EurJOC European Journal of Organic Chemistry

FULL PAPER

DOI: 10.1002/ejoc.201200715

Naphthyl Derivatives Functionalised with Electron Acceptor Units – Synthesis, Electronic Characterisation and DFT Calculations

Miquel Planells[a] and Neil Robertson*[a]

Keywords: Donor–acceptor systems / Organic photovoltaics / Density functional calculations / Electrochemistry / Luminescence

A series of unsymmetrical dyes containing a naphthyl unit connected to an electron acceptor moiety was designed and synthesised. By modifying the electron acceptor unit, a shift of the LUMO energy level as well as its distribution through the molecule were achieved. These dyes were fully characterised 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 (OPVs) was also 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 (OPVs). 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] Because of their high cost and limited light harvesting, however, replacing the fullerene derivative in OPVs is an important target and a significant current challenge. In this context, an interesting approach consists of developing new molecules containing electron withdrawing groups. By this approach, several materials have been synthesised, 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 characterisation and DFT calculations of a series of dyes containing the naphthyl π system as a core unit and the modification of 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 photoluminescence quenching with common electron donor polymers.

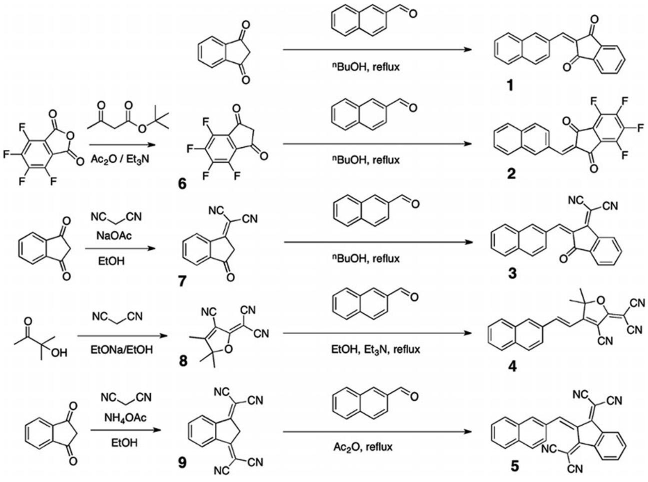
Results and Discussion

Electron acceptor units were synthesised as shown in Scheme 1. Indane derivatives **7** and **9** were prepared by condensation of malononitrile (2 or 3 equiv. 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) was prepared 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 procedures, depending on the nature of the acceptor, and collected by filtration.

---

[a] EastChem School of Chemistry, University of Edinburgh,
West Mains Road, Edinburgh EH9 3JJ, U.K.
Fax: +44-131 650 6453
E-mail: neil.robertson@ed.ac.uk

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201200715.



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

The stability of these new compounds was tested by keeping the dyes for a few days in $CDCl_3$ or $[D_6]DMSO$ solutions and monitoring them by ^1H NMR spectroscopy. All the chromophores showed good stability, except for molecule **5**. In this case, a peak at $\delta = 10$ ppm appeared after one day, which indicated that **5** had decomposed into starting materials 2-naphthaldehyde and acceptor **9**. This result is not unexpected, because chromophore **5** exhibits 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]

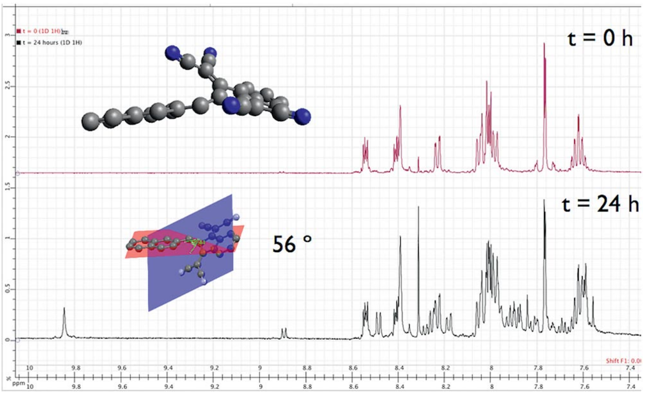


Figure 1. ^1H NMR spectra of pristine **5** (top) and after 24 h (bottom) in $[D_6]DMSO$. DFT calculations show a large ring twist of 56 degrees.

Optical properties were measured by UV/Vis 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 redshift was observed when fluorine atoms (molecule **2**) or cyano groups (molecules **3** and **4**) were introduced. This redshift reached up to 80 nm as we increased 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 blueshifted absorption maximum, indicating a reduction in the dipole moment of the excited state relative to that of the ground state of the dye.

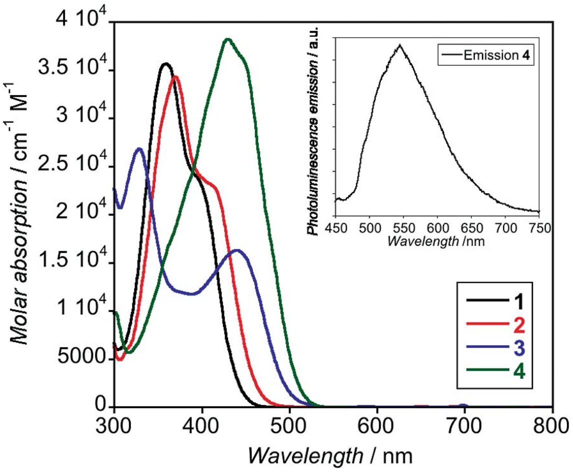


Figure 2. Absorption of **1** (black line), **2** (red line), **3** (blue line) and **4** (green line) recorded in CH_2Cl_2 at room temperature. Inset: Emission spectrum of **4** in CH_2Cl_2 at room temperature after excitation at 430 nm.

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_{gap}^{opt} /eV	E_{OX} /V[c]	E_{RED} /V[c]	E_{gap}^{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 5×10^{-5} M in CH_2Cl_2. [b] Measured at 5×10^{-6} M in CH_2Cl_2 and excited at λ_{max}. [c] Differential pulse voltammetry (DPV) measured from 0.1 M [TBA][PF_6] in CH_2Cl_2 and referenced to ferrocene. [d] Cyclic voltammetry: E_{gap} (CV) = $E_{OX} - E_{RED}$. [e] Low intensity. [f] The abbreviation n.o. means not observed.

Electrochemical behaviour was investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) in a CH_2Cl_2 solution containing 0.1 M [TBA][PF_6] 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 at the edge of the solvent window and can only be observed by the DPV technique (Figures S3 and S4 – Supporting Information). On the other hand, reduction potentials shifted to more positive potentials as the electron withdrawing ability of the molecule increased, that is, when the number of cyano/fluorinated units increased. All the first reduction processes could be observed by both CV and DPV, and they showed an irreversible wave (Figure 3). Although electrochemically irreversible waves indicate that 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.

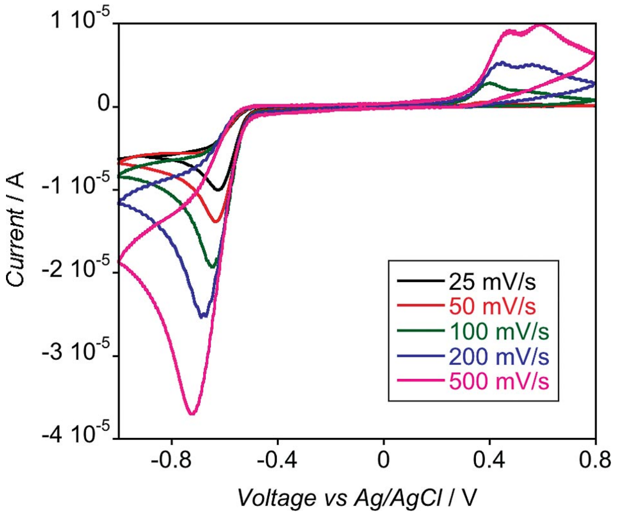


Figure 3. Cyclic voltammetry of **4** performed at different scan rates (CH_2Cl_2, 0.1 M [TBA][PF_6], V vs. Ag/AgCl).

DFT calculations were performed at the Gaussian 03, B3LYP 6-31G(d,p) level of theory. Computational details can be found in the Supporting Information. Figure 4 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. Fluorinated analogue **2** shows a lower LUMO energy relative 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, relative to that of **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 recrystallisation in hot 1-butanol for **1** and chlorobenzene for **2** and **4**. Multiple attempts were performed to obtain crystals from solution processing for molecule **3**, with no success. However, suitable crystals were obtained after sublimation.

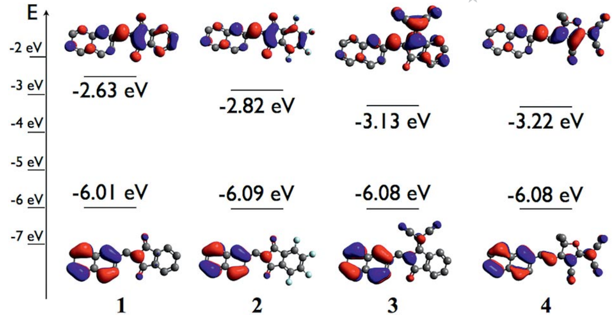


Figure 4. Molecular orbital distribution (isodensity = 0.03) and orbital energies calculated for molecules **1**–**4** (from left to right) at the B3LYP/6-31G(d,p) level of theory.

As shown 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 the TCF unit, which are out of plane.

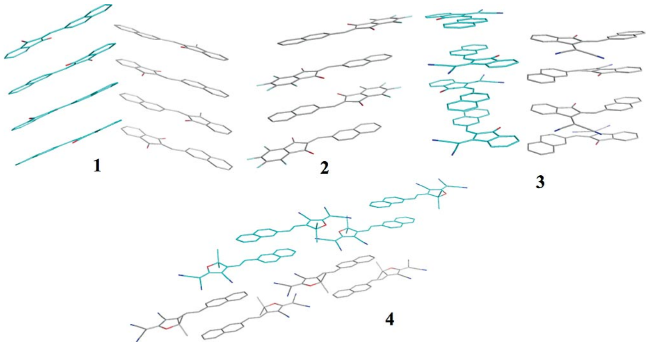


Figure 5. Packing of **1**, **2**, **3** and **4**. Additional asymmetric units (if any) are shown in different colours.

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 the 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 nonplanar 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 polymers P3HT and PCDTBT through spin coating of solutions containing 5 mg mL^{-1} of each component in chlorobenzene solvent. We discarded samples **2** and **5** because of their low solubility and low stability, respectively. Spin coating studies typically use concentrations around 10 mg mL^{-1} or higher; however, the solubility limit of **1** and **4** is around 5 mg mL^{-1}, and therefore blends were sonicated and vigorously stirred at 40 °C in order to dissolve them 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 (Figures 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).

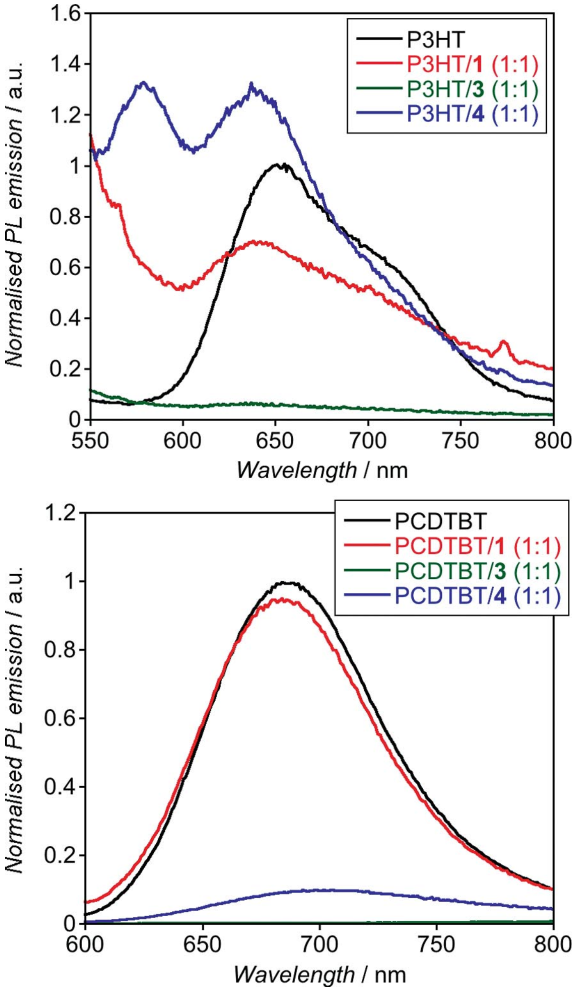


Figure 6. Photoluminescence quenching of P3HT (top) and PCDTBT (bottom) after blending with acceptor **1**, **3** and **4** at a ratio of 1:1 in chlorobenzene. Photoluminescence intensities have been corrected for the absorption of the film and then normalised to the maximum emission of the polymer.

Figure 4 shows good P3HT photoluminescence quenching for molecule **3**; however, the photoluminescence quenching for molecules **1** and **4** is inefficient, in spite of the fact that the LUMO energy levels suggest 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 it is blended with PCDTBT, which is considered to be a more amorphous polymer, molecule **3** shows a nearly complete photoluminescence quenching, but only a 90% quenching is observed for molecule **4**.[28] This suggests that molecule **3** intercalates better into the polymer than **4**, probably because of the lower tendency for molecules of **3** to pack with each other.[28–29] Although better photoluminescence quenching has been found for **3** because of its less crystalline nature, we note that its charge transport properties could also be affected. Finally, photoluminescence quenching of **1** with PCDTBT blend is not observed as a result of 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

We designed and synthesised four electron acceptor materials based on a naphthyl group with different electron withdrawing units. All these molecules were characterised by spectroscopic, electrochemical and computational techniques. These molecules possess an intense band between 350 and 500 nm, and most of them have 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 the 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 recrystallised from ethanol before use.

2-(Naphthalen-2-ylmethylene)-1*H*-indene-1,3(2*H*)-dione (1): 2-Naphthaldehyde (100 mg, 0.64 mmol) and 1,3-indanedione (103 mg, 1.1 mmol) were placed in a Schlenk tube with *n*-butyl alcohol (25 mL, 40 mL mmol^{-1}). The mixture was stirred under N_2 for 5 h. After cooling to room temp., a yellow precipitate was collected by filtration and washed with ethanol (50 mL). Yield 54 mg (30%). Melting point: 223 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.95 (s, 1 H), 8.62 (dd, J = 8.6, 1.9 Hz, 1 H), 8.07 (m, 4 H), 7.94 (d, J = 8.6 Hz, 1 H), 7.89 (d, J = 7.7 Hz, 1 H), 7.84 (m, 2 H), 7.62 (m, 1 H), 7.56 (m, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 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 (×2) ppm. MS EI (m/z): $[M]^+$ calcd. for $C_{20}H_{12}O_2$: 284.0837, found 284.08318. $C_{20}H_{12}O_2$ (284.31): calcd. C 84.49, H 4.25; found C 84.38, H 4.14.

Tetrafluoro-1,3-indanedione (6): Tetrafluorophthalic anhydride (2 g, 9.1 mmol) was added into a round-bottomed flask with acetic anhydride (9 mL, 1 mL mmol^{-1}) and triethylamine (4.5 mL, 0.5 mL mmol^{-1}). The mixture was stirred at room temp., and *tert*-butyl acetoacetate (1.66 mL, 10 mmol) was added. The reaction mixture was kept at room temp. and stirred overnight under N_2. Then, the crude mixture was poured into a 1:1 mixture (10 g) of ice-water and conc. HCl. An additional amount (16 mL) of HCl (5 M) was added, and the mixture was stirred at reflux for 3 h. After cooling at room temp., the crude was extracted by adding $CHCl_3$ (150 mL). The organic layer was washed with brine, dried with Na_2SO_4, and the solvent was removed to give a brown solid. The pure product was obtained by sublimation under high vacuum at 140 °C as a white solid (540 mg, 27%). ^{1}H NMR (400 MHz, $CDCl_3$): δ_H = 3.33 (s, 2 H) ppm. ^{19}F NMR (376 MHz, $CDCl_3$): δ_F = –135.2 (m, 2 F), –140.1 (m, 2 F) ppm. MS EI (m/z): $[M]^+$ calcd. for $C_9H_2O_2F_4$: 217.99854, found 217.99835. $C_9H_2F_4O_2$ (218.11): calcd. C 49.56, H 0.92; found C 49.57, H 1.00.

4,5,6,7-Tetrafluoro-2-(naphthalen-2-ylmethylene)-1*H*-indene-1,3-(2*H*)-dione (2): 2-Naphthaldehyde (155 mg, 1.0 mmol) and **6** (327 mg, 1.5 mmol) were placed in a Schlenk tube with *n*-butyl alcohol (20 mL, 20 mL mmol^{-1}). The mixture was stirred under N_2 overnight at reflux. After cooling to room temp. a yellow precipitate was collected by filtration and washed with ethanol (50 mL). Yield 77 mg (20%). Melting point: 300 °C. ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ_H = 9.04 (s, 1 H), 8.64 (dd, J = 8.88, 1.3 Hz, 1 H), 8.07 (m, 4 H), 7.73 (m, 1 H), 7.66 (m, 1 H) ppm. ^{19}F NMR (376 MHz, [D$_6$]DMSO): δ_F = 139.8 (m, 1 F), –141.1 (m, 1 F), –143.9 (m, 2 F) ppm. MS EI (m/z): $[M]^+$ calcd. for $C_{20}H_8F_4O_2$: 356.04604, found 356.045513. $C_{20}H_8F_4O_2$ (356.27): calcd. C 67.42, H 2.26; found C 67.51, H 2.17.

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-bottomed flask with ethanol (30 mL, 2 mL mmol^{-1}). The mixture was stirred at room temp., and sodium acetate (1.34 g, 16.4 mmol) was added. The reaction mixture was kept at room temp. and stirred for 40 min. Then, H_2O (130 mL) was added and the crude mixture was acidified by adding concentrated HCl dropwise until pH = 2. The mixture was stirred for an extra 10 min, and the grey precipitate was filtered off and washed with copious amounts of water. The solid was recrystallised twice with acetic acid and with ethanol to obtain a reddish solid (1.07 g, 41%). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.66 (d, J = 7.5 Hz, 1 H), 7.99 (d, J = 7.0 Hz, 1 H), 7.88 (m, 2 H), 3.73 (s, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 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 ppm. MS EI (m/z): $[M]^+$ calcd. for $C_{12}H_6ON_2$: 194.04856, found 194.04851. $C_{12}H_6N_2O$ (194.19): calcd. C 74.22, H 3.11, N 14.43; found C 74.02, H 3.05, N 14.36.

(*Z*)-2-[2-(Naphthalen-2-ylmethylene)-3-oxo-2,3-dihydro-1*H*-inden-1-ylidene]malononitrile (3): 2-Naphthaldehyde (72 mg, 0.47 mmol) and **7** (100 mg, 0.51 mmol) were placed in a Schlenk tube with *n*-butyl alcohol (20 mL, 40 mL mmol^{-1}). The mixture was stirred under N_2 for 3 h. After cooling to room temp., a red precipitate was collected by filtration and washed with ethanol (50 mL). Yield 50 mg (32%). Melting point = 196 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.80 (s, 1 H), 8.75 (d, J = 8.0 Hz, 1 H), 8.69 (s, 1 H), 8.26 (dd, J = 8.7, 1.9 Hz, 1 H), 7.99 (t, J = 9.0 Hz, 2 H), 7.92 (d, J = 8.6 Hz, 1 H), 7.89 (d, J = 8.3 Hz, 1 H), 7.85 (td, J = 7.5, 1.9 Hz, 1 H), 7.80 (td, J = 7.4, 0.9 Hz, 1 H), 7.63 (m, 1 H), 7.57 (m, 1 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 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 ppm. MS ESI (m/z): $[M – H]^–$ calcd. for $C_{23}H_{11}N_2O$: 331.08659, found 331.08777. $C_{23}H_{12}N_2O$ (332.36): calcd. C 83.12, H 3.64, N 8.43; found C 83.20, H 3.57, N 8.39.

2-[3-Cyano-4,5,5-trimethylfuran-2(5*H*)-ylidene]malononitrile (8):[30] 3-Hydroxy-3-methylbutanone (3.5 mL, 33.3 mmol) and malononitrile (4.4 g, 66.6 mmol) were added into a two-neck round-bottomed flask with ethanol (83 mL, 2.5 mL mmol^{-1}). Then, a freshly made sodium ethoxide solution (100 mg sodium in 1 mL ethanol) was added, and the mixture was stirred overnight under N_2 at 80 °C. After cooling down at room temp., the solvent was removed and the product was purified by column chromatography (CH_2Cl_2). An analytical sample was obtained by recrystallisation in ethanol as yellowish needles (3.2 g, 48%). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 2.36 (s, 3 H), 1.63 (s, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 182.2, 175.2, 111.1, 110.4, 109.1, 105.1, 99.7, 59.0, 24.6, 14.3 ppm. MS ESI (m/z): $[M + H]^+$ calcd. for $C_{11}H_{10}N_3O$: 200.08184, found 200.08207. $C_{11}H_9N_3O$ (199.21): calcd. C 66.32, H 4.55, N 21.09; found C 66.41, H 4.68, N 20.85.

(*E*)-2-{3-Cyano-5,5-dimethyl-4-[2-(naphthalen-2-yl)vinyl]furan-2(5*H*)-ylidene}malononitrile (4):[30] 2-Naphthaldehyde (155 mg, 1.0 mmol) and **8** (219 mg, 1.1 mmol) were placed in a Schlenk tube with ethanol (4 mL, 4 mL mmol^{-1}). Triethylamine (13 µL, 0.1 mmol) was added, and the mixture was stirred under N_2 overnight at reflux temperature. After cooling to room temp., a red precipitate was collected by filtration and washed with cold ethanol (20 mL). Yield 253 mg (75%). Melting point: 275 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.07 (s, 1 H), 7.92 (m, 2 H), 7.88 (d, J = 8.0 Hz, 1 H), 7.84 (d, J = 16.2 Hz, 1 H), 7.76 (dd, J = 8.8, 1.8 Hz, 1 H), 7.59 (m, 2 H), 7.15 (d, J = 16.3 Hz, 1 H), 1.84 (s, 6 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): 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 ppm. MS ESI (m/z): $[M – H]^–$ calcd. for $C_{22}H_{14}N_3O$: 336.11314, found 336.11438. $C_{22}H_{15}N_3O$ (337.38): calcd. C 78.32, H 4.48, N 12.46; found C 78.28, H 4.36, N 12.37.

(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-bottomed flask with ethanol (30 mL, 2 mL mmol^{-1}). The mixture was stirred at room temp., and ammonium acetate (1.05 g, 13.68 mmol) was added. The reaction mixture was heated up to 70 °C and stirred for 5 h. After cooling down to room temp., H_2O (40 mL) was added and the crude mixture was acidified by adding concentrated HCl dropwise until pH = 2. The crude mixture was stirred for an extra 10 min, and the grey precipitate was filtered off and washed with copious amounts of water. The solid was recrystallised with acetic acid to give brown crystals (1.15 g, 34%). ^{1}H NMR (500 MHz, $CDCl_3$): δ_H = 8.66 (m, 2 H), 7.92 (m, 2 H), 4.30 (s, 2 H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ_C = 165.4, 140.7, 136.4, 127.1, 111.9, 111.7, 79.4, 42.0 ppm. MS ESI (m/z): $[M – H]^–$ calcd. for $C_{15}H_5N_4$: 241.05197, found 241.05191. $C_{15}H_6N_4$ (242.24): calcd. C 74.37, H 2.50, N 23.13; found C 74.26, H 2.40, N 23.23.

2,2′-[2-(Naphthalen-2-ylmethylene)-1*H*-indene-1,3(2*H*)-diylidene]dimalononitrile (5): 2-Naphthaldehyde (155 mg, 1.0 mmol) and **9** (266 mg, 1.1 mmol) were placed in a Schlenk tube with acetic anhydride (8 mL, 8 mL mmol^{-1}). The mixture was stirred under N_2 for 4 h. at reflux temperature. After cooling to room temp., a red-brown precipitate was collected by filtration and washed with cold acetic anhydride (4 mL). Yield 39 mg (10 %). ^{1}H NMR (500 MHz, [D$_6$]DMSO): δ_H = 8.54 (m, 1 H), 8.40 (m, 1 H), 8.39 (s, 1 H), 8.23 (dd, J = 9.0, 2.0 Hz, 1 H), 8.01 (m, 5 H), 7.76 (d, J = 2.5 Hz, 2 H), 7.62 (m, 2 H) ppm.

Methods

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

Electrochemical Characterisation: All cyclic voltammetry measurements were carried out in freshly distilled CH_2Cl_2 by using [TBA][PF$_6$] electrolyte (0.1 M) in a three-electrode system, each solution being purged with N_2 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 room temp. with an μAUTOLAB Type III potentiostat, driven by the electrochemical software GPES. Cyclic voltammetry (CV) measurements used scan rates of 0.1 V s^{-1}, and DPV was carried out at a step potential of 0.01 V, a modulation amplitude of 0.1 V, a modulation time of 0.05 s and an interval time of 0.5 s. Ferrocene was used as internal standard in each measurement.

Optical Characterisation: Solution and solid-state UV/Vis absorption spectra were recorded with a Jasco V-670 UV/Vis/NIR spectrophotometer controlled with the SpectraManager software. Photoluminescence spectra were recorded with a Fluoromax-2 fluorimeter controlled by the ISAMain software. All samples were measured in a 1 cm cell at room temp. with dichloromethane as a solvent. Concentrations of 5×10^{-5} M and 5×10^{-6} M were used for UV/Vis and photoluminescence, respectively.

Computational Characterisation: The geometry of each system was calculated with CH_2Cl_2 included in the system by a polarisable continuum model.[31] All calculations were carried out with the Gaussian 03 program[32] with the Becke three-parameter hybrid exchange, at the 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 the Avogadro software package.

Supporting Information (see footnote on the first page of this article): UV/Vis spectra in 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. ^{1}H NMR, ^{19}F NMR and ^{13}C NMR spectra of all compounds.

Acknowledgments

We thank the Engineering and Physical Sciences Research Council (EPSRC) APEX project for financial support. We thank Dr. Gary Nichol (University of Edinburgh) for the crystal structure data collection, refinement and discussion. We thank Prof. James Durrant (Imperial College London) for providing us with P3HT and PCDTBT polymers.

---

[1] A. C. Mayer, S. R. Scully, B. E. Hardin, M. W. Rowell, M. D. McGehee, *Mater. Today* **2007**, *10*, 28–33.
[2] B. Kippelen, J.-L. Bredas, *Energy Environ. Sci.* **2009**, *2*, 251–261.
[3] H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu, G. Li, *Nature Photon.* **2009**, *3*, 649–653.
[4] M. D. McGehee, *Nature Photon.* **2009**, *3*, 250–252.
[5] S. H. Park, A. Roy, S. Beaupre, S. Cho, N. Coates, J. S. Moon, D. Moses, M. Leclerc, K. Lee, A. J. Heeger, *Nature Photon.* **2009**, *3*, 297–302.
[6] G. Dennler, M. C. Scharber, C. J. Brabec, *Adv. Mater.* **2009**, *21*, 1323–1338.
[7] P. Sonar, J. P. F. Lim, K. L. Chan, *Energy Environ. Sci.* **2011**, *4*, 1558–1574.
[8] D. Venkataraman, S. Yurt, B. H. Venkatraman, N. Gavvalapalli, *J. Phys. Chem. Lett.* **2010**, *1*, 947–958.
[9] S. van Bavel, S. Veenstra, J. Loos, *Macromol. Rapid Commun.* **2010**, *31*, 1835–1845.
[10] Y. Shu, Y.-F. Lim, Z. Li, B. Purushothaman, R. Hallani, J. E. Kim, S. R. Parkin, G. G. Malliaras, J. E. Anthony, *Chem. Sci.* **2011**, *2*, 363–368.
[11] Y.-F. Lim, Y. Shu, S. R. Parkin, J. E. Anthony, G. G. Malliaras, *J. Mater. Chem.* **2009**, *19*, 3049–3056.
[12] G. D. Sharma, P. Suresh, J. A. Mikroyannidis, M. M. Stylianakis, *J. Mater. Chem.* **2010**, *20*, 561–567.
[13] J. T. Bloking, X. Han, A. T. Higgs, J. P. Kastrop, L. Pandey, J. E. Norton, C. Risko, C. E. Chen, J.-L. Bredas, M. D. McGehee, A. Sellinger, *Chem. Mater.* **2011**, *23*, 5484–5490.
[14] C. H. Woo, T. W. Holcombe, D. A. Unruh, A. Sellinger, J. M. J. Frechet, *Chem. Mater.* **2010**, *22*, 1673–1679.
[15] H. Gommans, T. Aernouts, B. Verreet, P. Heremans, A. Medina, C. G. Claessens, T. Torres, *Adv. Funct. Mater.* **2009**, *19*, 3435–3439.
[16] N. Camaioni, G. Ridolfi, V. Fattori, L. Favaretto, G. Barbarella, *J. Mater. Chem.* **2005**, *15*, 2220–2225.
[17] F. G. Brunetti, X. Gong, M. Tong, A. J. Heeger, F. Wudl, *Angew. Chem.* **2010**, *122*, 542; *Angew. Chem. Int. Ed.* **2010**, *49*, 532–536.
[18] R. Andreu, J. Aramburo, M. A. Cerdan, J. Garin, J. Orduna, B. Villacampa, *Tetrahedron Lett.* **2006**, *47*, 661–664.
[19] P. Leriche, P. Frere, A. Cravino, O. Aleveque, J. Roncali, *J. Org. Chem.* **2007**, *72*, 8332–8336.
[20] D. R. Buckle, N. J. Morgan, J. W. Ross, H. Smith, B. A. Spicer, *J. Med. Chem.* **1973**, *16*, 1334–1339.
[21] S. Zheng, A. Leclercq, J. Fu, L. Beverina, L. A. Padilha, E. Zojer, K. Schmidt, S. Barlow, J. Luo, S.-H. Jiang, A. K. Y. Jen, Y. Yi, Z. Shuai, E. W. Van Stryland, D. J. Hagan, J.-L. Bredas, S. R. Marder, *Chem. Mater.* **2007**, *19*, 432–442.
[22] Z. Lu, N. Liu, S. J. Lord, S. D. Bunge, W. E. Moerner, R. J. Twieg, *Chem. Mater.* **2009**, *21*, 797–810.
[23] A. Capobianco, A. Esposito, T. Caruso, F. Borbone, A. Carella, R. Centore, A. Peluso, *Eur. J. Org. Chem.* **2012**, 2980–2989.
[24] S.-H. Kim, S.-Y. Lee, S.-Y. Gwon, Y.-A. Son, J.-S. Bae, *Dyes Pigm.* **2010**, *84*, 169–175.
[25] F. Würthner, S. Yao, T. Debaerdemaeker, R. Wortmann, *J. Am. Chem. Soc.* **2002**, *124*, 9431–9447.
[26] F. Würthner, K. Meerholz, *Chem. Eur. J.* **2010**, *16*, 9366–9373.
[27] Values in brackets correspond to the other asymmetric unit (if any).
[28] N. C. Cates, R. Gysel, J. E. P. Dahl, A. Sellinger, M. D. McGehee, *Chem. Mater.* **2010**, *22*, 3543–3548.
[29] N. C. Cates, R. Gysel, Z. Beiley, C. E. Miller, M. F. Toney, M. Heeney, I. McCulloch, M. D. McGehee, *Nano Lett.* **2009**, *9*, 4153–4157.

[30] P. Gopalan, H. E. Katz, D. J. McGee, C. Erben, T. Zielinski, D. Bousquet, D. Muller, J. Grazul, Y. Olsson, *J. Am. Chem. Soc.* **2004**, *126*, 1741–1747.

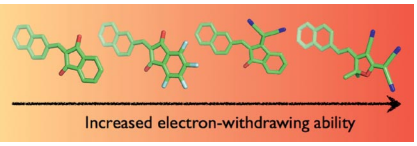
[31] B. Mennucci, J. Tomasi, R. Cammi, J. R. Cheeseman, M. J. Frisch, F. J. Devlin, S. Gabriel, P. J. Stephens, *J. Phys. Chem. A* **2002**, *106*, 6102–6113.

[32] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, A. Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, *Gaussian 03, Revision C.02*, Gaussian, Inc., Wallingford CT, **2004**.

Received: May 29, 2012

Organic Photovoltaics

A series of unsymmetrical dyes was synthesised and characterised. Their optical and electrochemical properties were tuned by modifying the electron acceptor unit.



M. Planells, N. Robertson* **1–8**

Naphthyl Derivatives Functionalised with Electron Acceptor Units – Synthesis, Electronic Characterisation and DFT Calculations

Keywords: Donor–acceptor systems / Organic photovoltaics / Density functional calculations / Electrochemistry / Luminescence