Electronic Supplementary Material (ESI) for RSC Advances.

Electronic Supplementary Information

Synthesis and properties of pteridine-2,4-dione-functionalised oligothiophenes

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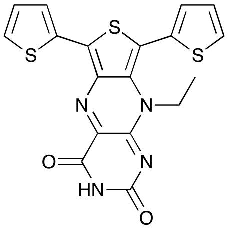
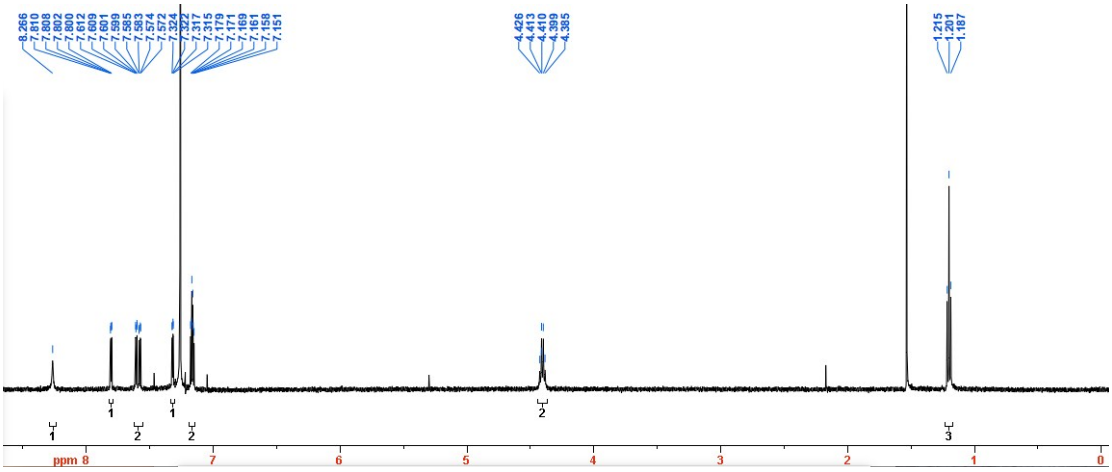
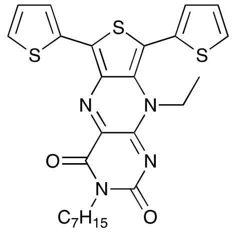
(1) NMR spectra ($CDCl_3$)

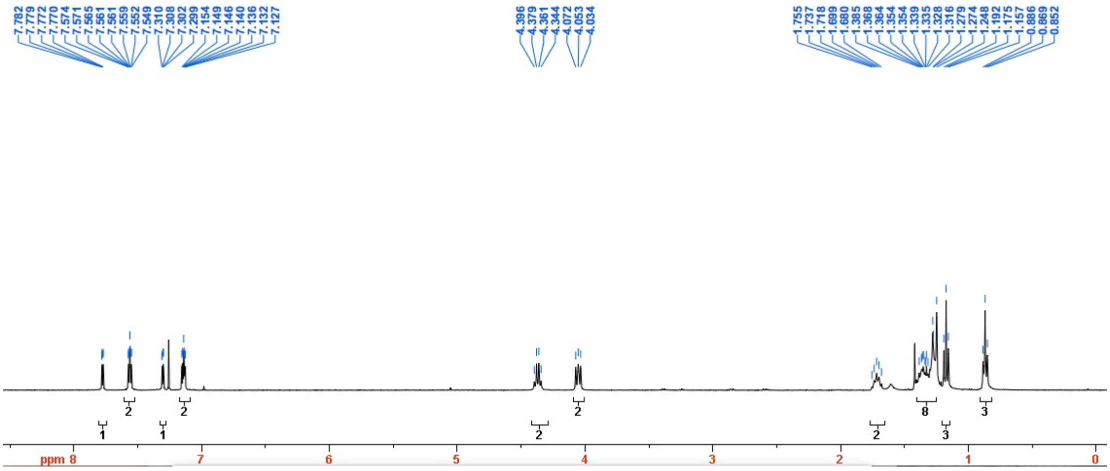
Compound 3:





Compound t3:





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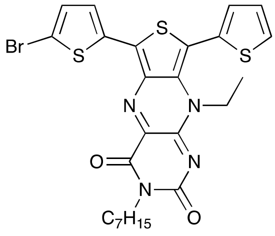
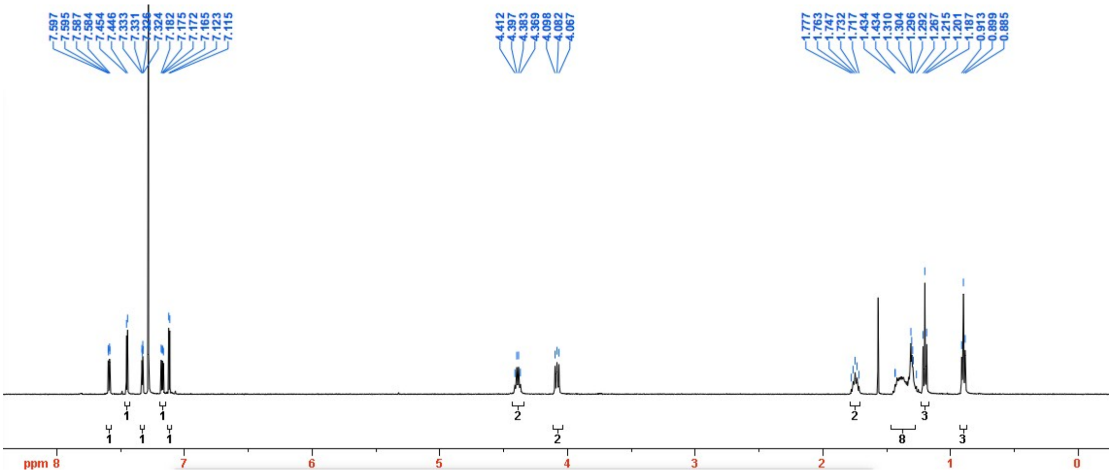
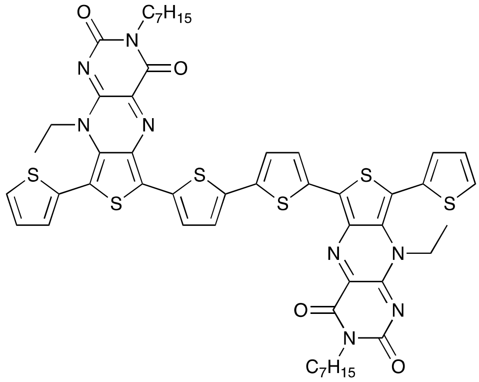
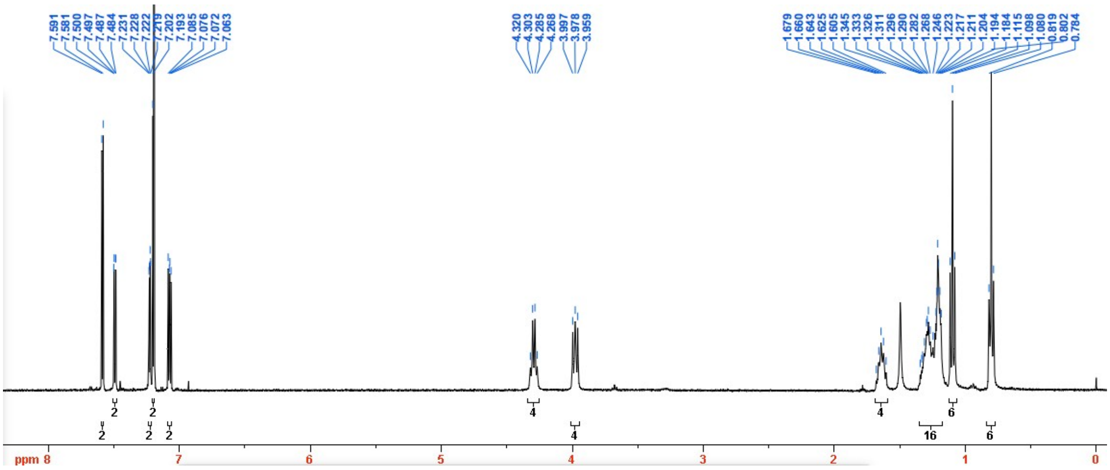


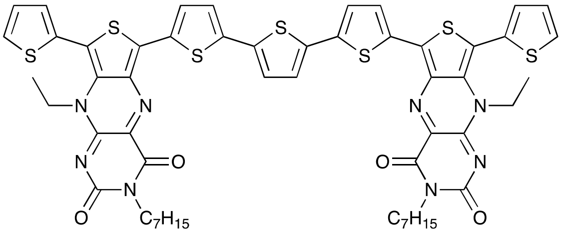


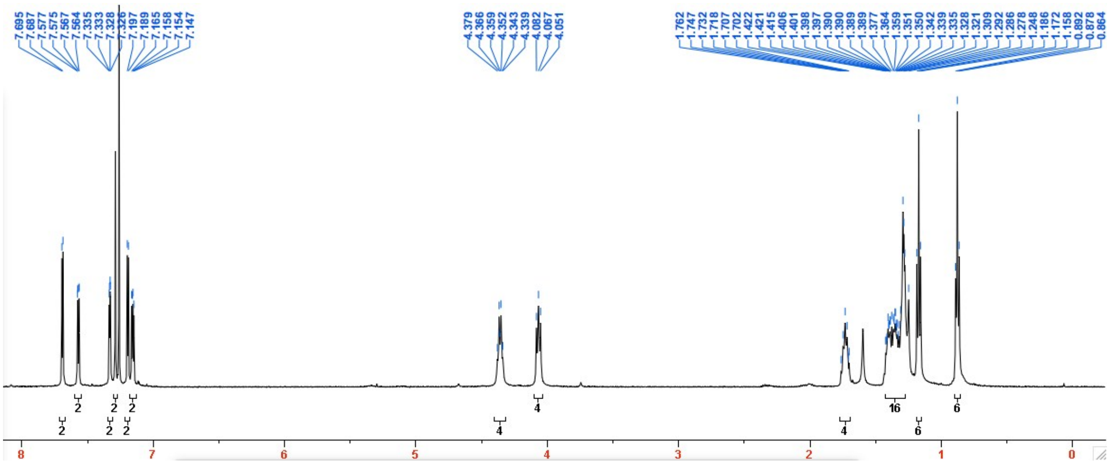
Compound t6:



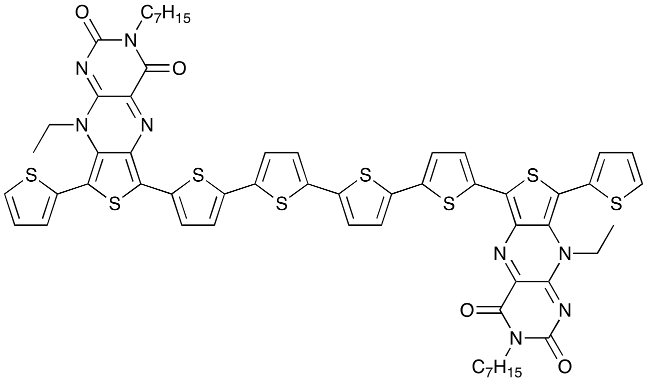


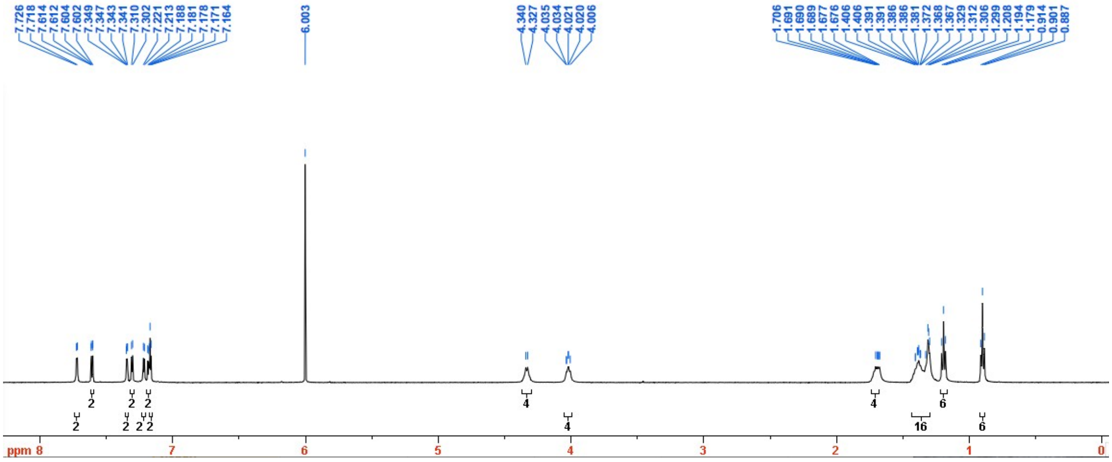
Compound t7:





Compound t8:





(2) NMR spectra of t3 and 4

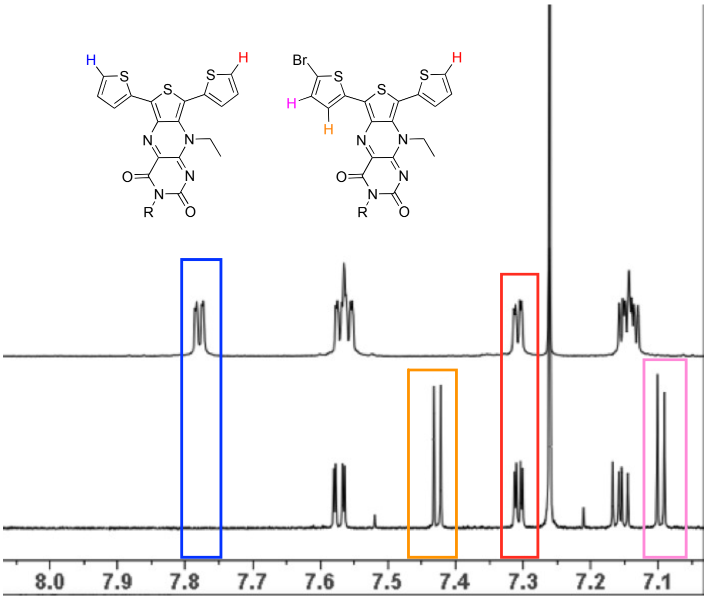


Figure S1. Partial ^{1}H NMR of compounds **t3** and **4**.

(3) Cyclic voltammetry

Voltammetry was recorded on a CH Instrument Electrochemical Workstation (CHI 440A), Austin, TX, USA. Samples were recorded as solutions in dry acetonitrile containing electrochemical grade tetrabutylammonium hexafluorophosphate (0.1M) as the supporting electrolyte. All measurements were undertaken under an oxygen-free nitrogen atmosphere. A platinum disc working electrode, a platinum wire counter electrode and a silver wire pseudo-reference electrode were used for all measurements. Ferrocene was used as an internal reference (Fc/Fc+ redox wave adjusted to 0.0 V).[2]

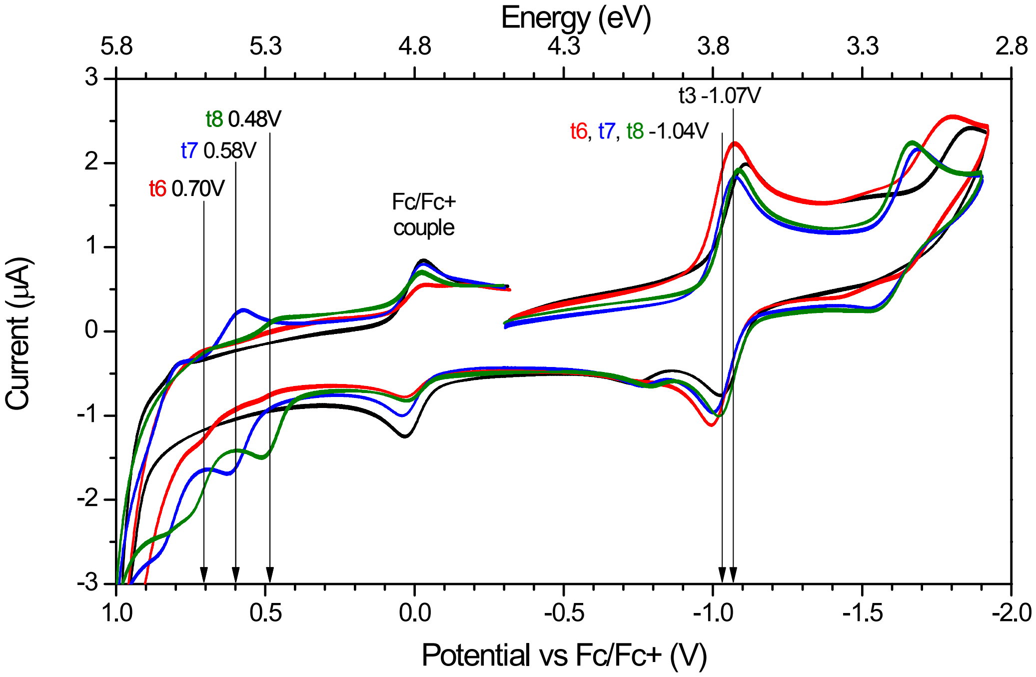


Figure S2. Cyclic voltammogram traces for compounds **t3**, **t6**, **t7** and **t8**.

(4) UV-vis spectroscopy

The optical gaps (E_{opt}) were obtained from the longest wavelength absorption edge (λ_{onset}) using the equation E_{opt} (eV) = $hc/\lambda_{onset} = 1240/\lambda_{onset}$. *h* = Planck's constant and *c* is the speed of light.

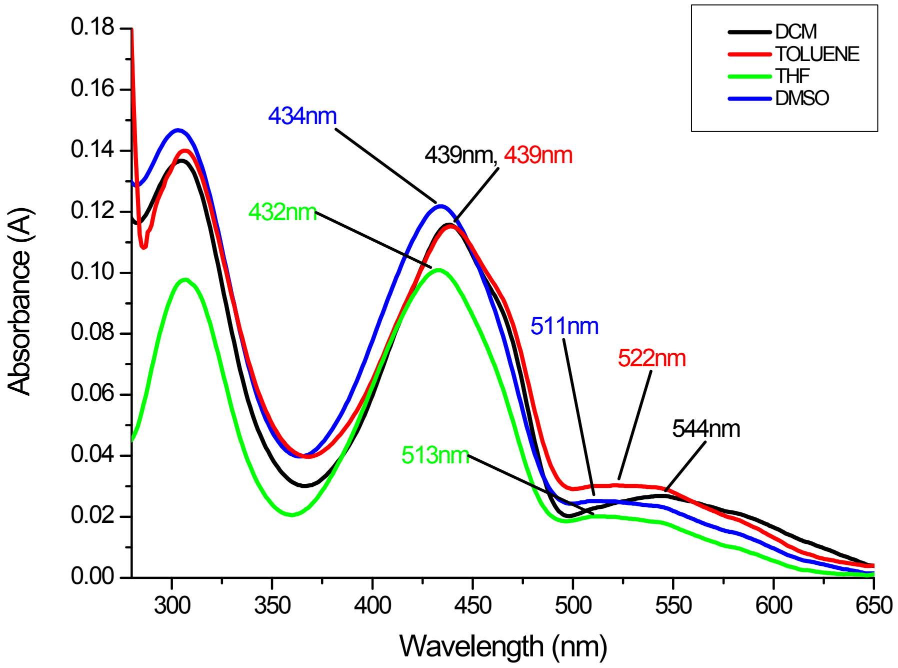
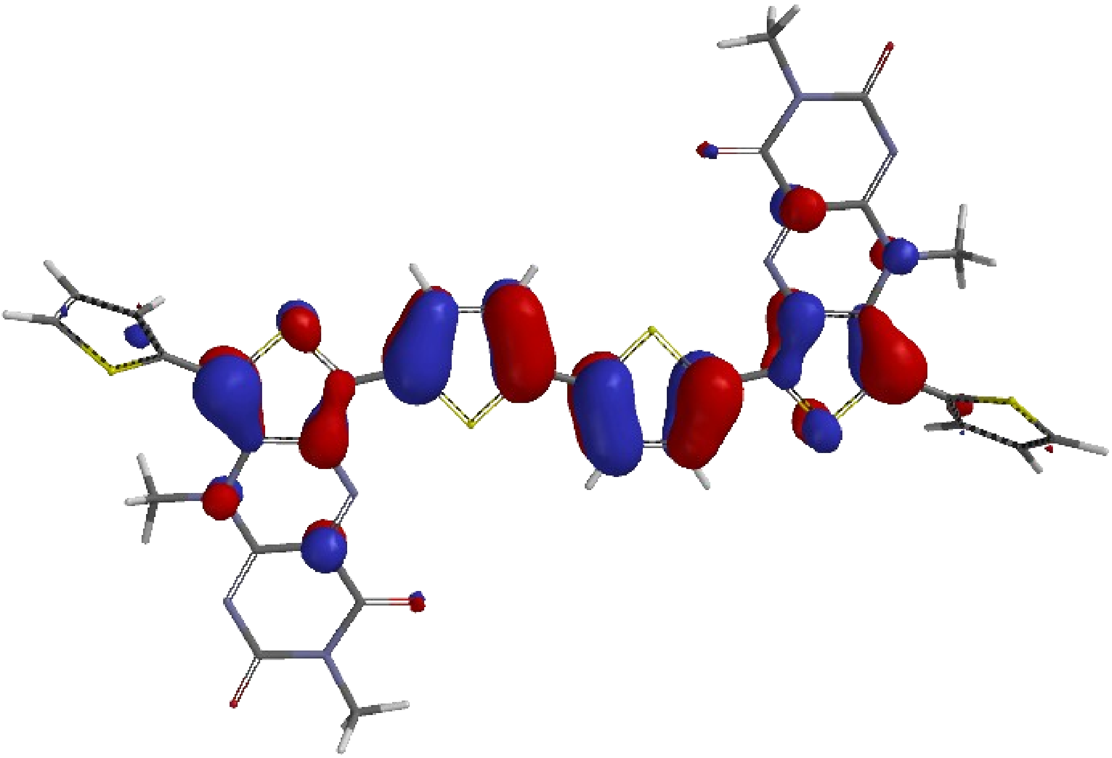


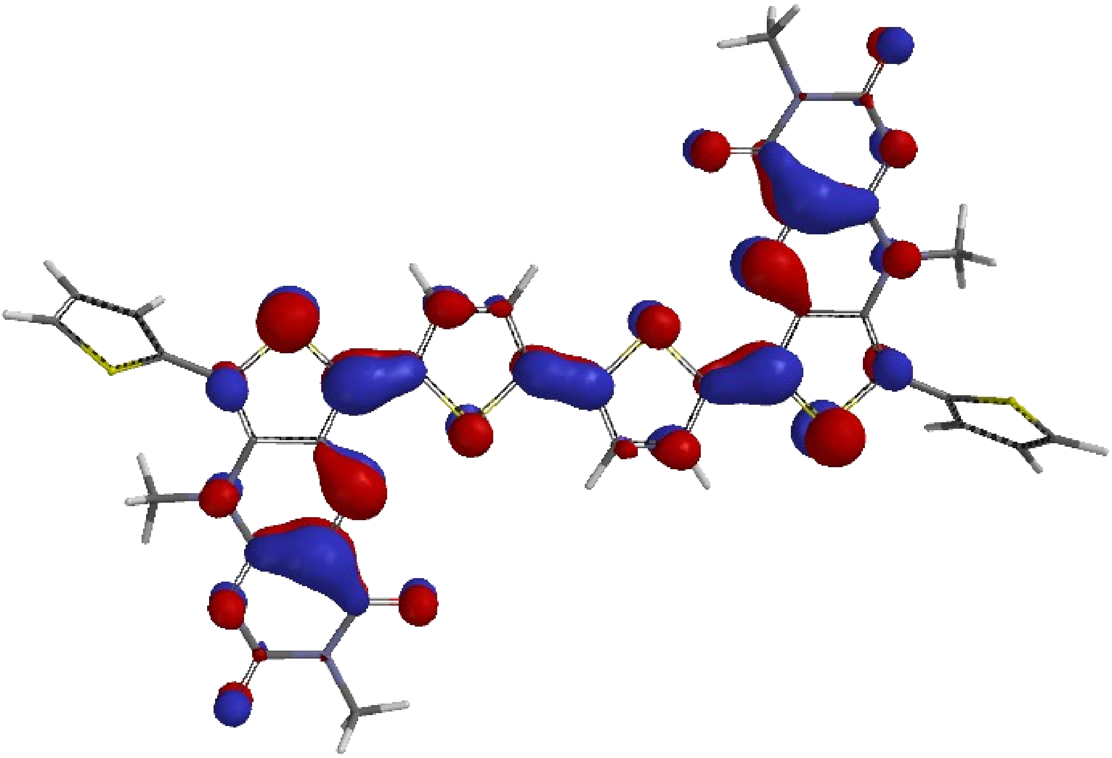
Figure S3. UV-vis spectra of **t3** recorded in toluene, DCM, THF and DMSO.

(5) DFT calculations t6 and t7 analogues

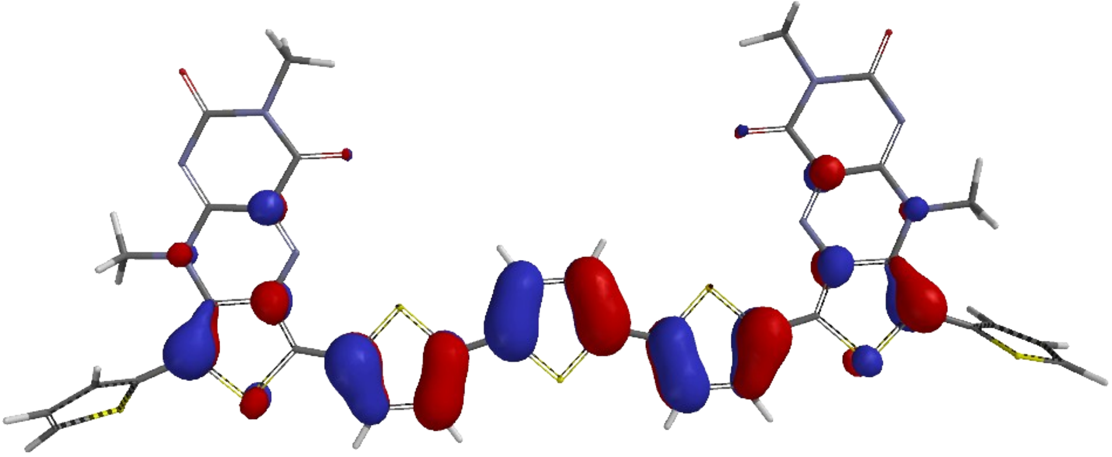
t6 HOMO (-5.4 eV)



t6 LUMO (-3.3 eV)



t7 HOMO (-5.2 eV)



t7 LUMO (-3.3 eV)

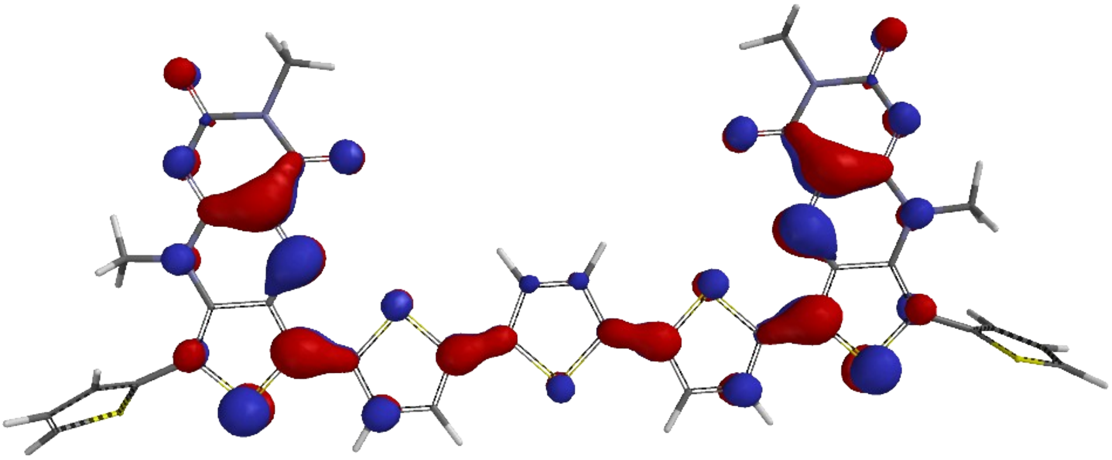


Figure S3. HOMO/ LUMO maps of short chain analogues of **t6** and **t7**.

(6) Fluorescence quenching

For quenching studies, a solution of P3HT (from Rieke metals) was prepared by dissolving 20 mg/ml in chlorobenzene. Solutions of **t3** and **t8** were prepared by dissolving 1 mg/ml in chlorobenzene. Both solutions were mixed by appropriate volumes to yield the desired ratio of P3HT and acceptors with the concentration given as the fraction of total mass. The solutions were then spin coated in a nitrogen filled glovebox at 1000 rpm. Quenching studies were performed by measuring the photoluminescence quantum yield with a Hamamatsu U6039-05 integrating sphere. At the excitation wavelength of 500 nm the total absorption was more than 60 % and the emission was collected in a range from 650 to 900 nm. PLQY was determined by the instrument and is given by the number of photons emitted divided by the number of photons absorbed.

(7) Single crystal X-ray data

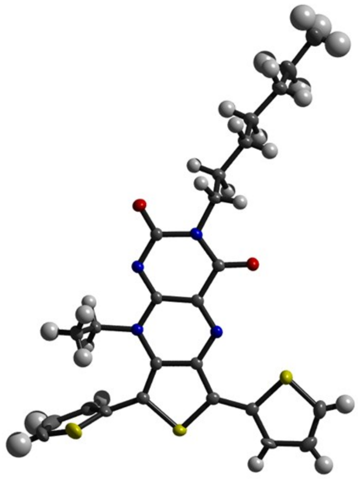


Figure S4: CPK representation of **t3**.

Compound t3: Crystal with size 0.39 x 0.37 x 0.34 was scanned on an Oxford Gemini Ultra A CCD diffractometer [(λ ($Mo_{K\alpha}$) = 0.71073 Å] at 150(2) K. The diffraction data were collected and processed using the CrysAlisPro software package. Corrections for incident and diffracted beam absorption effects were applied utilising analytical absorption correction.[3a] Structure solution and refinement were carried out with SHELXS-97[4] and SHELXL-97[4] using WinGX[5] *via* a full matrix least-squares on F^2 method. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were added and refined using riding models. Crystal data for **t3**: $C_{26}H_{28}Cl_2N_4O_2S_3$, M_r = 595.60, monoclinic system, space group $P2_1/c$, a = 14.3594(3), b = 22.1059(5), c = 8.8264(2) Å, β = 104.710(2), V = 2709.91(10) Å^3. Z = 4, ρ_{calcd} = 1.460 g cm^{-3}; $Mo_{K\alpha}$ radiation, λ = 0.71073 Å, μ = 0.504 mm^{-1}, T = 150 K. 21011 data collected, 5140 unique, R_{int} = 0.0421, θ < 25.7°; w$R2$ = 0.1775, $R1$ = 0.0576, S = 1.038 for 362 parameters; Residual electron density extrema were 0.72 and -0.86 e Å^{-3}.

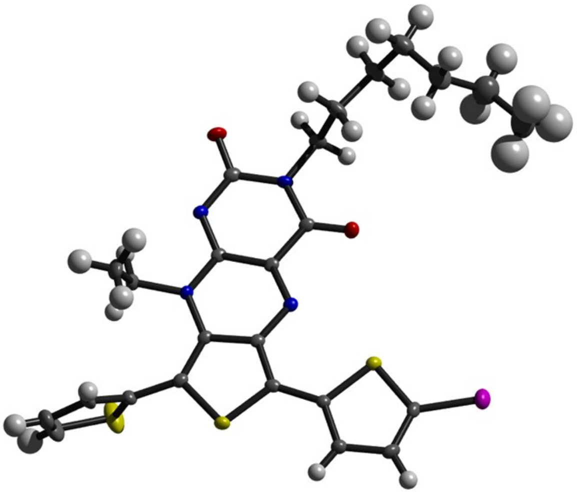


Figure S5: CPK representation of **4**.

Compound 4: Crystal with size 0.09 x 0.08 x 0.03 was scanned on a Bruker Apex II Quasar CCD diffractometer [(λ (Mo$_{K\alpha}$) = 0.71073 Å] at 150(2) K. The diffraction data were collected and processed using the Apex2 software package. Corrections for incident and diffracted beam absorption effects were applied utilising empirical absorption correction.[3b] Structure solution and refinement were carried out with SHELXS-97[4] and SHELXL-97[4] using WinGX[5] *via* a full matrix least-squares on F^2 method. All non-hydrogen atoms were refined anisotropically and hydrogen atoms were added and refined using riding models. Crystal data for **4**: $C_{25}H_{25}BrN_4O_2S_3$, M_r = 589.58, monoclinic system, space group $P2_1/c$, a = 14.7336(8), b = 18.2084(11), c = 9.4057(6) Å, β = 94.715(3), V = 2514.8(3) Å^3. Z = 4, ρ_{calcd} = 1.557 g cm^{-3}; Mo$_{K\alpha}$ radiation, λ = 0.71073 Å, μ = 1.915 mm^{-1}, T = 150 K. 19655 data collected, 4922 unique, R_{int} = 0.0406, θ < 26°; w$R2$ = 0.1037, $R1$ = 0.0396, S = 1.051 for 318 parameters; Residual electron density extrema were 0.96 and -0.56 e Å^{-3}.

The crystallographic data for compound t3 and 4 have been deposited with the Cambridge Crystallographic Data Centre with deposition number CCDC1053866-1053867. Copies of the data can be obtained, free of charge, via the internet (http://www.ccdc.cam.ac.uk/data_request/cif).
Email: data_request@ccdc.cam.ac.uk, or fax: +44 1223336033.

References.

1. Y. Xia *et al*, *Macromol. Chem. Phys.* **2006**, *207*, 511.
2. Pommerehne, *et al. Adv. Mater.* **1995**, *7*, 551.
3. (a) R. C. Clark, J. S. Reid, *Acta Cryst. A* **1995**, *51*, 887; (b) R. H. Blessing, *Acta Cryst. A* **1995**, *51*, 33.
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