energies calculated for molecules **1 - 4** (from left to right) at B3LYP/6-31G(d,p) level of theory.

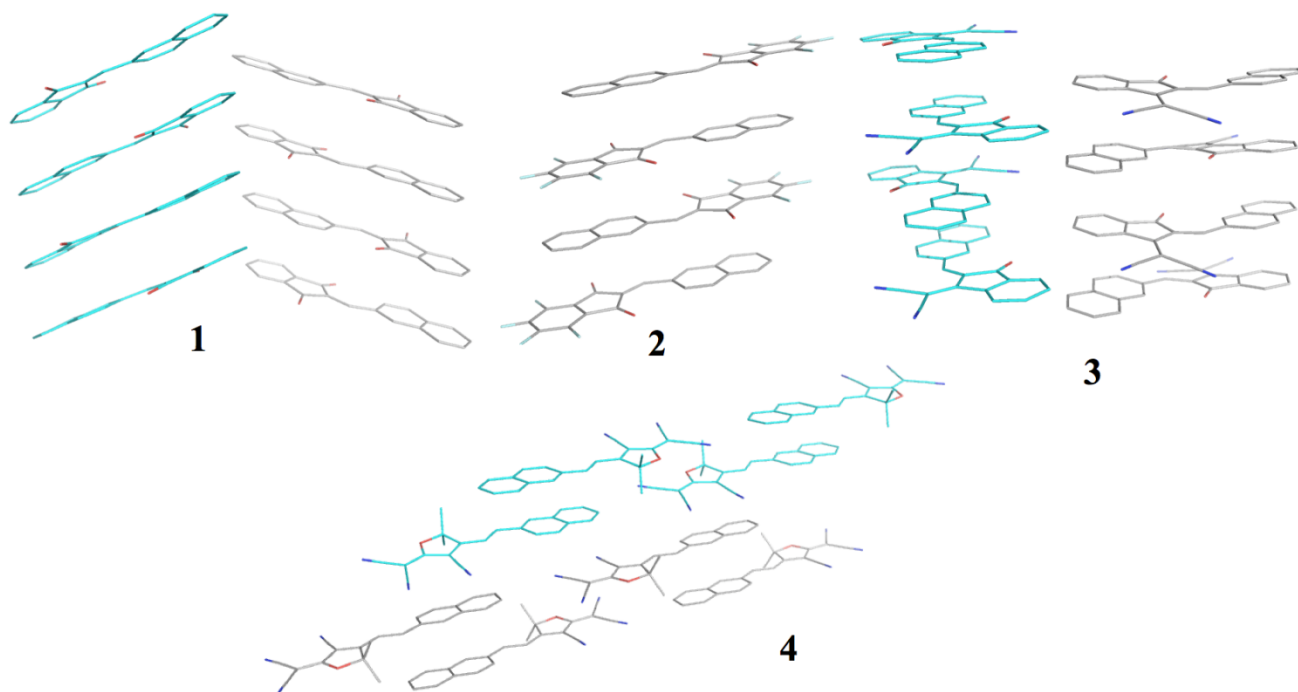


Figure 5. Packing of **1, 2, 3** and **4**. Additional asymmetric units (if any) are shown in different colour.

Intradimer distances were 3.29 (3.30), 3.24, 3.31 (3.41) and 3.42 (3.61) Å for **1**, **2**, **3** and **4**, respectively, showing a strong π - π interaction between units within the same range for all samples.^[27] However, the twist between the naphthyl unit and acceptor moiety is different. In this case, we observe a small twist of 2, 2 and 8 degrees for molecules **1**, **2** and **4**, respectively. On the other hand, molecule **3**, with similar packing to **1** and **2**, shows a twist angle as high as 18 degrees. This non-planar packing for a fully conjugated molecule **3** is consistent with its poorer crystallinity.

Photoluminescence quenching of blends is a useful and straightforward technique to screen the potential use of organic semiconductors in OPV applications. In this case, we formed 1:1 blends of acceptors **1**, **3** and **4** with both P3HT and PCDTBT polymers through spin coating of solutions containing 5 mg/mL of each component in chlorobenzene solvent. We discarded sample **2** and **5** due to low solubility and low stability, respectively. Spin coating studies typically use concentrations around 10 mg/mL or higher, however for **1** and **4** their solubility limit is around 5 mg/mL, and therefore, blends were sonicated and vigorously stirred at 40 °C in order to dissolve completely. The mixture was spin coated onto slightly warm glass to avoid microprecipitation. In order to study the thin-film stability as well as the light absorption contribution of the synthesised electron acceptor materials in the solid state, UV-Vis absorption spectra were recorded and monitored over four days for the acceptors blended with PCDTBT polymer (Figure S7 and S8 – supporting information). Bands due to the acceptor absorption can be observed at similar positions to solution experiments, and no significant changes were observed during the next four days. After proving the stability of the films, photoluminescence quenching was followed after excitation at 520 and 550 nm for P3HT and PCDTBT, respectively.

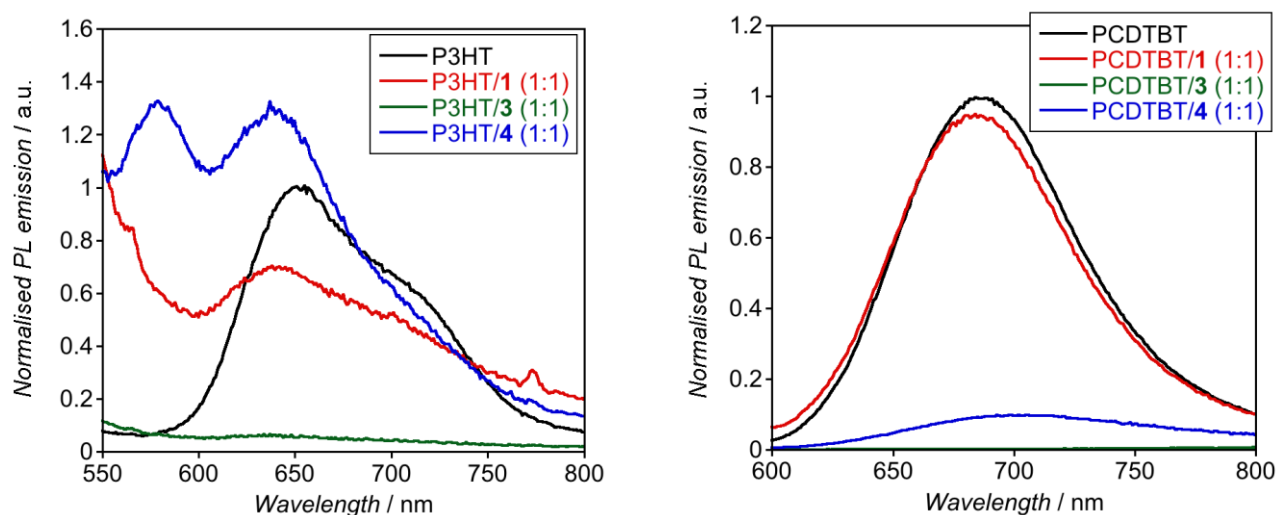


Figure 6. Photoluminescence quenching of P3HT (*top*) and PCDTBT (*bottom*) after blending with acceptor **1**, **3** and **4** at 1:1 ratio in chlorobenzene. PL intensity have been corrected considering the film absorption and then normalized to the polymer maximum emission.

Figure 4 shows good P3HT PL quenching for molecule **3**, however, inefficient PL quenching for molecules **1** and **4**, despite the LUMO energy levels suggesting a good energy offset for exciton splitting. We believe that P3HT, considered as a strongly crystalline polymer, did not blend well with the more crystalline acceptors **1** and **4**, but better with **3**, the acceptor we found most difficult to crystallise from solution. On the other hand, when they are blended with PCDTBT, considered as a more amorphous polymer, molecule **3** shows a nearly complete PL quenching, but only a 90% quenching for molecule **4**.^[28] This suggests that molecule **3** intercalates better into the polymer than **4**, probably due to its lower tendency for molecules of **3** to pack with each other.^[28-29] Although better PL quenching has been found for **3** due to its less crystalline nature, we note that its charge transport properties could also be affected. Finally, PL quenching of **1** with PCDTBT blend is not observed due to the very small energy offset, considering the low lying LUMO of PCDTBT. This is consistent with the results observed by electrochemistry and DFT calculations.

Conclusions

In summary, we have designed and synthesized four electron-acceptor materials based on a naphthyl group with different electron-withdrawing units. All these molecules have been characterized by spectroscopic, electrochemical and computational techniques. These molecules possess an intense band between 350 and 500 nm, and most of them a reduction potential suitable for mixing with typical electron-donor polymers. In spite of this, photoluminescence quenching clearly indicates other factors that should be taken in account, such as crystallinity of the materials used. In this case, only molecule **3** gave good quenching with both P3HT and PCDTBT, while **4** showed good quenching with just PCDTBT. We have interpreted this in terms of the crystal structure of **3**, which shows a larger twist in the molecule possibly enhancing its tendency to blend with the polymer. In general, we have demonstrated that π systems attached to electron-withdrawing groups can provide the right electrochemical and optical properties for a new approach to electron-acceptor materials for OPV. Further studies are in progress to explore their properties in OPV devices, and to prepare analogues that build on the morphological insight gained.

Experimental Section

Materials and Reagents. All reagents were purchased from either Sigma-Aldrich or Alfa-Aesar and they were used as received without further purification, except for 1,3-indanedione and 2-naphthaldehyde that were recrystallized from ethanol before use.

Synthesis of 2-(naphthalen-2-ylmethylene)-1H-indene-1,3(2H)-dione (1**):** 2-naphthaldehyde (100 mg, 0.64 mmol) and 1,3-indanedione (103 mg, 1.1 mmol) were placed in a schlenck tube with 25 mL of n-butanol (40 mL/mmol). The mixture was stirred under N₂ for 5 hours. After cooling to room temperature (r.t) a yellow

precipitate was collected by filtration and washed with 50 mL of ethanol (54 mg, 30% yield). Melting point: 223 °C. ¹H NMR (500 MHz, CDCl₃) δ_H: 8.95 (s, 1H); 8.62 (dd, *J* = 8.6 Hz, 1.9 Hz, 1H); 8.07 (m, 4H); 7.94 (d, *J* = 8.6 Hz, 1H); 7.89 (d, *J* = 7.7 Hz, 1H); 7.84 (m, 2H); 7.62 (m, 1H); 7.56 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ_C: 190.6; 189.4; 147.3; 142.8; 140.3; 136.9; 135.7; 135.6; 135.4; 133.2; 131.1; 130.0; 129.5; 129.3; 129.2; 128.6; 127.9; 126.9; 123.5 (x2). MS EI (m/z): [M]⁺ calcd for C₂₀H₁₂O₂: 284.0837; found: 284.08318. Anal. Calcd for C₂₀H₁₂O₂: C, 84.49; H, 4.25; Found: C, 84.38; H, 4.14.

Synthesis of tetrafluoro-1,3-indanedione (6): Tetrafluorophthalic anhydride (2 g, 9.1 mmol) was added in a round bottom flask with 9 mL of acetic anhydride (1 mL/mmol) and 4.5 mL triethylamine (0.5 mL/mmol). The mixture was stirred at r.t. and tert-butyl acetoacetate (1.66 mL, 10 mmol) was added. The reaction was kept at r.t. and stirred overnight under N₂. Then, the crude was poured into a mixture of 10 g ice-water/HCl conc (1:1). An additional 16 mL of HCl 5M was added and the mixture was stirred at reflux for 3 hours. After cooling at r.t., the crude was extracted by adding 150 mL of CHCl₃. The organic layer was washed with brine, dried over Na₂SO₄ and solvent removed, giving a brown solid. Pure product was obtained by sublimation under high vacuum at 140 °C as white solid (540 mg, 27%). ¹H NMR (400 MHz, CDCl₃) δ_H: 3.33 (s, 2H). ¹⁹F NMR (376 MHz, CDCl₃) δ_F: -135.2 (m, 2F); -140.1 (m, 2F). MS EI (m/z): [M]⁺ calcd for C₉H₂O₂F₄: 217.99854; found: 217.99835. Anal. Calcd for C₉H₂O₂F₄: C, 49.56; H, 0.92; Found: C, 49.57; H, 1.00.

Synthesis of 4,5,6,7-tetrafluoro-2-(naphthalen-2-ylmethylene)-1H-indene-1,3(2H)-dione (2): 2-naphthaldehyde (155 mg, 1.0 mmol) and **6** (327 mg, 1.5 mmol) were placed in a schlenk tube with 20 mL of n-butanol (20 mL/mmol). The mixture was stirred under N₂ overnight at reflux. After cooling to r.t. a yellow precipitate was collected by filtration and washed with 50 mL of ethanol (77 mg, 20% yield). Melting point: 300 °C. ¹H NMR (400 MHz, DMSO-*d*₆) δ_H: 9.04 (s, 1H); 8.64 (dd, *J* = 8.88 Hz, 1.3 Hz, 1H); 8.07 (m, 4H); 7.73 (m, 1H); 7.66 (m, 1H). ¹⁹F NMR (376 MHz, DMSO-*d*₆) δ_F: -139.8 (m, 1F); -141.1 (m, 1F); -143.9 (m, 2F). MS EI (m/z): [M]⁺ calcd for C₂₀H₈F₄O₂: 356.04604; found: 356.045513. Anal. Calcd for C₂₀H₈F₄O₂: C, 67.42; H, 2.26; Found: C, 67.51; H, 2.17.

Synthesis of 2-(3-oxo-indane-1-ylidene)-malononitrile (7): 1,3-indanedione (2 g, 13.68 mmol) and malononitrile (1.8 g, 66.06 mmol) were placed in a round bottom flask with 30 mL of ethanol (2 mL/mmol). The mixture was stirred at r.t. and sodium acetate (1.34 g, 16.4 mmol) was added. The reaction was kept at r.t. and stirred for 40 minutes. Then, H₂O (130 mL) was added and the crude was acidified by adding drop-wise concentrated HCl until pH = 2. The crude was stirred for an extra 10 and the grey precipitate was filtered off and washed with copious amounts of water. The solid was recrystallized twice with acetic acid and with ethanol, giving a reddish solid (1.07 g, 41%). ¹H NMR (500 MHz, CDCl₃) δ_H: 8.66 (d, *J* = 7.5 Hz, 1H); 7.99 (d, *J* = 7.0 Hz, 1H); 7.88 (m, 2H); 3.73 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ_C: 194.9; 166.4; 142.6; 140.7; 136.3; 135.9; 126.2; 124.9; 112.3; 122.2; 79.4; 43.4. MS EI (m/z): [M]⁺ calcd for C₁₂H₆ON₂: 194.04856; found: 194.04851. Anal. Calcd for C₁₂H₆ON₂: C, 74.22; H, 3.11; N, 14.43; Found: C, 74.02; H, 3.05; N, 14.36.

Synthesis of (Z)-2-(2-(naphthalen-2-ylmethylene)-3-oxo-2,3-dihydro-1H-inden-1-ylidene)malononitrile

(3): 2-naphthaldehyde (72 mg, 0.47 mmol) and **7** (100 mg, 0.51 mmol) were placed in a schlenck tube with 20 mL of n-butanol (40 mL/mmol). The mixture was stirred under N₂ for 3 hours. After cooling to room temperature (r.t) a red precipitate was collected by filtration and washed with 50 mL of ethanol (50 mg, 32% yield). Melting point = 196 °C. ¹H NMR (500 MHz, CDCl₃) δ_H: 8.80 (s, 1H); 8.75 (d, *J* = 8.0 Hz, 1H); 8.69 (s, 1H); 8.26 (dd, *J* = 8.7 Hz, 1.9 Hz, 1H); 7.99 (t, *J* = 9.0 Hz, 2H); 7.92 (d, *J* = 8.6 Hz, 1H); 7.89 (d, *J* = 8.3 Hz, 1H); 7.85 (td, *J* = 7.5 Hz, 1.9 Hz, 1H); 7.80 (td, *J* = 7.4 Hz, 0.9 Hz, 1H); 7.63 (m, 1H); 7.57 (m, 1H). ¹³C NMR (125 MHz, CDCl₃) δ_C: 186.6; 161.9; 148.2; 140.0; 137.6; 136.8; 135.9; 135.7; 135.3; 132.9; 130.4; 130.0; 129.9; 129.5; 129.5; 129.1; 128.2; 128.0; 127.1; 125.6; 124.6; 114.3; 114.0; 72.7.

MS ESI (m/z): [M-H]⁻ calcd for C₂₃H₁₁N₂O: 331.08659; found: 331.08777. Anal. Calcd for C₂₃H₁₂N₂O C, 83.12; H, 3.64; N, 8.43; Found: C, 83.20; H, 3.57; N, 8.39.

Synthesis of 2-(3-cyano-4,5,5-trimethylfuran-2(5H)-ylidene)malononitrile (8):^[30] 3-hydroxy-3-

methylbutanone (3.5 mL, 33.3 mmol) and malononitrile (4.4 g, 66.6 mmol) were added in a two neck round bottom flask with 83 mL of ethanol (2.5 mL/mmol). Then, a freshly made sodium ethoxide solution (100 mg of sodium in 1 mL of ethanol) was added and the mixture was stirred overnight under N₂ at 80 °C. After cooling down at r.t., the solvent was removed and the product was purified by column chromatography (CH₂Cl₂). Analytical sample was obtained by recrystallization in ethanol as yellowish needles (3.2 g, 48%). ¹H NMR (500 MHz, CDCl₃) δ_H: 2.36 (s, 3H); 1.63 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ_C: 182.2; 175.2; 111.1; 110.4; 109.1; 105.1; 99.7; 59.0; 24.6; 14.3. MS ESI (m/z): [M+H]⁺ calcd for C₁₁H₁₀N₃O: 200.08184; found: 200.08207. Anal. Calcd for C₁₁H₉N₃O C, 66.32; H, 4.55; N, 21.09; Found: C, 66.41; H, 4.68; N, 20.85.

Synthesis of (E)-2-(3-cyano-5,5-dimethyl-4-(2-(naphthalen-2-yl)vinyl)furan-2(5H)-ylidene)malononitrile

(4):^[30] 2-naphthaldehyde (155 mg, 1.0 mmol) and **8** (219 mg, 1.1 mmol) were placed in a schlenck tube with 4 mL of ethanol (4 mL/mmol). Triethylamine (13 μL, 0.1 mmol) was added and the mixture was stirred under N₂ overnight at reflux temperature. After cooling to r.t. a red precipitate was collected by filtration and washed with 20 mL of cold ethanol (253 mg, 75% yield). Melting point: 275 °C. ¹H NMR (500 MHz, CDCl₃) δ_H: 8.07 (s, 1H); 7.92 (m, 2H); 7.88 (d, *J* = 8.0 Hz, 1H); 7.84 (d, *J* = 16.2 Hz, 1H); 7.76 (dd, *J* = 8.8 Hz, 1.8 Hz, 1H); 7.59 (m, 2H); 7.15 (d, *J* = 16.3 Hz, 1H); 1.84 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ_C: 175.4; 173.8; 147.6; 135.5; 133.4; 132.9; 131.5; 129.8; 129.3; 129.2; 128.3; 127.7; 122.9; 115.1; 111.8; 111.0; 110.4; 100.1; 97.8; 58.2; 26.7. MS ESI (m/z): [M-H]⁻ calcd for C₂₂H₁₄N₃O: 336.11314; found: 336.11438. Anal. Calcd for C₂₂H₁₅N₃O C, 78.32; H, 4.48; N, 12.46; Found: C, 78.28; H, 4.36; N, 12.37.

Synthesis of (indan-1,3-diylidene)dimalononitrile (9): 1,3-indanedione (2 g, 13.68 mmol) and malononitrile

(2.7 g, 41.04 mmol) were placed in a round bottom flask with 30 mL of ethanol (2 mL/mmol). The mixture was stirred at r.t. and ammonium acetate (1.05 g, 13.68 mmol) was added. The reaction was heated up to 70 °C and stirred for 5 hours. After cooling down to r.t., H₂O (40 mL) was added and the crude was acidified by adding drop-wise concentrated HCl until pH = 2. The crude was stirred for an extra 10 and the grey precipitate

was filtered off and washed with copious amounts of water. The solid was recrystallized with acetic acid, giving a brown crystals (1.15 g, 34%). ¹H NMR (500 MHz, CDCl₃) δ_H: 8.66 (m, 2H), 7.92 (m, 2H); 4.30 (s, 2H). ¹³C NMR (125 MHz, CDCl₃) δ_C: 165.4; 140.7; 136.4; 127.1; 111.9; 111.7; 79.4; 42.0. MS ESI (m/z): [M-H]⁻ calcd for C₁₅H₅N₄: 241.05197; found: 241.05191. Anal. Calcd for C₁₅H₆N₄: C, 74.37; H, 2.50; N, 23.13; Found: C, 74.26; H, 2.40; 23.23.

Synthesis of 2,2'-(2-(naphthalen-2-ylmethylene)-1H-indene-1,3(2H)-diylidene)dimalononitrile (5): 2-naphthaldehyde (155 mg, 1.0 mmol) and **9** (266 mg, 1.1 mmol) were placed in a schlenk tube with 8 mL of acetic anhydride (8 mL/mmol). The mixture was stirred under N₂ for 4 h. at reflux temperature. After cooling to r.t. a red-brown precipitate was collected by filtration and washed with 4 mL of cold acetic anhydride (39 mg, 10% yield). ¹H NMR (500 MHz, DMSO-*d*₆) δ_H: 8.54 (m, 1H); 8.40 (m, 1H); 8.39 (s, 1H); 8.23 (dd, J = 9.0 Hz, 2.0 Hz, 1H); 8.01 (m, 5H); 7.76 (d, J = 2.5 Hz, 2H); 7.62 (m, 2H).

Methods

Chemical characterization. ¹H and ¹³C NMR spectra were recorded on Bruker Advance 500 spectrometer (500 MHz for ¹H and 125 MHz for ¹³C). ¹⁹F NMR spectra were recorded on Bruker Advance 400 spectrometer (376 MHz for ¹⁹F). The deuterated solvents are indicated; chemical shifts, δ, are given in ppm, referenced to the solvent residual signal (¹H, ¹³C). MS were recorded both on ThermoElectron MAT 900 using electron impact (EI) or LCQ Thermo Finnegan using electrospray ionization (ESI), depending on the sample. Elemental analyses were carried out by Stephen Boyer at London Metropolitan University using a Carlo Erba CE1108 Elemental Analyser.

Electrochemical characterization. All cyclic voltammetry measurements were carried out in freshly distilled CH₂Cl₂ using 0.1 M [TBA][PF₆] electrolyte in a three electrode system, with each solution being purged with N₂ prior to measurement. The working electrode was a Pt disk. The reference electrode was Ag/AgCl and the counter electrode was a Pt rod. All measurements were made at r.t. using an μAUTOLAB Type III potentiostat, driven by the electrochemical software GPES. Cyclic voltammetry (CV) measurements used scan rates of 0.1 V/s, and DPV was carried out at a step potential of 0.01 V, modulation amplitude of 0.1 V, modulation time of 0.05 s and an interval time of 0.5 s. Ferrocene was used as internal standard in each measurement.

Optical characterization. Solution and solid state UV-Visible absorption spectra were recorded using Jasco V-670 UV/Vis/NIR spectrophotometer controlled using the SpectraManager software. Photoluminescence (PL) spectra were recorded with Fluoromax-2 fluorimeter controlled by the ISAMain software. All samples were measured in a 1 cm cell at r.t. with dichloromethane as a solvent. Concentration of 5 · 10⁻⁵ M and 5 · 10⁻⁶ M were used for UV/Vis and PL, respectively.

Computational characterization. The geometry of each system was calculated with CH₂Cl₂ included in the system via a polarisable continuum model.^[31] All calculations were carried out using the Gaussian 03 program^[32] with the Becke three parameter hybrid exchange, Lee Yang-Parr correlation functional (B3LYP) level of theory. All atoms were described by the 6-31G(d,p) basis set. All structures were input and processed through Avogadro software package.

Supporting Information: UV-Visible spectra upon different solvents. Differential pulse voltammetry scans. Top view of crystal packing. Chemical structures of P3HT and PCDTBT and thin-film UV-Vis spectra. Crystallographic data. ¹H NMR, ¹⁹F NMR and ¹³C NMR spectra of all compounds.

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