

Electronic Supporting Information

α,β -Unsubstituted *meso*-Positioning Thienyl BODIPY: A Promising Electron Deficient Building Block for the Development of Near Infrared (NIR) *p*-type Donor-Acceptor (D-A) Conjugated Polymers

Benedetta M. Squeo,^[a] Vasilis G. Gregoriou,^[a,b] Yang Han^[c] Alex Palma-Cando,^[d] Sybille Allard,^[d] Efthymis Serpetzoglou,^[e] Ioannis Konidakis,^[e] Emmanuel Stratakis,^[e] Apostolos Avgeropoulos,^[f] Thomas D. Anthopoulos,^[g,h] Martin Heeney,^[c] Ullrich Scherf,^[d] Christos L. Chochos^{[a,f]*}

^[a] Advent Technologies SA, Patras Science Park, Stadiou Street, Platani-Rio, 26504, Patra, Greece.

^[b] National Hellenic Research Foundation (NHRF), 48 Vassileos Constantinou Avenue, Athens 11635, Greece.

^[c] Department of Chemistry and Centre for Plastic Electronics, Imperial College London, Exhibition Road, South Kensington, London, SW7 2AY, UK.

^[d] Macromolecular Chemistry Group (buwmakro) and Institute for Polymer Technology, Bergische Universität Wuppertal, Gaußstraße 20, D-42119 Wuppertal, Germany.

^[e] Institute of Electronic Structure and Laser, Foundation for Research and Technology – Hellas, P. O. Box 1527, Heraklion, Crete, Greece

^[f] Department of Materials Science Engineering, University of Ioannina, Ioannina 45110, Greece.

^[g] Department of Physics and Centre for Plastic Electronics, Imperial College London, Exhibition Road, South Kensington, London, SW7 2AY, UK.

^[h] Division of Physical Sciences and Engineering, King Abdullah University of Science and Technology, Thuwal 23955-6900, Saudi Arabia.

E-mail address: cchochos@advent-energy.com

Contents	Page
S1. Experimental Section	S3
S1.1. General Experimental Procedures	S3
S1.2. Synthesis of BODIPY starting precursors	S3
S1.3. Stille Couplings Polymerisations	S5
S1.4. Instrumentation	S6
S2. Computational data	S10
S3. NMR spectra of all new compounds	S33
S4. Mass spectrum of the final compound	S38
S5. Absorption spectra of the monomers	S39
S6. Gel permeation chromatography (GPC) graphs of the polymers	S40
S7. Hole mobility measurements	S42
S8. Electron mobility measurements	S43
S9. References	S44

S1. Experimental Section

S1.1. General Experimental Procedures

All glassware was washed using detergent (Teepol), rinsed with excess water, acetone and methylene dichloride and dried in an oven at *ca.* 120 °C. *N*-Bromosuccinimide (NBS) was recrystallized from water. Acetonitrile and toluene were distilled over CaH₂ before use. Reactions were protected from moisture with CaCl₂ drying tubes or carried out under an Ar atmosphere. Anhydrous Na₂SO₄ was used for drying organic extracts and all volatiles were removed under reduced pressure. All reaction mixtures and column eluents were monitored by thin layer chromatography (TLC) using commercial glass backed TLC plates (Merck Kieselgel 60 F₂₅₄). The plates were observed under UV light at 254 and 365 nm. The technique of dry flash chromatography was used throughout for all non-TLC scale chromatographic separations using Merck Silica Gel 60 (less than 0.063 mm).^{S1} (4,4'-didodecyl-2,2'-bithiophene-5,5'-diyl)bis(trimethylstannane) (**16**) and (3,3'-didodecyl-2,2'-bithiophene-5,5'-diyl)bis(trimethylstannane) (**17**) (Scheme 1) were purchased from Solarmer Materials Inc. and used as received. The 2,8-dibromo-5,5-difluoro-10-(5-octylthiophen-2-yl)-5*H*-4λ⁴,5λ⁴-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (**13**) in Scheme 1 was prepared according to literature procedure.^{S2}

S1.2. Synthesis of BODIPY starting precursors

1.2.1 5,5-difluoro-10-(5-octylthiophen-2-yl)-2,8-di(thiophen-2-yl)-5*H*-4λ⁴,5λ⁴-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (**14**).

A solution of the commercially available 2-tributylstannylthiophene (2.3 mol) and the 2,8-dibromo-5,5-difluoro-10-(5-octylthiophen-2-yl)-5*H*-4λ⁴,5λ⁴-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (**13**) (0.92 mol) were combined in dry deoxygenated toluene in the presence

of tris(dibenzylideneacetone)dipalladium(0) [Pd₂(dba)₃] (2 mol%) and tri-*o*-tolylphosphine [P(*o*-Tol)₃] (4 mol%) and the mixture was heated to ca. 120 °C for 4 hours. Then, the reaction mixture was filtered through a pad of celite and the toluene solution was evaporated and dried under high vacuum. Purification was achieved by silica gel chromatography using as eluent a hexane/chloroform mixture (1:1). The resulting pure compound is an orange solid with yield 79% (0.40 g).

¹H NMR (CDCl₃, 300 MHz): δ 8.14 (s, 2H), 7.53 (d, 1H), 7.33 (s, 2H), 7.24 (dd, ³J = 7.24, 2H), 7.21 (dd, ³J = 7.21, 2H), 7.05 (dd, ³J = 7.05, 2H), 7.04 (d, 1H), 2.97 (t, 2H), 1.80 (quintuplet, 2H), 1.46 (m, 12H), 0.90 (t, 3H).

¹³C NMR (CDCl₃, 100 MHz): δ 154.72 (s), 140.74 (s), 139.03 (s), 135.90 (s), 134.57 (s), 134.08 (s), 131.98 (s), 128.02 (m), 127.90 (s), 126.14 (s), 124.69 (s), 124.28 (s), 123.35 (s), 99.51 (s), 31.82 (s), 31.44 (s), 30.48 (s), 29.69 (m), 29.26-29.18 (t), 22.63 (s), 14.08 (s)

1.2.2 2,8-bis(5-bromothiophen-2-yl)-5,5-difluoro-10-(5-octylthiophen-2-yl)-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (15).

In a predegassed flask, **14** (0.72 mol) was dissolved in fresh dried DMF, then recrystallized NBS (1.44 mol) was added portion wise (three times) in a period of 30 minutes. The mixture was stirred at room temperature for 3 hours. The mixture was diluted in chloroform and washed with water three times. The solvent were removed under reduced pressure and the crude compound was purified through silica gel chromatography using as eluent a hexane/chloroform mixture (7:3). The resulting pure compound is a red-orange solid with yield 68%.

¹H NMR (CDCl₃, 300 MHz): δ 8.07 (s, 2H), 7.51 (d, 1H), 7.04 (d, 2H), 7.0 (d, 1H), 6.95 (d, 2H), 2.97 (t, 2H), 1.80 (quintuplet, 2H), 1.31 (m, 12H), 0.90 (t, 3H).

^{13}C NMR (CDCl_3 , 100 MHz): δ 155.28 (s), 140.37 (s), 139.36 (s), 137.47 (s), 134.53-134.36 (d), 131.83 (s), 130.73 (s), 127.21 (s), 126.30 (s), 124.60 (s), 123.53 (s), 110.95 (s), 31.81 (s), 31.42 (s), 30.50 (s), 29.67 (s), 29.25-29.17 (t), 22.63 (s), 14.07 (s)

m/z [FD+(eiFI)]: 704.98 (M^+-1 , 12%), 705.97 (M^+ , 50%), 706.97 (MH^+ , 40%), 707.97 (MH^++1 , 100%), 708.97 (MH^++2 , 49%), 709.97 (MH^++3 , 77%), 710.97 (MH^++4 , 22%), 711.97 (MH^++5 , 11%)

S1.3. Stille Couplings Polymerizations

1.3.1. Polymer of BODIPY-*q*Ti (Typical procedure).

A solution of monomer **15** (1 eq) and 4,4'-didodecyl-2,2'-bithiophene-5,5'-diyl)bis(trimethylstannane) **16** (1 eq), were combined in dry deoxygenated toluene in the presence of tris(dibenzylideneacetone)dipalladium(0) [$\text{Pd}_2(\text{dba})_3$] (2 mol%) and tri-*o*-tolylphosphine [$\text{P}(\text{o-Tol})_3$] (4 mol%) and the mixture was heated to ca. 120°C for 48 h to provide the desired crude polymer. The polymer was purified by precipitation in methanol, filtered and washed on Soxhlet extraction with ethylacetate (200 mL, 1 d), dichloromethane (200 mL, 1 d), chloroform (200 mL, 1 d) and chlorobenzene (150 mL, 1d). The chlorofobenzene fraction was then concentrated under reduced pressure, precipitated in methanol, filtered and dried in vacuum. The resulting greenish polymer solid (74 mg, 33%) is readily soluble in hot chlorobenzene and *o*-dichlorobenzene (*o*-DCB).

1.3.2. Polymer of bis(trimethylstannyl)tetra(5-*n*-hexyl)thien-2-yl-IDT and 3,5-dichloro-4H-1,2,6-thiadiazin-4-one (**6**).

A solution of monomer **15** (1 eq) and readily available 3,3'-didodecyl-2,2'-bithiophene-5,5'-diyl)bis(trimethylstannane) **17** (1 eq), were combined in dry deoxygenated toluene in the presence

of tris(dibenzylideneacetone)dipalladium(0) [Pd₂(dba)₃] (2 mol%) and tri-*o*-tolylphosphine [P(*o*-Tol)₃] (4 mol%) and the mixture was heated to ca. 120°C for 48 h to provide the desired crude polymer. The polymer was purified by precipitation in methanol, filtered and washed on Soxhlet extraction with ethylacetate (200 mL, 1 d), dichloromethane (200 mL, 1 d) and chloroform (200 mL, 1 d). The chloroform fraction was then concentrated under reduced pressure, precipitated in methanol, filtered and dried in vacuum. The resulting greenish polymer solid (152 mg, 67%) is readily soluble in chloroform, chlorobenzene and *o*-dichlorobenzene (*o*-DCB).

S1.4. Instrumentation

¹H-, and ¹³C- NMR spectra were recorded on a Varian V300 MHz. Deuterated solvent (chloroform) was used for homonuclear lock and the signals are referenced to the deuterated solvent peaks. Field desorption (FD) and field ionization (FI) mass spectra were recorded on a JEOL Ltd. JMS-T200GC AccuTOF GCx High Performance Gas Chromatograph – Time-of-Flight Mass Spectrometer with sample inlet FI/FD.

Gel Permeation Chromatography (GPC): Average molecular weights per number (\overline{M}_n) and dispersity (\mathcal{D}) were determined with Gel Permeation Chromatography (GPC) at 150 °C on a high temperature PL-GPC 220 system using a PL-GEL 10 μm guard column, two PL-GEL 10 μm Mixed-B columns and *ortho*-dichlorobenzene (*o*-DCB) as the eluent. The instrument was calibrated with narrow polystyrene standards with M_p ranging from 4830 g/mol to 3242000 g/mol.

The UV-Vis absorption spectra of the examined polymer solutions and pristine films were measured using a LAMBDA 950 UV/VIS/NIR (Perkin Elmer) spectrophotometer from 300 nm to 2000 nm with 1 nm resolution. All measurements were performed at room temperature.

Micro-photoluminescence (μ PL) studies were performed at 295 K, using a setup in backscattering geometry with a He–Ne 543 nm continuous wave laser as the excitation source. The laser beam was focused down to 1 μ m on the sample through an objective lens (Mitutoyo 50 \times), placed on an XYZ translation stage, at normal incidence and the power was 760 μ W.

Transient absorption spectroscopy (TAS) measurements were performed on a Newport (TAS-1) transient absorption spectrometer, equipped with a source pulsed laser beam generated from an Yb:KGW-based laser system (PHAROS, Light Conversion), emitting at 1026 nm, with a pulse duration of 170 fs and 1 KHz repetition rate. The fundamental beam is split, so that the probe beam component (10% of the source) passes through a delay line and routed on a YAG crystal, which generates a super continuum white light of 500-1000 nm. The other part of the incident beam (90% of the source), is used as the pump beam for sample excitation. The energy of the pump beam can be controlled by a variable reflective neutral density filter inside the TAS instrument, or by altering the power of the employed 1026 nm fundamental laser beam. For all measurements, the probe light is coupled through an optical fiber to a multichannel detector and monitored as a function of wavelength. In a typical TAS pump-probe experiment, the sample is excited by the pump beam, and the corresponding decay dynamics of the sample's relative optical density are recorded as a function of wavelength at various time delays after photo-excitation.

Electrochemical measurements: Cyclic Voltammetry was employed to determine the E_{HOMO} and E_{LUMO} levels of **BODIPY-qTi** and **BODIPY-qTo** by their corresponding oxidation (E^{ox}) and reduction (E^{red}) potentials. A three electrode electrochemical cell was used with a modified glassy carbon disk as working electrode, Pt wire as counter electron and Ag/AgCl (1 M KCl) as reference electrode in pre-dried and deaerated acetonitrile solution containing *n*-Bu₄NPF₆ (0.1 M) as an electrolyte. Polished Pt disk electrodes were coated with **BODIPY-qTi** and **BODIPY-qTo** via a

drop casting method. Concentrated solutions of **BODIPY-qTi** and **BODIPY-qTo** (0.5 mg) in *o*-DCB (0.2 ml) were prepared and were drop casted ($3 \times 1 \mu\text{l}$ aliquots) onto the Pt disk electrodes. Thin films of **BODIPY-qTi** and **BODIPY-qTo** were formed onto the electrode's surface after evaporation of the *o*-DCB solutions under standard conditions (*i.e. ca.* 20 °C, 1 atm). All electrodes were washed with distilled acetonitrile prior to use. Scan rate 50 mV s⁻¹. Temperature = 20 °C. Fc/Fc⁺ was used as an internal reference. Both the oxidation (E^{ox}) and reduction (E^{red}) potentials are calculated from their corresponding onsets. The E_{HOMO} and E_{LUMO} levels were estimated by $E_{\text{LUMO/HOMO}} = -(4.7 + E_{\text{on}}^{\text{red/ox}}) \text{ eV}$.^{S3}

Theoretical Calculations: All calculations of the model compounds studied in this work have been performed using the Gaussian 03 software package.^{S4} The alkyl side chains substituents anchored onto the DPP and the peripheral thienyl rings have been replaced with methyl groups in the model compounds for our calculations. While the presence of these long alkyl chains enhances the solubility of these polymers and affects the charge carrier mobility and photovoltaic behavior of the polymer,^{S5-S7} from a computational point of view their replacement with shorter chains does not affect their optoelectronic properties (HOMO, LUMO and band gap) and thus the optimized structures of the molecules.^{S8,S9} The ground-state geometry of each model compound has been determined by a full geometry optimization of its structural parameters using the DFT calculations, upon energy minimization of all possible isomers. In this work, the DFT calculations were performed using the Becke's three-parameter hybrid functional, B3, with non-local correlation of Lee-Yang-Parr, LYP, abbreviated as B3LYP^{S10,S11} in conjunction with the 6-311G(d,p) split valence polarized basis set. All calculations were performed taking into account that the system is under vacuum conditions. No symmetry constraints were imposed during the optimization process. The geometry optimizations have been performed with a tight threshold that corresponds to root

mean square (rms) residual forces smaller than 10^{-5} au for the optimal geometry. The visualization of the molecular orbitals has been performed using GaussView 5.0.

OFET device fabrication procedures: Hole mobility measurements: Bottom contact/top gate (BC/TG) devices were fabricated on glass substrates using Au (40 nm) source-drain electrodes and CYTOP dielectric. Au electrodes were treated with pentafluorobenzene thiol (PFBT) SAM to increase the work function. Polymers were dissolved in chloroform at a concentration of 10 mg/mL, and spun cast at 2000 rpm onto the substrate for 60 s. The obtained polymer films were thermally annealed at 100 °C for 30 min, before spin coating of CYTOP dielectric (900 nm). The devices were completed by evaporation of Al (40 nm) gate through shadow masks. The channel width and length of the transistors are 1000 μm and 50 μm , respectively. A Keithley 4200 parameter analyzer was used to characterise the transistors under nitrogen. Linear mobility was calculated according

to the equation below: $\mu_{lin} = \frac{L}{WC_i V_D} \left(\frac{\partial I_{D lin}}{\partial V_G} \right)$

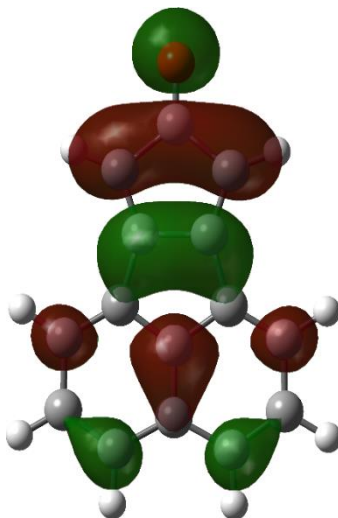
And saturation mobility was extracted from the slope of $I_D^{1/2}$ vs. V_G : $\mu_{sat} = \frac{2L}{WC_i} \left(\frac{\partial \sqrt{I_{D sat}}}{\partial V_G} \right)^2$

Performance parameters were averaged over ~6 devices.

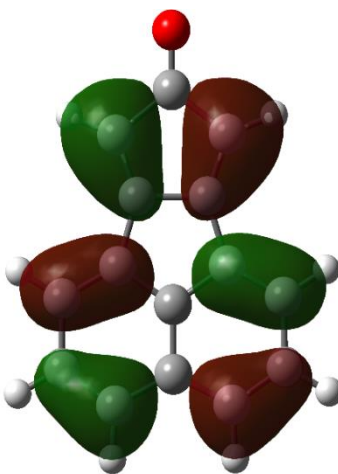
Electron mobility measurements: Bottom gate/top contact devices were fabricated on heavily doped n⁺-Si (100) wafers with 400 nm-thick thermally grown SiO₂. The Si/SiO₂ substrates were treated with BCB^{S12} to improve electron transport. Polymers were dissolved in chloroform at a concentration of 10 mg/mL, and spun cast at 2000 rpm onto the substrate for 60 s. The obtained polymer films were thermally annealed at 100 °C for 30 min. Al (40nm) source and drain electrodes were deposited onto the polymer film under vacuum through shadow masks. The channel width and length of the transistors are 1000 μm and 40 μm , respectively.

S2. Computational data

S2.1 Molecular Orbitals and Atomic coordinates of the geometry optimized structures



$$E_{\text{LUMO}} = -2.86 \text{ eV}$$



$$E_{\text{HOMO}} = -5.93 \text{ eV}$$

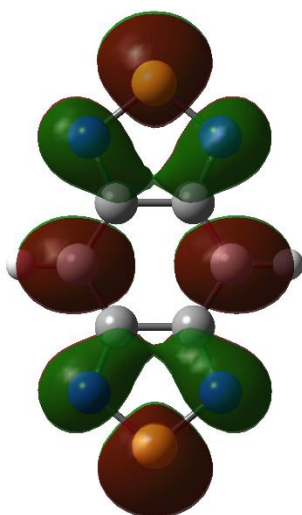
$$\text{Dipole moment } (\mu) = 4.6925 \text{ D}$$

Fig. S1 Molecular Orbitals for the Singlet Ground State of cyclopentadienone as calculated with DFT RB3LYP/6-311G(d,p). Hydrogens are omitted for clarity.

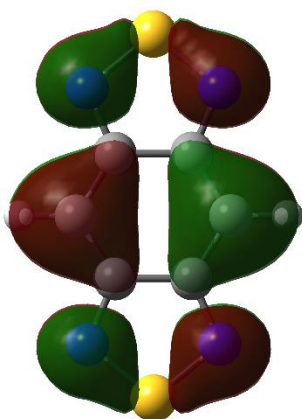
Atomic coordinates of the optimised geometry of cyclopentadienone using DFT/B3LYP/6-311G(d,p)

Center Number	Atomic Number	Forces (Hartrees/Bohr)			
		X	Y	Z	

1	6	0.000000000	0.000061453	0.000038464	
2	6	0.000000000	0.000083764	-0.000578930	
3	6	0.000000000	-0.000383620	0.000441602	
4	6	0.000000000	0.000069266	0.000021403	
5	6	0.000000000	0.000533949	0.000244539	
6	6	0.000000000	-0.000015758	0.000693141	
7	6	0.000000000	-0.000040030	-0.000018333	
8	6	0.000000000	0.000514520	-0.000464718	
9	6	0.000000000	0.000032741	-0.000030867	
10	6	0.000000000	0.000029692	-0.000309888	
11	6	0.000000000	0.000088973	0.000307508	
12	6	0.000000000	-0.000569788	-0.000260952	
13	6	0.000000000	0.000290951	-0.000133510	
14	6	0.000000000	-0.000215236	0.000224912	
15	6	0.000000000	-0.000001983	0.000044953	
16	8	0.000000000	-0.000302884	-0.000138715	
17	1	0.000000000	-0.000093724	0.000014026	
18	1	0.000000000	-0.000050604	-0.000080125	
19	1	0.000000000	0.000017985	-0.000021410	
20	1	0.000000000	-0.000017075	0.000026789	
21	1	0.000000000	-0.000019464	-0.000006706	
22	1	0.000000000	-0.000017792	-0.000010357	
23	1	0.000000000	0.000009129	-0.000030428	
24	1	0.000000000	-0.000004462	0.000027604	



$$E_{\text{LUMO}} = -3.74 \text{ eV}$$



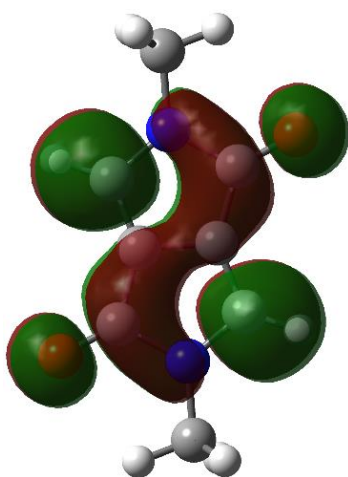
$$E_{\text{HOMO}} = -6.40 \text{ eV}$$

$$\text{Dipole moment } (\mu) = 0.0014 \text{ D}$$

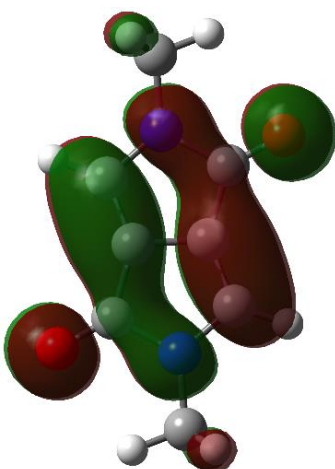
Fig. S2 Molecular Orbitals for the Singlet Ground State of benzobisthiadiazole as calculated with DFT RB3LYP/6-311G(d,p). Hydrogens are omitted for clarity.

Atomic coordinates of the optimised geometry of benzobisthiadiazole using DFT/B3LYP/6-311G(d,p)

Center Number	Atomic Number	Forces (Hartrees/Bohr)		
		X	Y	Z
1	6	0.000015130	-0.000107358	0.000117851
2	6	-0.000022152	-0.000105802	0.000471751
3	6	0.000070624	-0.000084203	-0.000471335
4	6	0.000038271	-0.000101970	-0.000117392
5	6	-0.000070162	0.000347402	-0.000177914
6	6	-0.000105018	0.000339287	0.000176408
7	7	0.000106952	-0.000268738	-0.000367808
8	16	0.000020512	-0.000080404	0.000000176
9	7	0.000034467	-0.000285614	0.000369023
10	7	-0.000054014	0.000246324	-0.000085214
11	16	0.000074979	-0.000293911	0.000000645
12	7	-0.000070674	0.000242445	0.000084142
13	1	-0.000019233	0.000076323	-0.000002446
14	1	-0.000019681	0.000076219	0.000002111



$$E_{\text{LUMO}} = -2.40 \text{ eV}$$



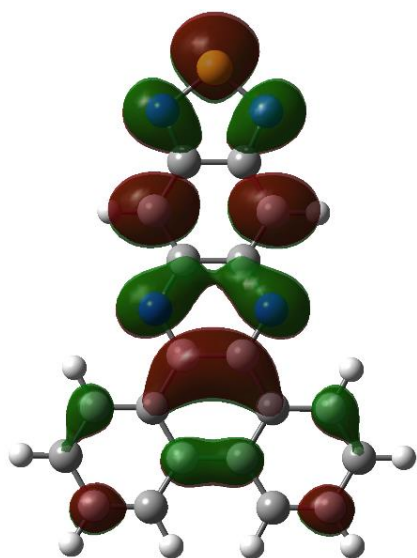
$$E_{\text{HOMO}} = -5.73 \text{ eV}$$

$$\text{Dipole moment } (\mu) = 0.0019 \text{ D}$$

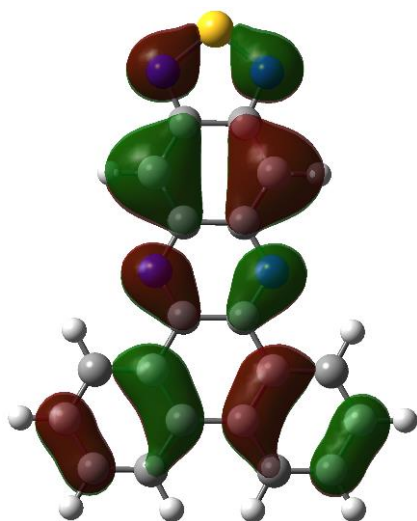
Fig. S3 Molecular Orbitals for the Singlet Ground State of diketopyrrolopyrrole as calculated with DFT RB3LYP/6-311G(d,p). Hydrogens are omitted for clarity.

Atomic coordinates of the optimised geometry of diketopyrrolopyrrole using DFT/B3LYP/6-311G(d,p)

Center Number	Atomic Number	Forces (Hartrees/Bohr)		
		X	Y	Z
1	6	0.000018634	-0.000062870	0.000007100
2	6	-0.000028516	-0.000030538	-0.000045760
3	6	-0.000028516	0.000030538	0.000045760
4	6	0.000016544	-0.000003954	-0.000023218
5	7	0.000001574	0.000059012	0.000017463
6	6	0.000016544	0.000003954	0.000023218
7	7	0.000001574	-0.000059012	-0.000017463
8	6	0.000018634	0.000062870	-0.000007100
9	8	-0.000003171	-0.000021014	-0.000006190
10	8	-0.000003171	0.000021014	0.000006190
11	6	-0.000001318	-0.000040963	-0.000011800
12	6	-0.000001318	0.000040963	0.000011800
13	1	-0.000003916	-0.000006984	-0.000001687
14	1	-0.000003916	0.000006984	0.000001687
15	1	0.000004453	0.000011656	0.000001557
16	1	-0.000004329	0.000010692	0.000001023
17	1	0.000000044	0.000015328	0.000004028
18	1	0.000004453	-0.000011656	-0.000001557
19	1	-0.000004329	-0.000010692	-0.000001023
20	1	0.000000044	-0.000015328	-0.000004028



$$E_{\text{LUMO}} = -3.41 \text{ eV}$$



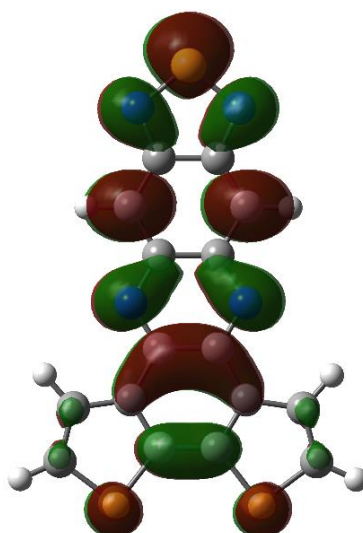
$$E_{\text{HOMO}} = -6.15 \text{ eV}$$

$$\text{Dipole moment } (\mu) = 3.2016 \text{ D}$$

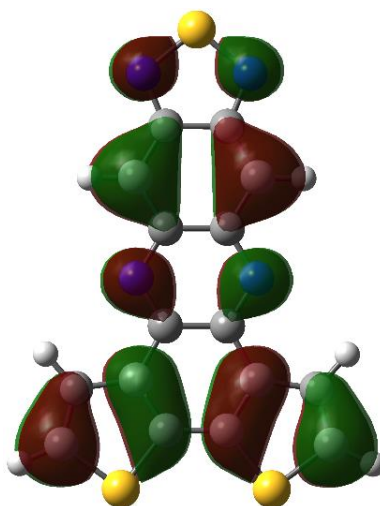
Fig. S4 Molecular Orbitals for the Singlet Ground State of phenanthrene-condensed thiadiazoloquinoxaline as calculated with DFT RB3LYP/6-311G(d,p). Hydrogens are omitted for clarity.

Atomic coordinates of the optimised geometry of phenanthrene-condensed thiadiazoloquinoxaline using DFT/B3LYP/6-311G(d,p)

Center Number	Atomic Number	Forces (Hartrees/Bohr)		
		X	Y	Z
1	6	0.000000000	-0.000063455	-0.000015987
2	6	0.000000000	-0.000011221	0.000185011
3	6	0.000000000	-0.000045653	-0.000179640
4	6	0.000000000	-0.000059341	0.000027582
5	6	0.000000000	-0.000210404	0.000083614
6	6	0.000000000	-0.000222336	-0.000042752
7	7	0.000000000	0.000216790	0.000113071
8	16	0.000000000	0.000066840	-0.000006311
9	7	0.000000000	0.000191794	-0.000151652
10	7	0.000000000	0.000075756	-0.000070626
11	6	0.000000000	0.000062691	-0.000079709
12	6	0.000000000	0.000076502	0.000066566
13	7	0.000000000	0.000087637	0.000055198
14	6	0.000000000	-0.000223669	-0.000033575
15	6	0.000000000	0.000129837	0.000055614
16	6	0.000000000	0.000117132	-0.000078934
17	6	0.000000000	-0.000213431	0.000074848
18	6	0.000000000	-0.000033504	0.000015433
19	6	0.000000000	0.000033193	-0.000039256
20	6	0.000000000	-0.000039018	0.000012159
21	6	0.000000000	0.000042060	0.000004281
22	6	0.000000000	0.000040515	-0.000012078
23	6	0.000000000	-0.000040605	-0.000004641
24	6	0.000000000	0.000039954	0.000032349
25	6	0.000000000	-0.000035801	-0.000008889
26	1	0.000000000	-0.000006897	0.000007357
27	1	0.000000000	-0.000008152	-0.000005936
28	1	0.000000000	0.000001717	-0.000034349
29	1	0.000000000	0.000001111	-0.000020170
30	1	0.000000000	-0.000016721	-0.000003054
31	1	0.000000000	0.000023609	-0.000014693
32	1	0.000000000	0.000025942	0.000010015
33	1	0.000000000	-0.000015854	0.000006129
34	1	0.000000000	0.000004867	0.000019605
35	1	0.000000000	0.000008116	0.000033421



$$E_{\text{LUMO}} = -3.48 \text{ eV}$$



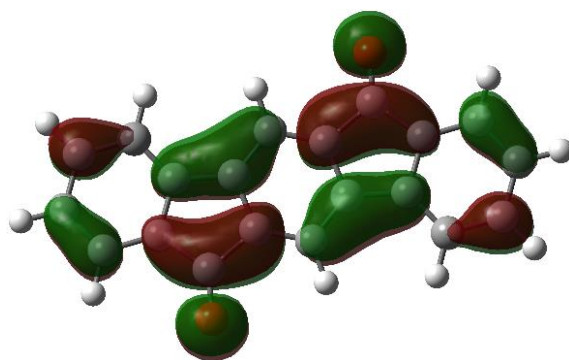
$$E_{\text{HOMO}} = -5.94 \text{ eV}$$

$$\text{Dipole moment } (\mu) = 2.2495 \text{ D}$$

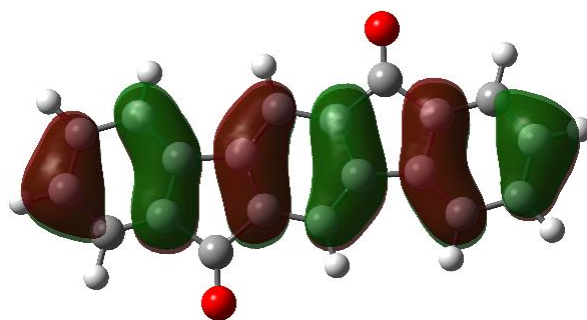
Fig. S5 Molecular Orbitals for the Singlet Ground State of benzodithiophene-condensed thiadiazoloquinoxaline as calculated with DFT RB3LYP/6-311G(d,p). Hydrogens are omitted for clarity.

Atomic coordinates of the optimised geometry of benzodithiophene-condensed thiadiazoloquinoxaline using DFT/B3LYP/6-311G(d,p)

Center Number	Atomic Number	Forces (Hartrees/Bohr)		
		X	Y	Z
1	6	0.000000000	-0.000073654	-0.000002848
2	6	0.000000000	-0.000047162	0.000111584
3	6	0.000000000	-0.000049559	-0.000110540
4	6	0.000000000	-0.000073576	0.000004437
5	6	0.000000000	-0.000249821	0.000043314
6	6	0.000000000	-0.000250698	-0.000037912
7	7	0.000000000	0.000230681	0.000106602
8	16	0.000000000	0.000060512	-0.000000653
9	7	0.000000000	0.000228327	-0.000111555
10	7	0.000000000	0.000102901	-0.000037616
11	6	0.000000000	-0.000018138	0.000070767
12	6	0.000000000	-0.000019661	-0.000070359
13	7	0.000000000	0.000103689	0.000035386
14	6	0.000000000	-0.000156554	-0.000109010
15	6	0.000000000	0.000197160	-0.000044039
16	6	0.000000000	0.000198064	0.000039774
17	6	0.000000000	-0.000154164	0.000112363
18	16	0.000000000	-0.000042818	-0.000025779
19	6	0.000000000	-0.000010958	-0.000054993
20	6	0.000000000	0.000047920	-0.000029503
21	6	0.000000000	0.000048546	0.000028462
22	6	0.000000000	-0.000009768	0.000055217
23	16	0.000000000	-0.000042252	0.000026697
24	1	0.000000000	-0.000006526	0.000008372
25	1	0.000000000	-0.000006705	-0.000008229
26	1	0.000000000	-0.000025225	0.000017757
27	1	0.000000000	0.000022408	-0.000010758
28	1	0.000000000	0.000022635	0.000010271
29	1	0.000000000	-0.000025602	-0.000017209



$E_{\text{LUMO}} = -3.13 \text{ eV}$



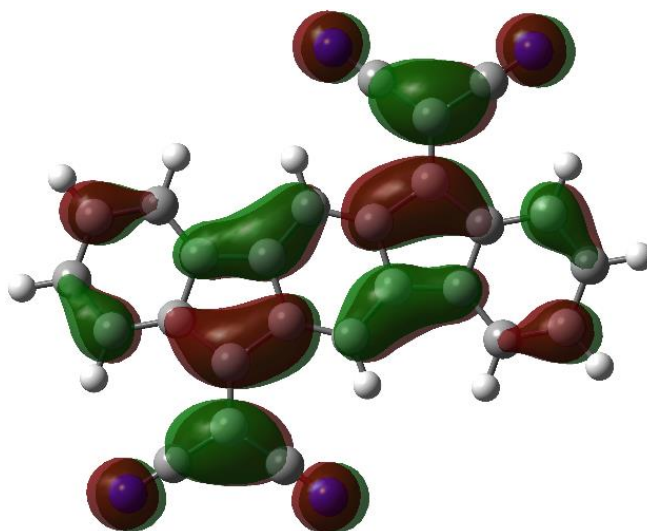
$E_{\text{HOMO}} = -6.30 \text{ eV}$

Dipole moment (μ) = 0.0000 D

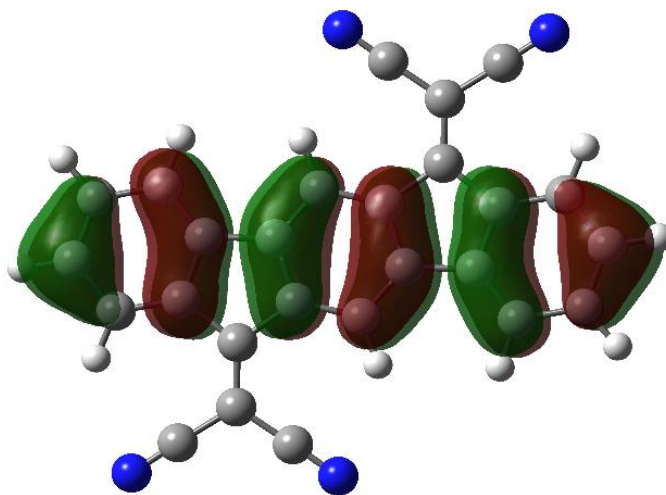
Fig. S6 Molecular Orbitals for the Singlet Ground State of indeno[1,2-*b*]fluorene-6,12-dione as calculated with DFT RB3LYP/6-311G(d,p). Hydrogens are omitted for clarity.

Atomic coordinates of the optimised geometry of indeno[1,2-*b*]fluorene-6,12-dione using DFT/B3LYP/6-311G(d,p)

Center Number	Atomic Number	Forces (Hartrees/Bohr)		
		X	Y	Z
1	6	0.000000000	0.000091576	0.000096419
2	6	0.000000000	-0.000089065	-0.000083981
3	6	0.000000000	-0.000032445	-0.000045509
4	6	0.000000000	0.000077942	0.000052919
5	6	0.000000000	-0.000151051	-0.000052355
6	6	0.000000000	0.000068887	0.000182963
7	6	0.000000000	-0.000077942	-0.000052919
8	6	0.000000000	0.000032445	0.000045509
9	6	0.000000000	-0.000068887	-0.000182963
10	6	0.000000000	-0.000047018	-0.000098794
11	6	0.000000000	0.000066002	-0.000024757
12	6	0.000000000	-0.000019022	0.000090868
13	6	0.000000000	0.000054199	-0.000067664
14	6	0.000000000	0.000151051	0.000052355
15	6	0.000000000	-0.000091576	-0.000096419
16	6	0.000000000	0.000089065	0.000083981
17	6	0.000000000	0.000047018	0.000098794
18	6	0.000000000	-0.000066002	0.000024757
19	6	0.000000000	0.000019022	-0.000090868
20	6	0.000000000	-0.000054199	0.000067664
21	8	0.000000000	0.000091805	0.000071031
22	8	0.000000000	-0.000091805	-0.000071031
23	1	0.000000000	-0.000022860	-0.000034428
24	1	0.000000000	0.000022860	0.000034428
25	1	0.000000000	0.000006212	0.000041143
26	1	0.000000000	-0.000019793	0.000008219
27	1	0.000000000	0.000001876	-0.000013222
28	1	0.000000000	-0.000000913	0.000026567
29	1	0.000000000	-0.000006212	-0.000041143
30	1	0.000000000	0.000019793	-0.000008219
31	1	0.000000000	-0.000001876	0.000013222
32	1	0.000000000	0.000000913	-0.000026567



$$E_{\text{LUMO}} = -4.18 \text{ eV}$$



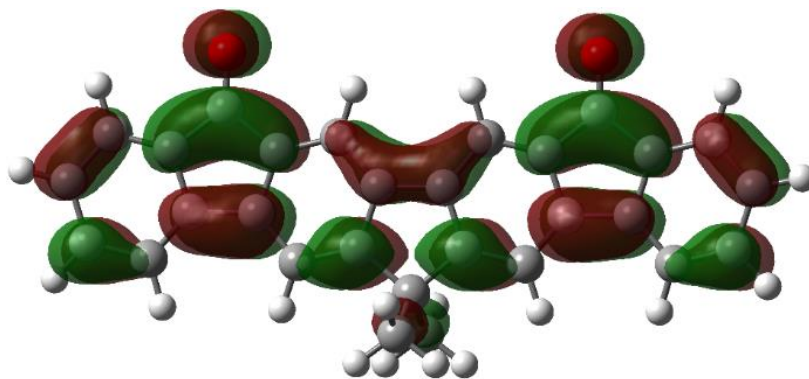
$$E_{\text{HOMO}} = -6.73 \text{ eV}$$

$$\text{Dipole moment } (\mu) = 0.0000 \text{ D}$$

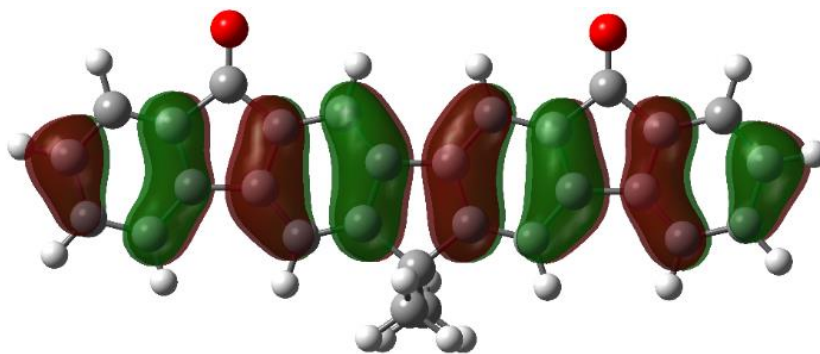
Fig. S7 Molecular Orbitals for the Singlet Ground State of 2,2'-(indeno[1,2-*b*]fluorene-6,12-diylidene) dimalononitrile as calculated with DFT RB3LYP/6-311G(d,p). Hydrogens are omitted for clarity.

Atomic coordinates of the optimised geometry of 2,2'-(indeno[1,2-*b*]fluorene-6,12-diylidene) dimalononitrile using DFT/B3LYP/6-311G(d,p)

Center Number	Atomic Number	Forces (Hartrees/Bohr)		
		X	Y	Z
1	6	-0.000005498	0.000039013	-0.000052955
2	6	0.000004965	-0.000044195	0.000041863
3	6	-0.000005630	0.000054030	-0.000044871
4	6	0.000005124	-0.000048327	0.000041389
5	6	0.000003033	-0.000002107	0.000042119
6	6	0.000005218	-0.000053088	0.000039584
7	6	-0.000005124	0.000048327	-0.000041389
8	6	0.000005630	-0.000054030	0.000044871
9	6	-0.000005218	0.000053088	-0.000039584
10	6	0.000003130	-0.000012301	0.000036724
11	6	-0.000000848	0.000000076	-0.000012116
12	6	0.000002338	-0.000034208	0.000010803
13	6	-0.000003626	0.000033759	-0.000029585
14	6	-0.000003033	0.000002107	-0.000042119
15	6	0.000005498	-0.000039013	0.000052955
16	6	-0.000004965	0.000044195	-0.000041863
17	6	-0.000003130	0.000012301	-0.000036724
18	6	0.000000848	-0.000000076	0.000012116
19	6	-0.000002338	0.000034208	-0.000010803
20	6	0.000003626	-0.000033759	0.000029585
21	6	-0.000002061	0.000060785	0.000010833
22	6	0.000002061	-0.000060785	-0.000010833
23	6	0.000000773	-0.000064242	-0.000031598
24	6	-0.000001818	-0.000042700	-0.000054461
25	6	0.000001818	0.000042700	0.000054461
26	6	-0.000000773	0.000064242	0.000031598
27	7	0.000000219	0.000024504	0.000019419
28	7	0.000000501	0.000023776	0.000022994
29	7	-0.000000501	-0.000023776	-0.000022994
30	7	-0.000000219	-0.000024504	-0.000019419
31	1	-0.000000981	0.000009869	-0.000007509
32	1	0.000000981	-0.000009869	0.000007509
33	1	-0.000000764	0.000005752	-0.000007132
34	1	-0.000000089	0.000002299	0.000000255
35	1	-0.000000442	-0.000000214	-0.000006489
36	1	0.000000500	-0.000007299	0.000002321
37	1	0.000000764	-0.000005752	0.000007132
38	1	0.000000089	-0.000002299	-0.000000255
39	1	0.000000442	0.000000214	0.000006489
40	1	-0.000000500	0.000007299	-0.000002321



$$E_{\text{LUMO}} = -2.60 \text{ eV}$$



$$E_{\text{HOMO}} = -5.91 \text{ eV}$$

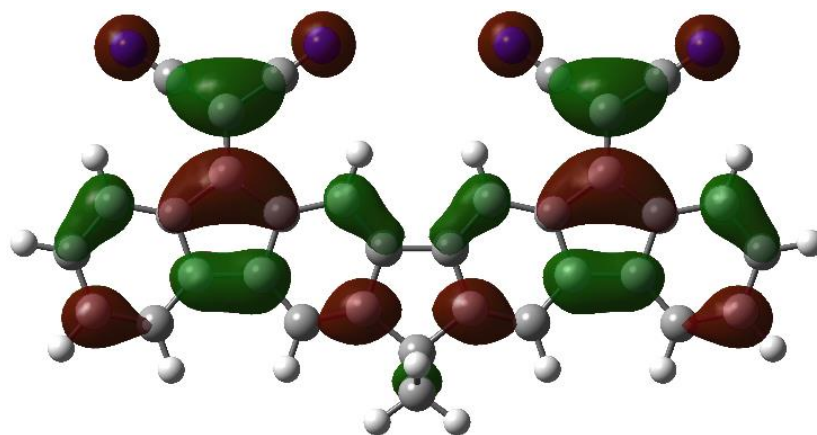
$$\text{Dipole moment } (\mu) = 7.1132 \text{ D}$$

Fig. S8 Molecular Orbitals for the Singlet Ground State of bisindenofluorene-12,15-dione as calculated with DFT RB3LYP/6-311G(d,p). Hydrogens are omitted for clarity.

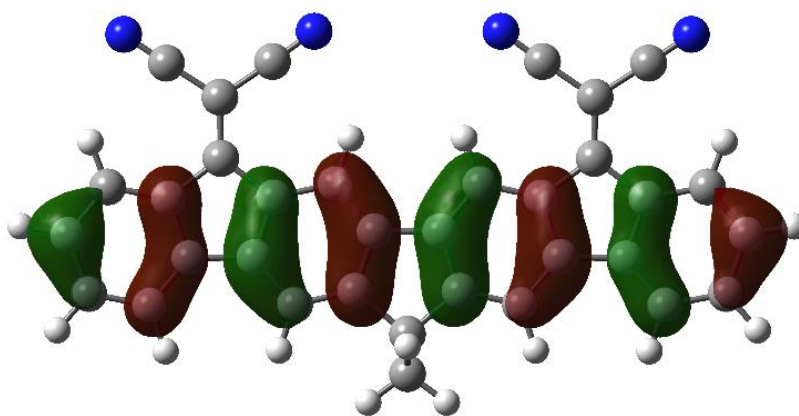
Atomic coordinates of the optimised geometry of bisindenofluorene-12,15-dione using DFT/B3LYP/6-311G(d,p)

Center Number	Atomic Number	Forces (Hartrees/Bohr)		
		X	Y	Z
1	6	-0.000048096	0.000107676	0.000095250
2	6	0.000027980	-0.000099961	-0.000064757
3	6	0.000036266	-0.000006065	-0.000053010
4	6	-0.000025793	0.000059550	0.000051533
5	6	0.000017621	-0.000089233	-0.000047362
6	6	-0.000086339	-0.000059104	0.000107786
7	6	0.000020026	0.000180538	0.000016775
8	6	-0.000039142	-0.000092007	0.000032535
9	6	0.000062129	-0.000022697	-0.000093895
10	6	0.000044011	-0.000069600	-0.000079916
11	6	0.000024227	0.000058575	-0.000019730
12	6	-0.000050285	-0.000021932	0.000065903
13	6	0.000052952	0.000057775	-0.000060715
14	6	0.000064567	-0.000185142	-0.000138034
15	6	-0.000097389	0.000041296	0.000148615
16	6	0.000061637	0.000027505	-0.000080625
17	6	0.000064981	0.000120347	-0.000062125
18	6	-0.000012053	-0.000063366	0.000001245
19	6	-0.000018683	0.000067981	0.000043549
20	6	-0.000014575	-0.000113660	-0.000007767
21	8	-0.000021226	0.000064211	0.000046216
22	6	0.000037716	-0.000088416	-0.000075689
23	6	-0.000033177	0.000125369	0.000078498
24	6	0.000036720	-0.000066584	-0.000068808
25	6	-0.000050475	-0.000064878	0.000055419
26	6	0.000031683	0.000075273	-0.000026135
27	6	-0.000038953	-0.000016350	0.000051212
28	6	0.000016084	-0.000102719	-0.000048557
29	6	-0.000028560	0.000054632	0.000032265
30	6	-0.000008300	0.000051059	0.000046534
31	8	-0.000022878	0.000062253	0.000048070
32	1	0.000022482	0.000005435	-0.000030559
33	1	-0.000001707	0.000034879	0.000011158
34	1	-0.000019370	0.000009874	0.000029974
35	1	-0.000006956	-0.000022775	0.000004173
36	1	0.000008478	0.000000222	-0.000011982
37	1	-0.000014892	-0.000002789	0.000020446
38	1	-0.000012008	-0.000035467	0.000008168
39	1	-0.000016502	0.000017334	0.000027770
40	1	0.000007554	0.000023830	-0.000004758
41	1	-0.000003627	-0.000014133	0.000001610

42	1	0.000014124	0.000002223	-0.000019496
43	1	0.000003164	0.000036597	0.000004672
44	1	-0.000001452	-0.000014370	-0.000005231
45	1	0.000005430	-0.000006208	-0.000012959
46	1	-0.000007564	-0.000001104	-0.000007902
47	1	0.000009375	-0.000004091	0.000004029
48	1	0.000008838	-0.000006809	-0.000010559
49	1	0.000001956	-0.000014971	-0.000002831



$E_{\text{LUMO}} = -3.49 \text{ eV}$



$E_{\text{HOMO}} = -6.25 \text{ eV}$

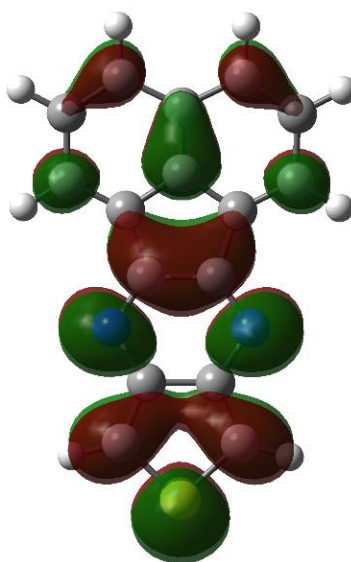
Dipole moment (μ) = 13.3020 D

Fig. S9 Molecular Orbitals for the Singlet Ground State of 2,2'-(bisindenofluorene-12,15-diylidene) dimalononitrile as calculated with DFT RB3LYP/6-311G(d,p). Hydrogens are omitted for clarity.

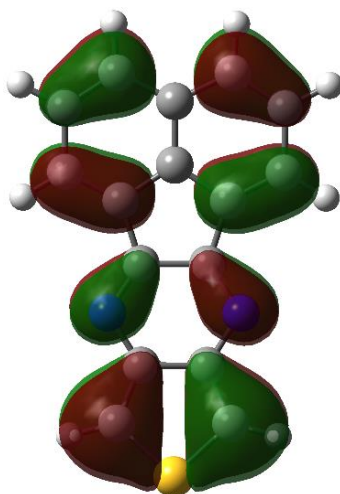
Atomic coordinates of the optimised geometry of 2,2'-(bisindenofluorene-12,15-diylidene) dimalononitrile using DFT/B3LYP/6-311G(d,p)

Center Number	Atomic Number	Forces (Hartrees/Bohr)		
		X	Y	Z
1	6	-0.000000423	-0.000000965	-0.000002690
2	6	-0.000002480	-0.000000091	0.000000275
3	6	0.000001339	0.000000394	0.000001770
4	6	-0.000000768	0.000001448	0.000000838
5	6	0.000001580	-0.000003039	0.000000541
6	6	0.000001040	0.000002789	-0.000001148
7	6	-0.000000339	-0.000006726	-0.000001953
8	6	-0.000000064	-0.000000425	-0.000000292
9	6	0.000001173	0.000003528	-0.000001914
10	6	-0.000000503	0.000000289	0.000003153
11	6	0.000000833	-0.000000431	-0.000001090
12	6	0.000000238	-0.000000279	-0.000000148
13	6	0.000000730	-0.000001741	0.000000272
14	6	-0.000002743	0.000010317	0.000008021
15	6	0.000003054	-0.000003572	-0.000006021
16	6	0.000000505	-0.000000071	-0.000000564
17	6	-0.000001571	-0.000001001	0.000002501
18	6	-0.000001860	0.000002203	0.000000429
19	6	0.000000593	0.000001563	0.000000516
20	6	-0.000002805	-0.000002687	0.000004310
21	6	0.000001991	0.000000572	0.000000393
22	6	0.000002064	-0.000000903	-0.000000633
23	6	-0.000002780	-0.000003406	-0.000001181
24	6	0.000000024	-0.000000108	-0.000001978
25	6	-0.000000011	-0.000000362	-0.000000404
26	6	-0.000000418	-0.000001098	-0.000000078
27	6	-0.000000109	0.000003027	-0.000000771
28	6	0.000003545	-0.000004616	-0.000001629
29	6	-0.000001341	-0.000003441	-0.000004757
30	6	0.000001445	0.000005745	-0.000000551
31	7	-0.000000821	-0.000002265	0.000000388
32	6	-0.000002200	0.000004786	0.000002221
33	6	-0.000004750	-0.000008525	0.000002186
34	7	0.000004077	0.000003279	-0.000002571
35	6	0.000000542	0.000002579	-0.000002409
36	7	-0.000000796	-0.000003283	0.000000139
37	6	0.000005168	0.000002501	-0.000000624
38	6	-0.000005044	0.000000398	0.000005029
39	7	0.000002671	-0.000000400	-0.000002498
40	1	-0.000000571	-0.000000115	0.000000225
41	1	0.000000444	-0.000000590	0.000000308

42	1	0.000000374	-0.000000889	-0.000001706
43	1	-0.000000186	-0.000000462	0.000000433
44	1	-0.000000147	0.000000434	0.000000242
45	1	0.000000229	0.000000934	-0.000000481
46	1	0.000000422	0.000000363	0.000000074
47	1	-0.000000233	0.000001413	-0.000000031
48	1	-0.000000357	-0.000000248	0.000000926
49	1	-0.000000085	0.000000347	0.000000376
50	1	0.000000183	0.000000569	-0.000000375
51	1	0.000000121	-0.000001055	0.000000200
52	1	-0.000000584	0.000000689	0.000000495
53	1	-0.000000442	0.000000856	0.000000322
54	1	-0.000000268	0.000000288	0.000000070
55	1	0.000000127	0.000000191	0.000000318
56	1	0.000000159	0.000000716	0.000000651
57	1	0.000000027	0.000000579	0.000000878



$$E_{\text{LUMO}} = -2.39 \text{ eV}$$



$$E_{\text{HOMO}} = -5.97 \text{ eV}$$

$$\text{Dipole moment } (\mu) = 1.5845 \text{ D}$$

Fig. S10 Molecular Orbitals for the Singlet Ground State of fused aromatic thieno[3,4-*b*]pyrazine as calculated with DFT RB3LYP/6-311G(d,p). Hydrogens are omitted for clarity.

Atomic coordinates of the optimised geometry of fused aromatic thieno[3,4-*b*]pyrazine using DFT/B3LYP/6-311G(d,p)

Center Number	Atomic Number	Forces (Hartrees/Bohr)		
		X	Y	Z
1	6	0.000000000	0.000296162	-0.000024593
2	6	0.000000000	-0.000263237	0.000282512
3	6	0.000000000	-0.000122579	-0.000366171
4	6	0.000000000	0.000259376	0.000145054
5	16	0.000000000	-0.000282754	-0.000061311
6	7	0.000000000	0.000378351	-0.000113722
7	6	0.000000000	-0.000044091	-0.000313875
8	6	0.000000000	-0.000170138	0.000267423
9	7	0.000000000	0.000297266	0.000260220
10	6	0.000000000	-0.000182650	0.000249232
11	6	0.000000000	-0.000092057	-0.000019961
12	6	0.000000000	-0.000063014	-0.000302501
13	6	0.000000000	0.000096365	-0.000068373
14	6	0.000000000	-0.000066965	-0.000000847
15	6	0.000000000	-0.000008659	0.000030468
16	6	0.000000000	0.000006934	0.000001504
17	6	0.000000000	0.000004739	-0.000031318
18	6	0.000000000	-0.000061301	-0.000026966
19	6	0.000000000	0.000059390	0.000102146
20	1	0.000000000	-0.000018881	0.000012540
21	1	0.000000000	-0.000011991	-0.000019235
22	1	0.000000000	-0.000003960	0.000014167
23	1	0.000000000	0.000005374	0.000011077
24	1	0.000000000	-0.000011355	-0.000004183
25	1	0.000000000	-0.000012068	-0.000000896
26	1	0.000000000	0.000009480	-0.000007856
27	1	0.000000000	0.000002263	-0.000014535

S2.2 Optimized geometry structures of the trimer model compounds

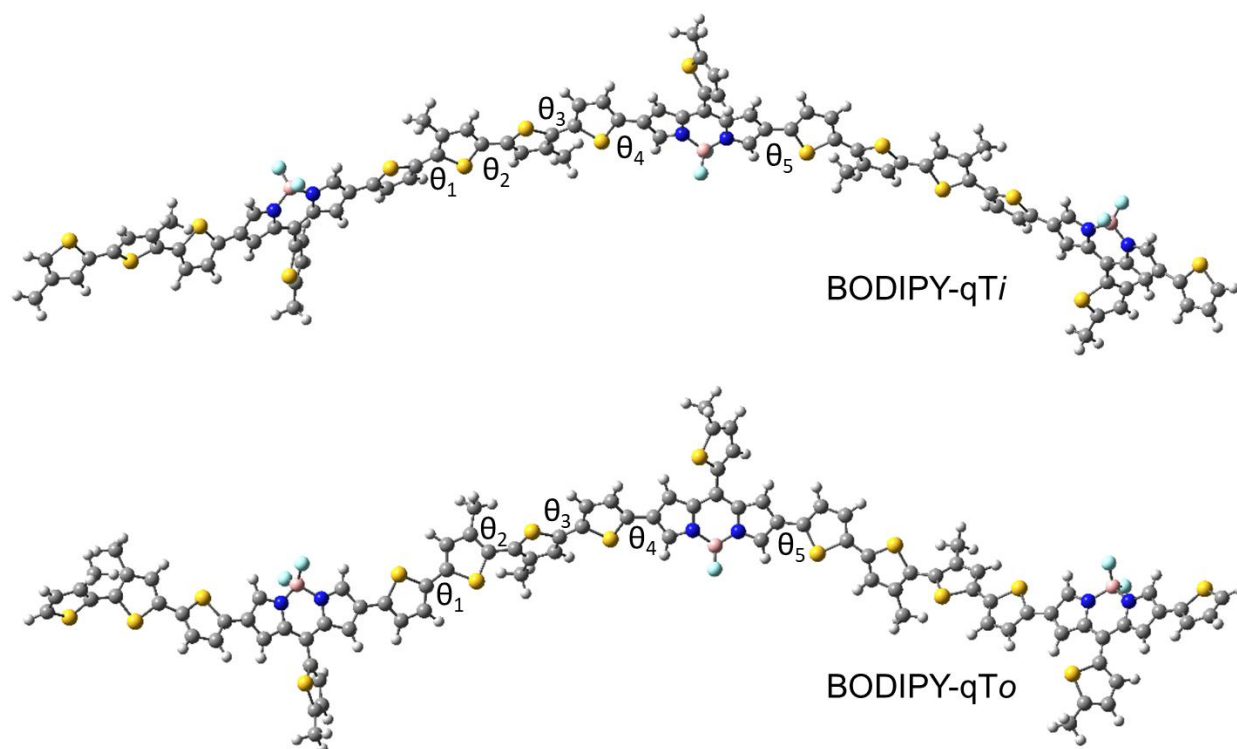


Fig. S11 Ground state geometry optimizations of BODIPY-qTi and BODIPY-qTo. Color scheme: carbon, gray; nitrogen, blue; sulfur, orange; boron, pink; fluorine, cyan. Optimized structures calculated using DFT at the B3LYP/6-311G(d,p) level of theory. θ_1 , θ_2 , θ_3 , θ_4 and θ_5 are the calculated dihedral angles.

S3. Nuclear Magnetic Resonance (NMR) spectra of all new compounds

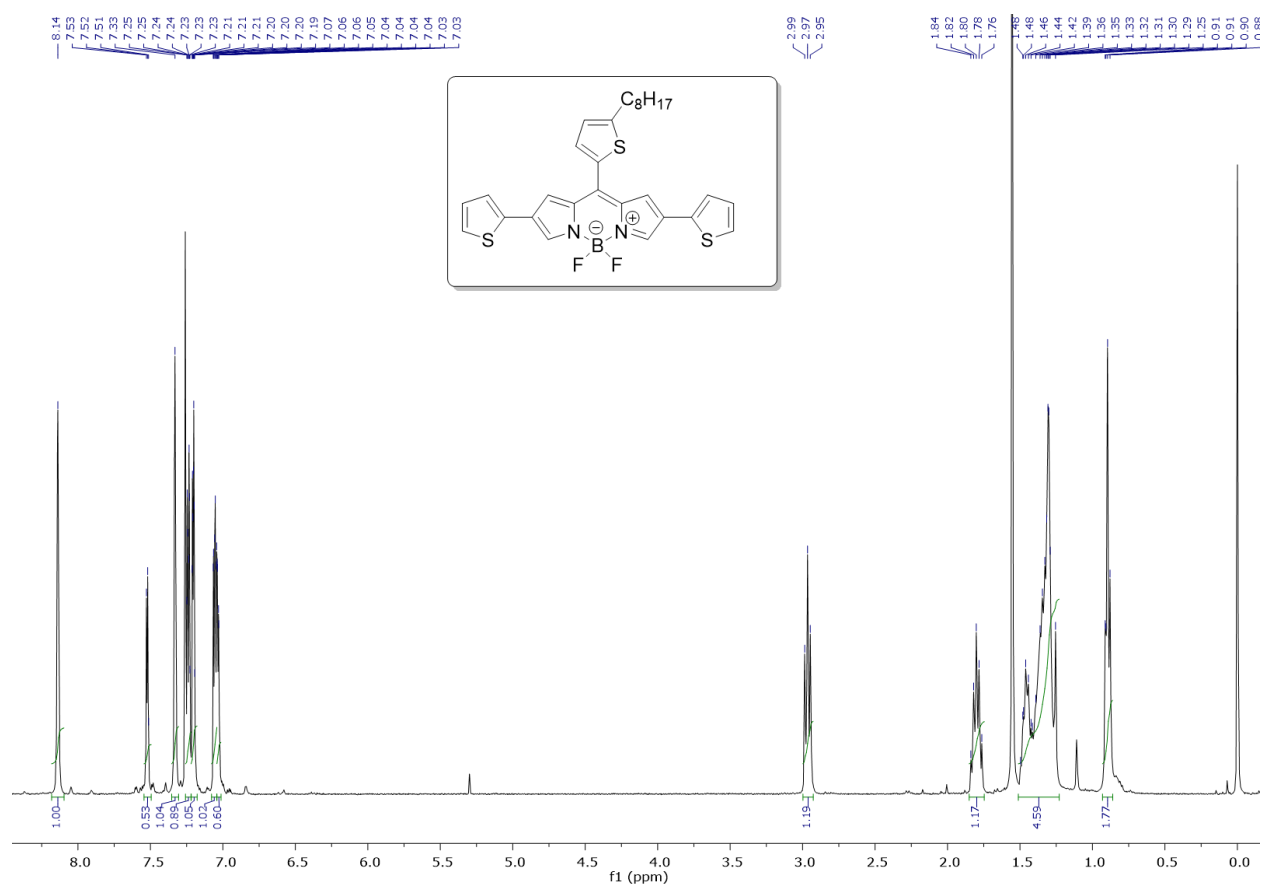


Fig. S12 ¹H-NMR spectrum of 5,5-difluoro-10-(5-octylthiophen-2-yl)-2,8-di(thiophen-2-yl)-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (**14**).

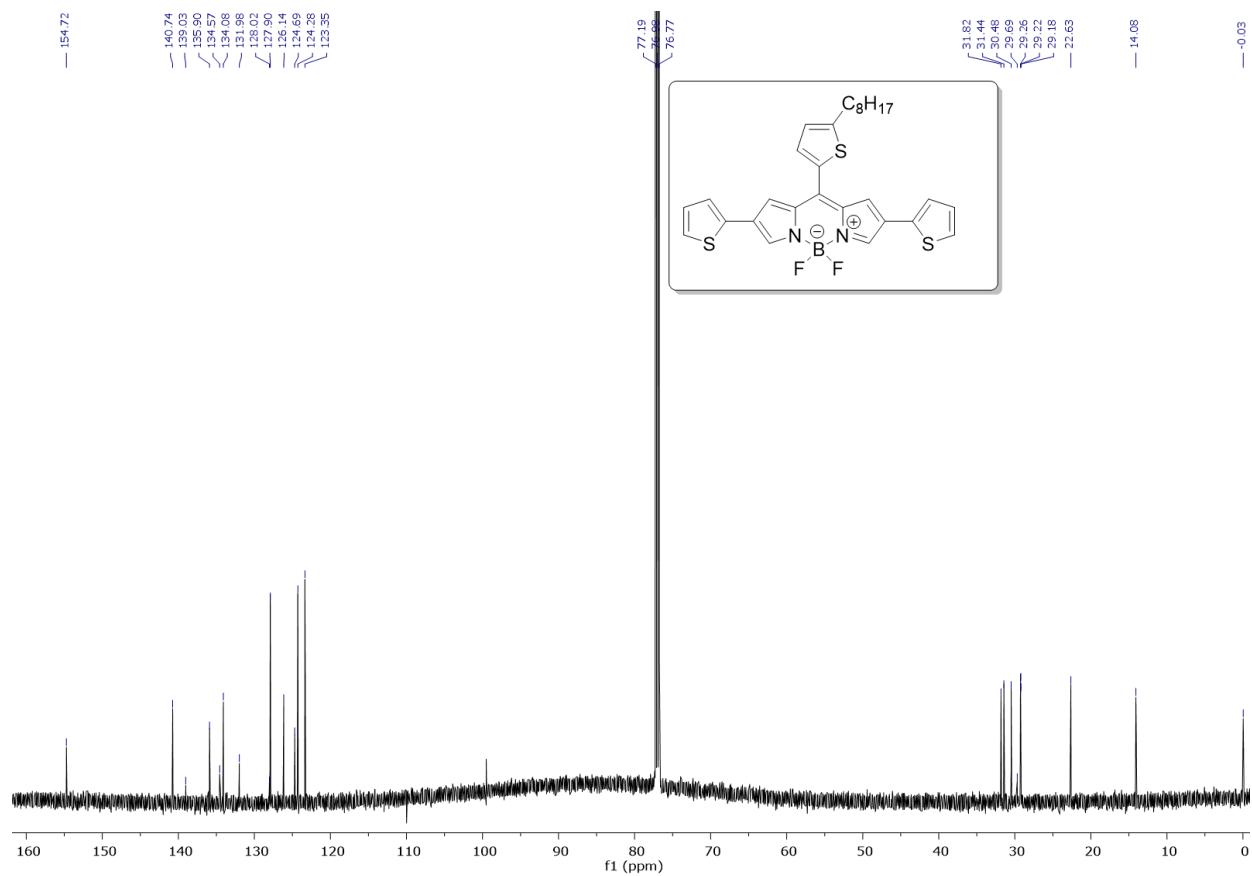


Fig. S13 ¹³C-NMR spectrum of 5,5-difluoro-10-(5-octylthiophen-2-yl)-2,8-di(thiophen-2-yl)-5H-4λ⁴,5λ⁴-dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (**14**).

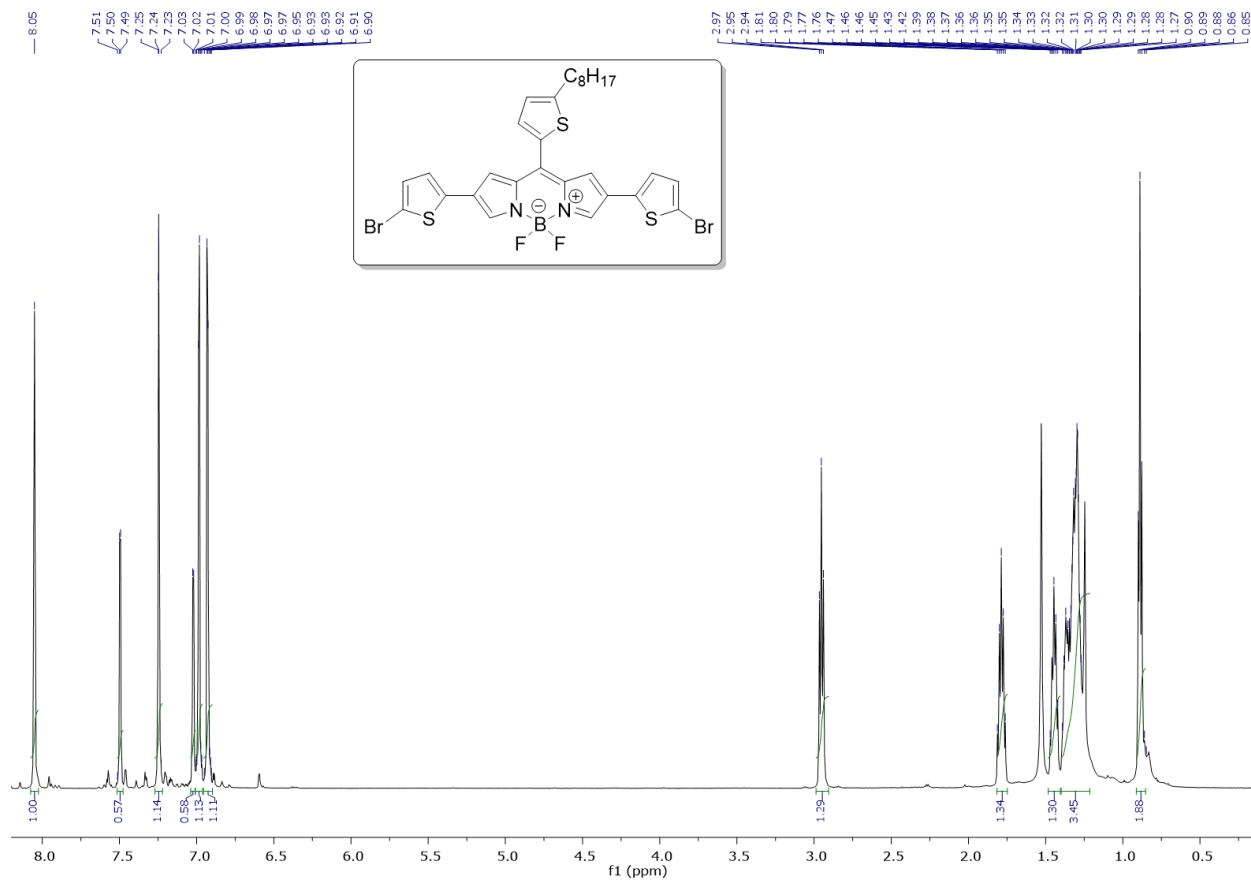


Fig. S14 $^1\text{H-NMR}$ spectrum of 2,8-bis(5-bromothiophen-2-yl)-5,5-difluoro-10-(5-octylthiophen-2-yl)-5*H*-4 λ^4 ,5 λ^4 -dipyrrolo[1,2-*c*:2',1'-*f*][1,3,2]diazaborinine (**15**).

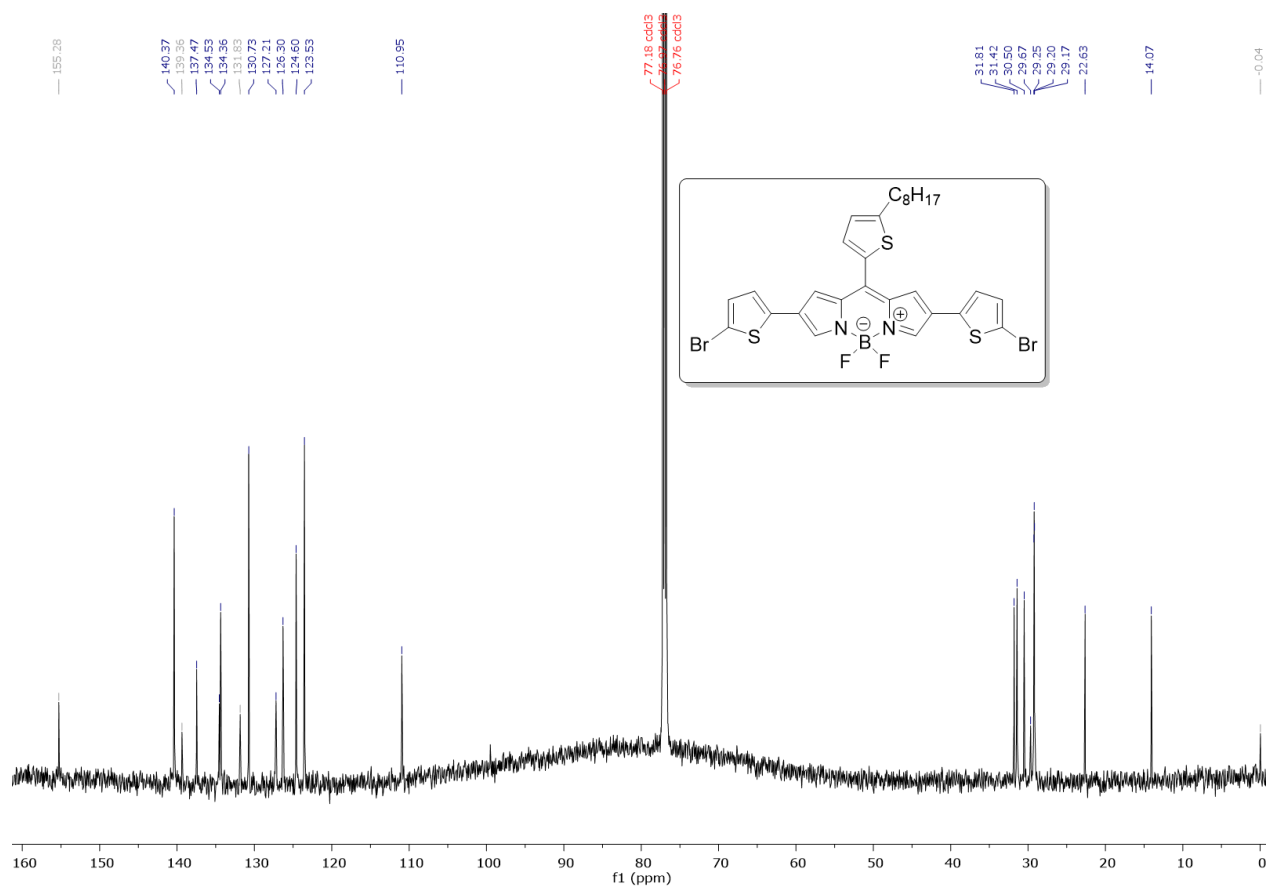


Fig. S15 ^{13}C -NMR spectrum of 2,8-bis(5-bromothiophen-2-yl)-5,5-difluoro-10-(5-octylthiophen-2-yl)-5H-4 λ^4 ,5 λ^4 -dipyrrolo[1,2-c:2',1'-f][1,3,2]diazaborinine (**15**).

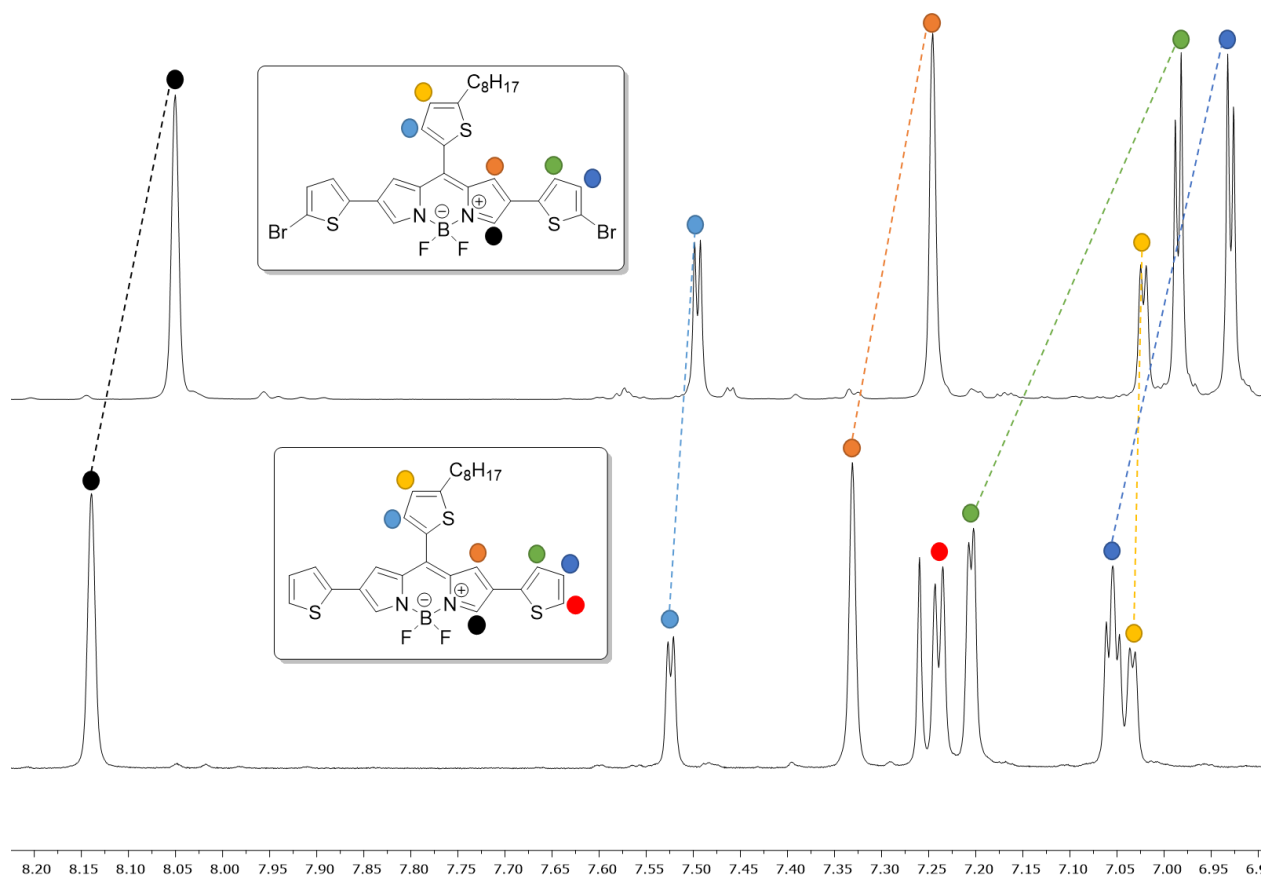


Fig. S16 Aromatic region (6.90–8.20 ppm) of the ¹H-NMR spectra of monomers **14** and **15** with assignment of the representative protons.

S4. Mass spectrum of the final compound

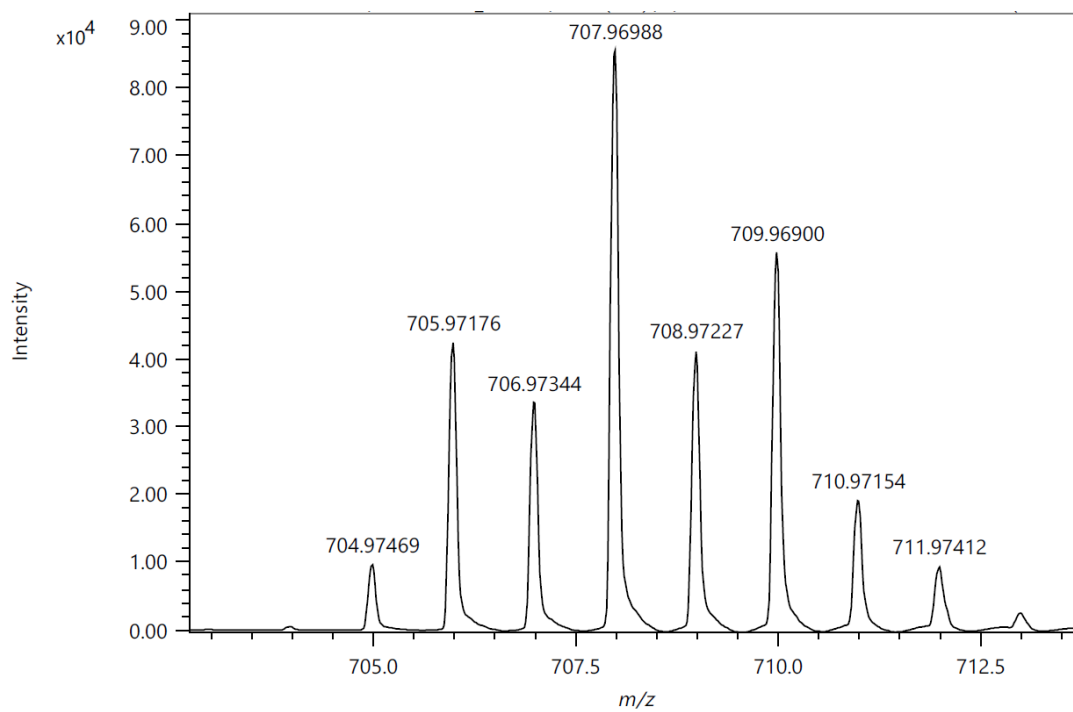


Fig. S17 FD+(eiFI) mass spectrum of 15.

S5. Absorption spectra of the monomers

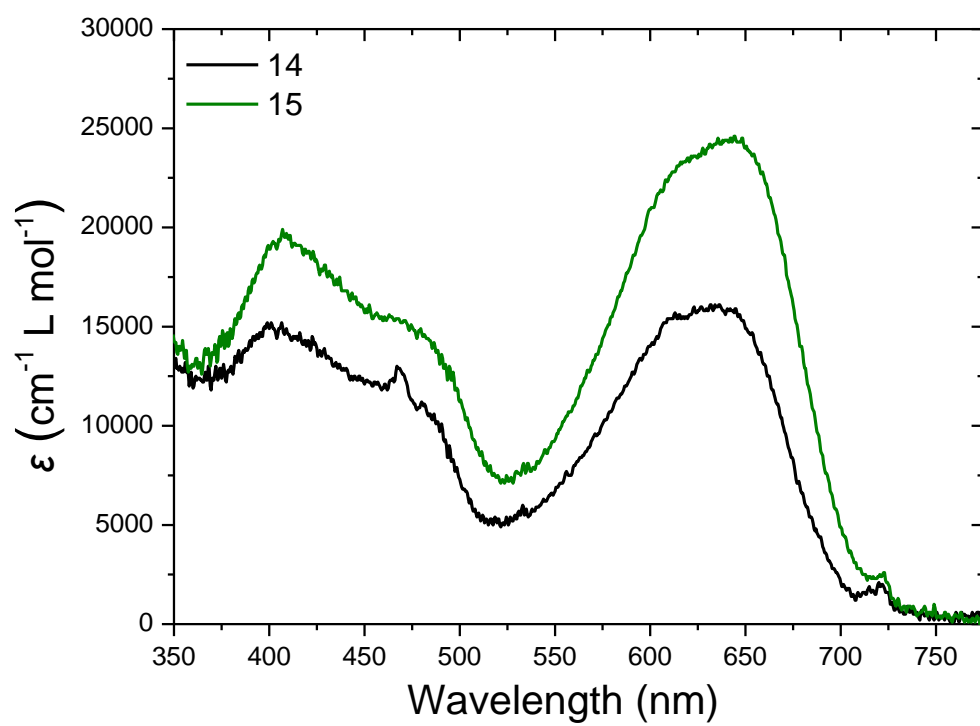


Fig. S18 Absorption spectra in chloroform solution of monomers 14 and 15.

S6. Gel permeation chromatography (GPC) graphs of the polymers

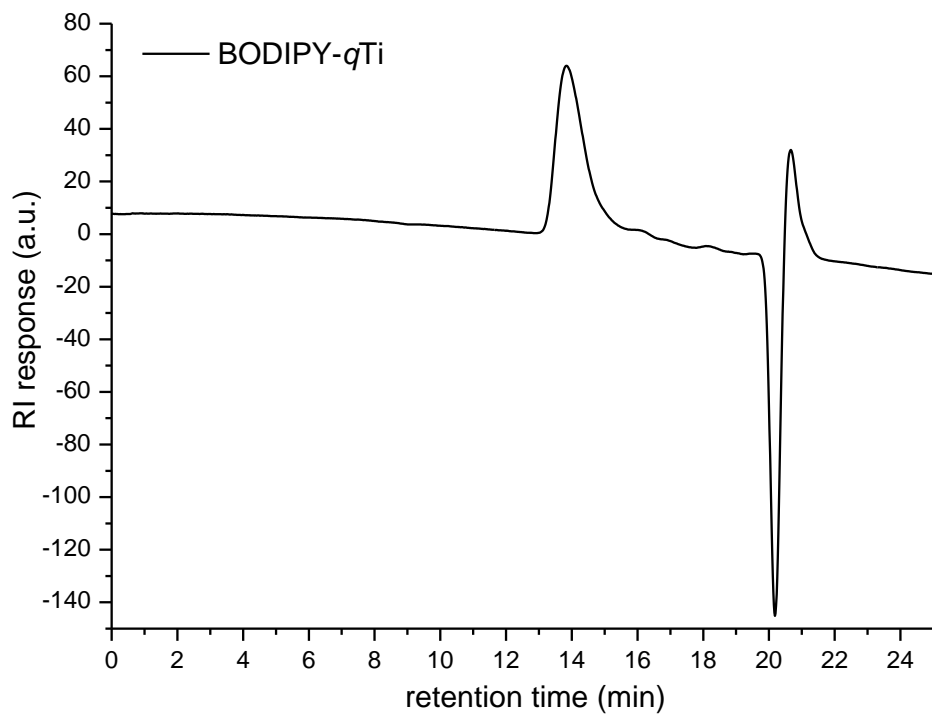


Fig. S19 Gel Permeation Chromatography (GPC) graph of BODIPY-qTi

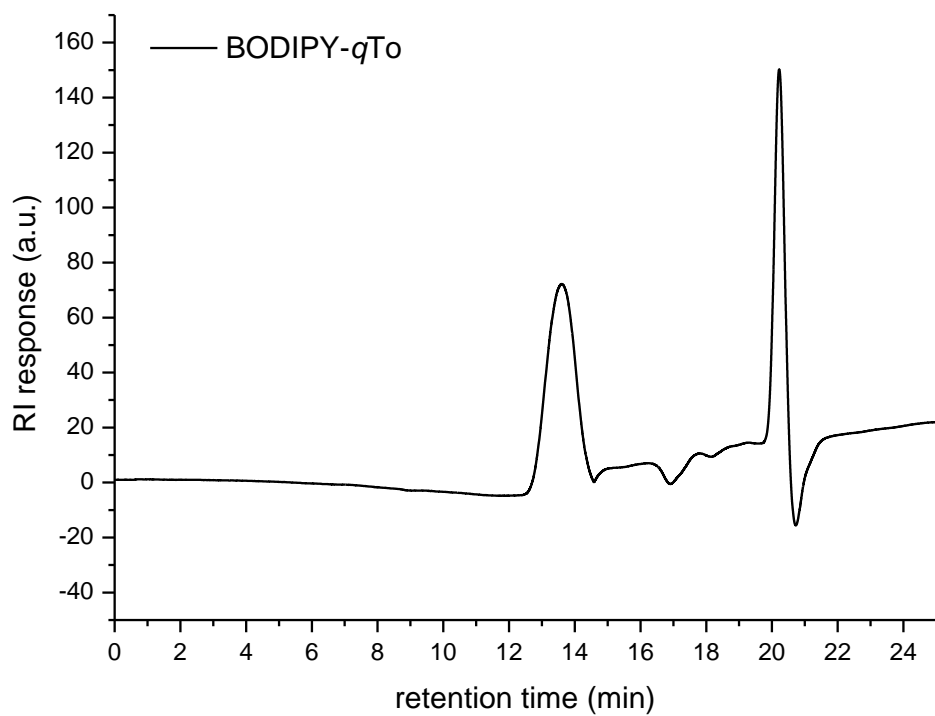


Fig. S20 Gel Permeation Chromatography (GPC) graph of BODIPY-qTo

S7. Hole mobility measurements

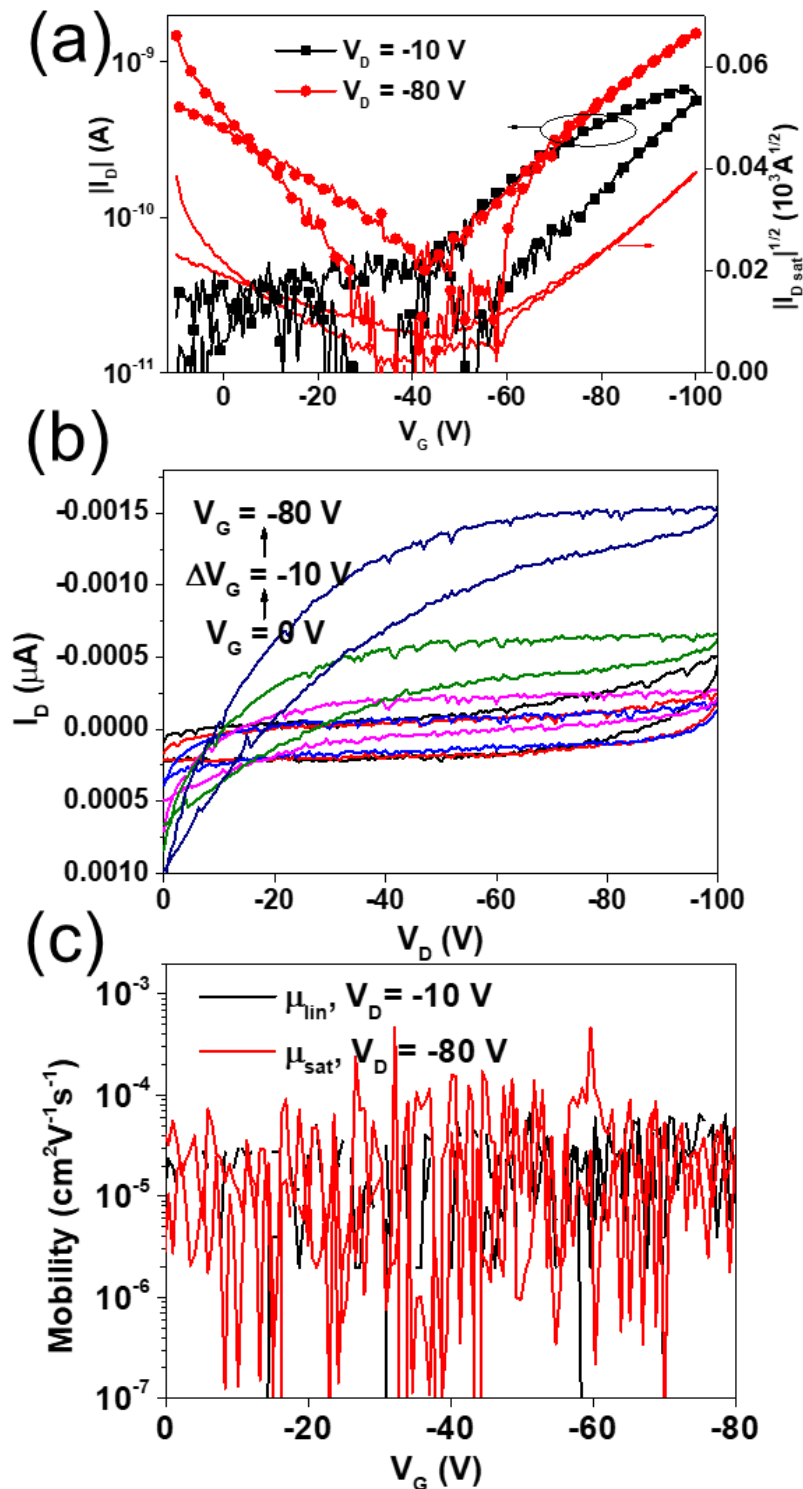


Fig. S21 Transfer (a), output (b) characteristics of BC/TG configuration OFET device and mobility calculation based on first derivative of the linear regime transfer curve and first derivative of the square root of the saturation regime transfer curve (c) for the with BODIPY-qT_o.

S8. Electron mobility measurements

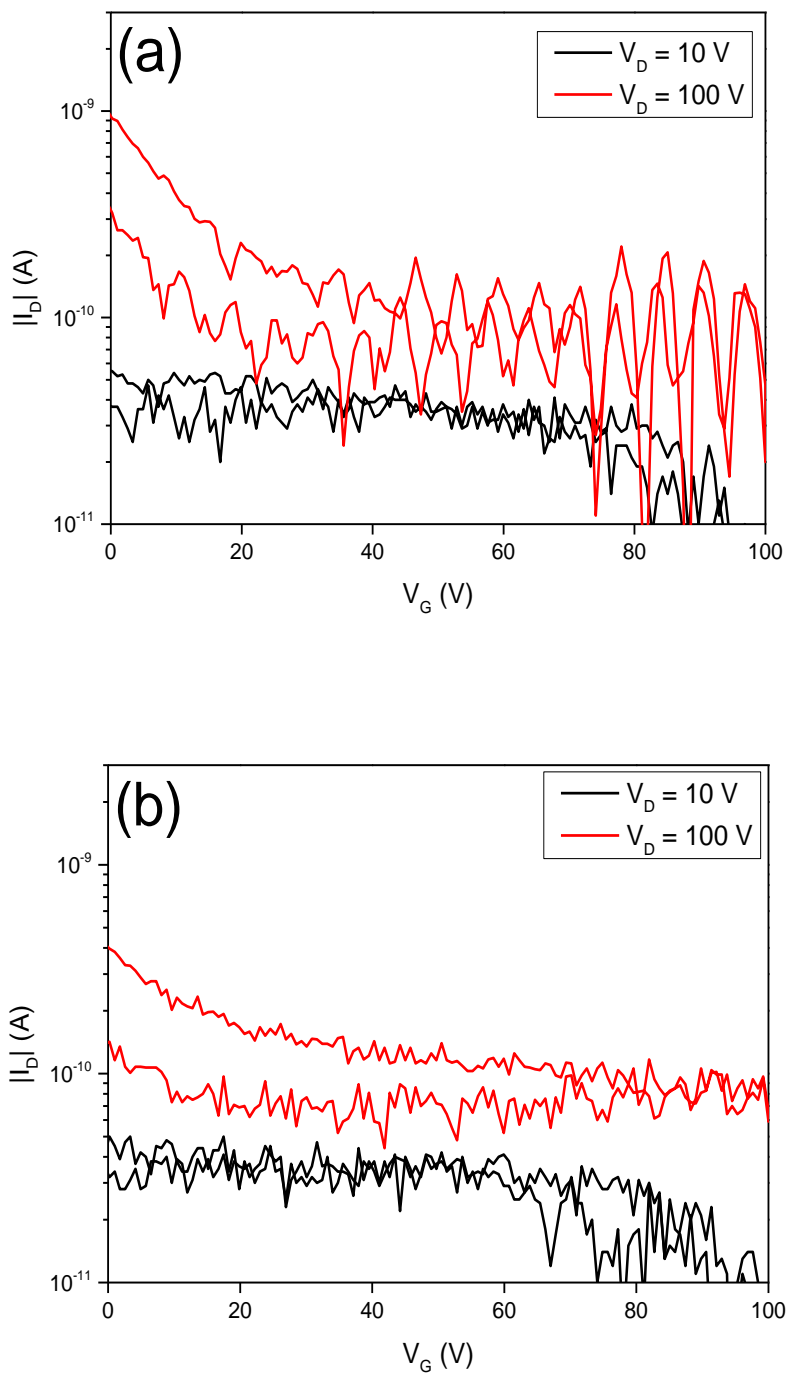


Fig. S22 Transfer curves of BG/TC configuration OFET device of (a) BODIPY-qTi and (b) BODIPY-qTo.

S9. References

- [S1] L. M. Harwood, *Aldrichim. Acta*, 1985, **18**, 25.
- [S2] B. M. Squeo, N. Gasparini, T. Ameri, A. Palma-Caldo, S. Allard, V. G. Gregoriou, C. J. Brabec, U. Scherf and C. L. Chochos, *J. Mater. Chem. A*, 2015, **3**, 16279.
- [S3] C. M. Cardona, W. Li, A. E. Kaifer, D. Stockdale and G. C. Bazan, *Adv. Mater.*, 2011, **23**, 2367.
- [S4] Gaussian 03, Revision C.02, Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; and Pople, J. A., Gaussian, Inc., Wallingford CT, **2004**.
- [S5] H. Bronstein, D. S. Leem, R. Hamilton, P. Woebkenberg, S. King, W. Zhang, R. S. Ashraf, M. Heeney, T. D. Anthopoulos, J. de Mello and I. McCulloch, *Macromolecules*, 2011, **44**, 6649.
- [S6] L. Biniek, C. L. Chochos, N. Leclerc, O. Boyron, S. Fall, P. Lévêque and T. Heiser, *J. Polym. Sci. Part A: Polym. Chem.*, 2012, **50**, 1861.

- [S7] L. Biniek, S. Fall, C. L. Chochos, N. Leclerc, P. Lévêque and T. Heiser, *Org. Electron.*, 2012, **13**, 114.
- [S8] J. Ku, Y. Lansac and Y. H. Jang, *J. Phys. Chem. C*, 2011, **115**, 21508.
- [S9] C. Risko, M. D. McGehee and J.-L. Brédas, *Chem. Sci.*, 2011, **2**, 1200.
- [S10] A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.
- [S11] C. T. Lee, W. T. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.
- [S12] L.-L. Chua, J. Zaumseil, J.-F. Chang, E. C.-W. Ou, P. K.-H. Ho, H. Sirringhaus and R. H. Friend, *Nature*, 2005, **434**, 194.