Supplementary information section

General

Melting points were taken using Stuart Scientific apparatus and are uncorrected.

^{1}H NMR spectra were recorded on AVANCE/DPX 400 and AVANCE 400 instruments at 400 MHz and on AVANCE/DRX500 instrument at 500 MHz; and ^{13}CNMR at 100 MHz; chemical shifts (δ_H) are given in parts per million (ppm). Peak multiplicities are denoted by s (singlet), d (doublet), t (triplet) and m (multiplet) or by a combination of these: dd (doublet of doublets), dt (doublet of triplets) and td (triplet of doublets) with coupling constants (J) given in Hertz (Hz).

Elemental analyses were conducted on a Perkin Elmer 2400.

Electron impact mass spectra were recorded on TraceGC – FinniganPolaris Q.

ES mass spectra were recorded on ThermoFinnigan LCQ DUO.

Infrared spectra were recorded on a Perkin Elmer Spectrum One FT-IR spectrometer (thin film deposited onto a diamond plate). Only selected absorptions (ν_{max}) are reported.

For all reactions that required anhydrous conditions, glassware was dried in an oven at 120 ^{o}C.

Column chromatography was performed with commercially available solvents and using VWR silica gel (40-63 µm). Thin layer chromatography (TLC) was performed using aluminium plates precoated with Merck silica gel 60 (F_{254}) and visualized by ultra-violet radiation and/or iodine vapor.

The chemicals were purchased from Sigma-Aldrich and used without further purification, unless stated otherwise. 2-Bromo-1-indanone was purified by column chromatography using silica gel (DCM/petroleum ether, 2:1, then DCM).

Anhydrous solvents were obtained from a PureSolv solvent purification system.

Known compounds are indicated by a reference to a previous literature procedure.

Cyclic voltammetry measurements were performed on a CH Instruments 660A Electrochemical Workstation with iR compensation, using anhydrous dichloromethane as the solvent for oxidation and tetrahydrofuran as the solvent for reduction.

Absorption spectra were recorded on a UNICAM UV 300 instrument in chloroform solution.

Synthetic procedures and data

3. 2,2'-(Thiophene-3,4-diylbis(sulfanediyl))bis(2,3-dihydro-1*H*-inden-1-one)
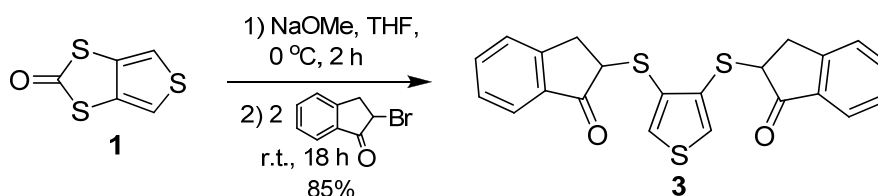
Method A

Thieno[3,4-*d*][1,3]dithiol-2-one **1**[17] (1.77 g, 10.15 mmol) was dissolved in dry THF (450 ml) and cooled to 0°C under N_2. Sodium methoxide (25 wt% sol in MeOH, 4.76 ml, 20.81 mmol) was added (mixture turned milky yellow) and the mixture was stirred for 1 hour. Purified 2-bromo-1-indanone (4.5 g, 21.32 mmol) was added, the mixture allowed to reach room temperature and then the reaction stirred for 18 hours. The solvent was removed, the remaining solid dissolved in DCM (350 ml), washed with water (5 × 100 ml), dried over $MgSO_4$, filtered and evaporated. The crude product was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate, 2:1), yielding 3.51 g (85%) of the desired compound as a pale yellow viscous oil.
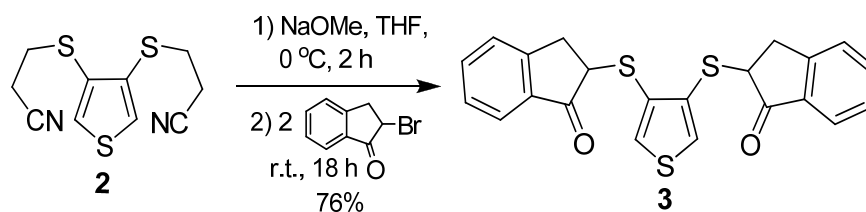
Method B

3,3'-(Thiophene-3,4-diylbis(sulfanediyl))dipropanenitrile **2**[5e,18] (4.70 g, 0.019 mol) was dissolved in dry THF (500 ml) and cooled to 0°C under N_2. Sodium methoxide (25 wt% sol in MeOH, 8.92 ml, 0.039 mmol) was added (mixture turned milky yellow) and the mixture was stirred for 1 hour. Purified 2-bromo-1-indanone (8.42 g, 0.040 mol) was added, the mixture allowed to reach room temperature and then the reaction stirred for 18 hours. The solvent was removed, the remaining solid dissolved in DCM (1200 ml), washed with water (5 × 400 ml), dried over $MgSO_4$, filtered and evaporated. The crude product was subjected to column chromatography on silica gel (petroleum ether/ethyl acetate, 2:1), yielding 5.88 g (76%) of the desired compound as a pale yellow viscous oil.

^{1}H NMR 500 MHz (CDCl$_3$) δ 7.79 (1H, d, ^3J = 7.55 Hz), 7.78 (1H, d, ^3J = 7.8 Hz), 7.61 (2H, t, ^3J = 7.5 Hz), 7.46 (s, 1H), 7.43 (s, 1H), 7.40 (4H, t, ^3J = 8.65 Hz), 4.20 (1H, dd, $^3J_1$ = 7.8 Hz, $^3J_2$ = 3.4 Hz), 4.19 (1H, dd, $^3J_1$ = 7.8 Hz, $^3J_2$ = 3.5 Hz), 3.62 (2H, dd, ^2J = 17.7 Hz, ^3J = 7.8 Hz), 3.16 (1H, dd, $^3J_1$ = 17.7 Hz, $^3J_2$ = 3.4 Hz), 3.15 (1H, dd, $^3J_1$ = 17.7 Hz, $^3J_2$ = 3.4 Hz) ppm. **^{13}C NMR** 100 MHz (CDCl$_3$) δ , 202.0, 201.95, 152.0, 135.43, 135.4, 135.2, 131.5, 131.4, 128.9, 128.8, 127.9, 126.42, 126.4, 124.58, 49.8, 49.7, 34.40, 34.38 ppm. **MS (EI$^+$)** m/z 408.0314 (M$^+$)(found), 408.0312 (calc.). **IR** ν = 2923 (sp^{3}C—H), 1698 (unsaturated C=O), 1594 (aromatic C=C), 1092 (S=C), 848 and 746 (aromatic C—H) cm^{-1}.
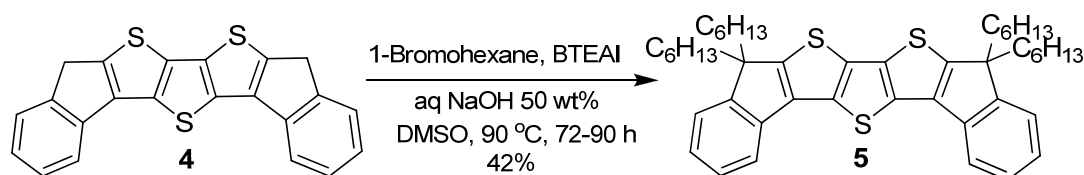
4. [1,2-*b*:2′,1′-*g*]Dihydrodiindeno-(dithieno)-[3,2-*b*:2,3-*d*]-thiophene
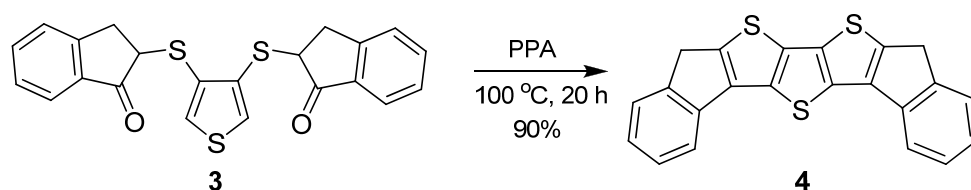
2,2'-(Thiophene-3,4-diylbis(sulfanediyl))bis(2,3-dihydro-1*H*-inden-1-one) **3** (1.55 g, 3.79 mmol) was placed in a round bottomed flask along with polyphosphoric acid (30 g), heated to *ca.* 100°C under N_2 and stirred at this temperature for 20 hours. Water (400 ml) was added and the product was extracted with DCM (5 × 300 ml), washed with water (3 × 300 ml), dried over $MgSO_4$, filtered and evaporated. The crude product was dissolved and boiled in toluene (*ca* 400 ml) with charcoal, filtered through a silica plug and left to crystallize, yielding 1.27 g (90%) of the product as pale-pink fine needle-like crystals. The product can be sublimed at 220°C and 0.3 mm Hg.

M. p. decomposes at 268-270°C. **^{1}H NMR** 400 MHz ($CDCl_3$) δ 7.65 (2H, d, ^3J = 6.4 Hz), 7.55 (2H, d, ^3J = 7.6 Hz), 7.45 (2H, t, ^3J = 7.4 Hz), 7.28 (2H, dt, $^3J_1$ = 7.4 Hz, $^3J_2$ = 1.2 Hz), 4.00 (4H, s) ppm. **MS (EI$^+$)** m/z 372.0107 (M$^+$) (found), 372.0101 (calc.). **IR** ν = 1602 (aromatic C=C), 1440 (sp^{3}C—H), 1183 (S=C), 754 (aromatic C—H) cm$^-$^{1}. **Anal. calcd**. for ($C_{22}H_{12}S_3$): C, 70.93; H, 3.25; S, 25.82%. Found: C, 70.81; H, 2.99; S, 26.01%.

5. [1,2-*b*:2′,1′-*g*]Dihexyldiindeno-(dithieno)-[3,2-*b*:2,3-*d*]-thiophene
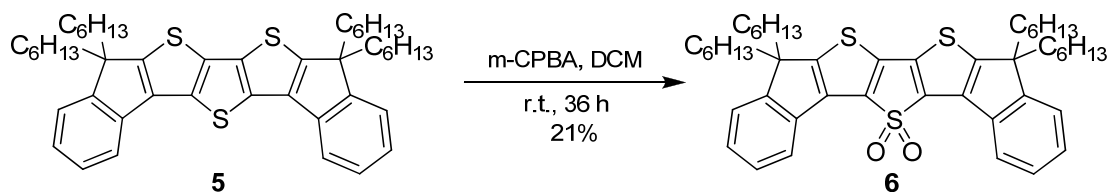

[1,2-*b*:2′,1′-*g*]Dihydrodiindeno-(dithieno)-[3,2-*b*:2,3-*d*]-thiophene **4** (50 mg, 0.134 mmol), benzyltriethylammonium iodide (BTEAI, *ca.* 10 mg), 1-bromohexane (0.15 ml, 1.072 mmol) and DMSO (11.5 ml) were placed in a round bottomed flask and degassed for 20 minutes with N_2. Degassed aqueous NaOH solution (50 wt%, 0.1 ml)

was added dropwise to the flask and the mixture was heated to 90-95°C until all of the solid dissolved; the mixture was then left to stir for a further 72 hours. The reaction was monitored by TLC (petroleum ether). When most of the starting material was converted, the mixture was poured over a saturated solution of ammonium chloride (15 ml) and extracted with DCM (3 × 25 ml). The organic layers were washed with water (3 × 25 ml), dried over MgSO$_4$, filtered and evaporated. The crude product was subjected to column chromatography on silica gel (petroleum ether) yielding 40 mg (42%) of the product as a pale viscous oil.

^{1}H NMR 400 MHz (CDCl$_3$) δ 7.58 (2H, d, ^3J = 7.2 Hz), 7.39 (2H, dt, $^3J_1$ = 7.6 Hz, $^3J_2$ = 0.8 Hz), 7.35 (2H, d, ^3J = 7.2 Hz), 7.27 (2H, dt, $^3J_1$= 7.6 Hz, $^3J_2$ = 0.8 Hz), 1.99 (8H, m), 1.22-0.84 (32H, br m), 0.8 (12H, t, ^3J = 6.8 Hz) ppm. **^{13}C NMR** 100 MHz (CD$_2$Cl$_2$) δ 154.30, 153.84, 137.63, 137.46, 134.83, 131.93, 127.23, 125.39, 122.76, 119.53, 57.03, 40.26, 31.91, 29.92, 24.43, 22.92, 14.11 ppm. **MS (FAB$^+$)** m/z 709.393 (M+H)$^+$ (found), 708.386 (calc.). **IR** ν = 2929 and 2857 (sp^{3}C—H), 1602 (aromatic C=C), 1457 (sp^{3}C—H), 1177 (S=C), 752 (aromatic C—H) cm^{-1}.

6. [1,2-*b*:2′,1′-*g*]Dihexyldiindeno-(dithieno)-[3,2-*b*:2,3-*d*]-*S,S*-dioxy-thiophene


[1,2-*b*:2′,1′-*g*]Dihexyldiindeno-(dithieno)-[3,2-*b*:2,3-*d*]-thiophene **5** (90 mg, 0.127 mmol) and meta-chloroperoxybenzoic acid (270 mg, 1.27 mmol) were dissolved in dry DCM (11 ml) and stirred for 36 hours at room temperature. The mixture was poured over a saturated solution of sodium sulfite Na$_2$SO$_3$ (30 ml) and the product extracted with DCM (150 ml). The organic layer was washed with water (3 × 50 ml) and brine (60 ml), dried over MgSO$_4$, filtered and evaporated. The crude product was

subjected to column chromatography on silica gel (DCM/petroleum ether, 1:3) and precipitated with acetonitrile yielding 20 mg (21 %) of a bright yellow powder.

M. p. 72-74°C. **^{1}H NMR** 400 MHz (CD$_2$Cl$_2$) δ 7.70 (2H, d, ^3J = 7.2 Hz), 7.43-7.33 (6H, m), 1.98 (8H, m), 1.28-0.88 (32H, br m), 0.83 (12H, t, ^3J = 7.0 Hz) ppm. **^{13}C NMR** 100 MHz (CD$_2$Cl$_2$) δ 156.68, 154.08, 140.19, 138.29, 135.32, 134.13, 127.78, 127.01, 123.00, 121.47, 57.53, 39.89, 31.85, 29.84, 24.52, 22.91, 14.11 ppm. **MS (FAB$^+$)** m/z 741.384 (M+H)$^+$ (found), 740.3755 (calc.). **IR** ν = 2929 and 2852 (sp^{3}C—H), 1679 (aromatic C=C), 1314 and 1141 (-SO$_2$-), 754 (aromatic C—H) cm^{-1}. **Anal. calcd.** for (C$_{46}$H$_{60}$O$_2$S$_3$): C, 74.54; H, 8.16; O, 4.32; S, 12.98%. Found: C, 74.02; H, 7.87; S, 12.48%

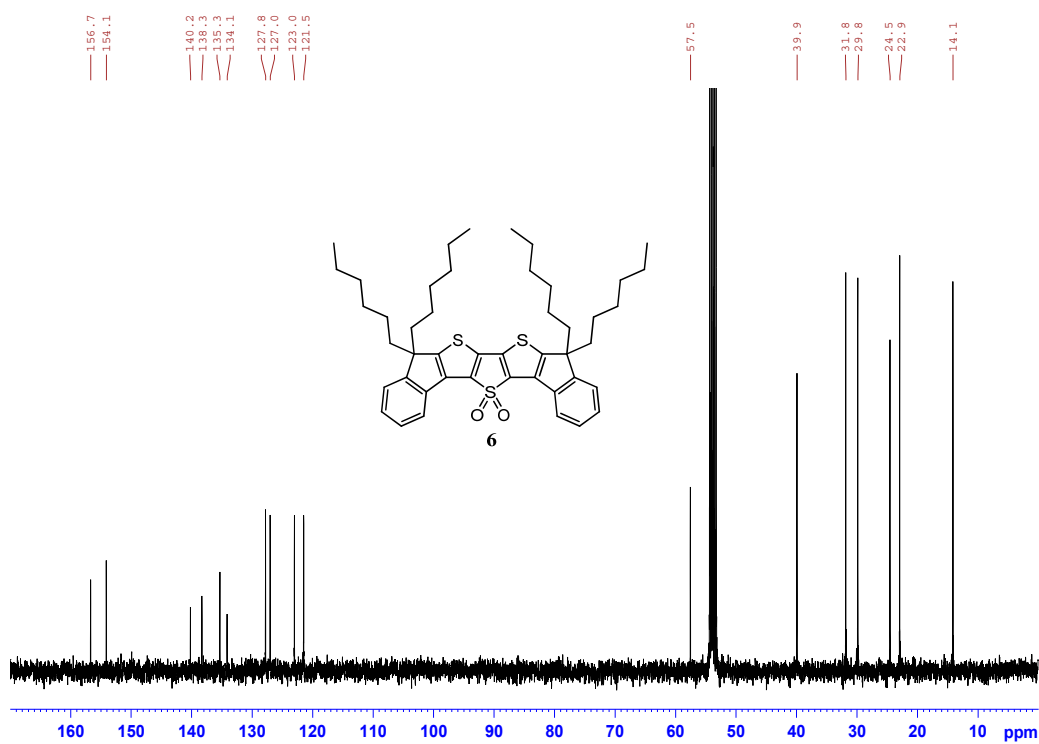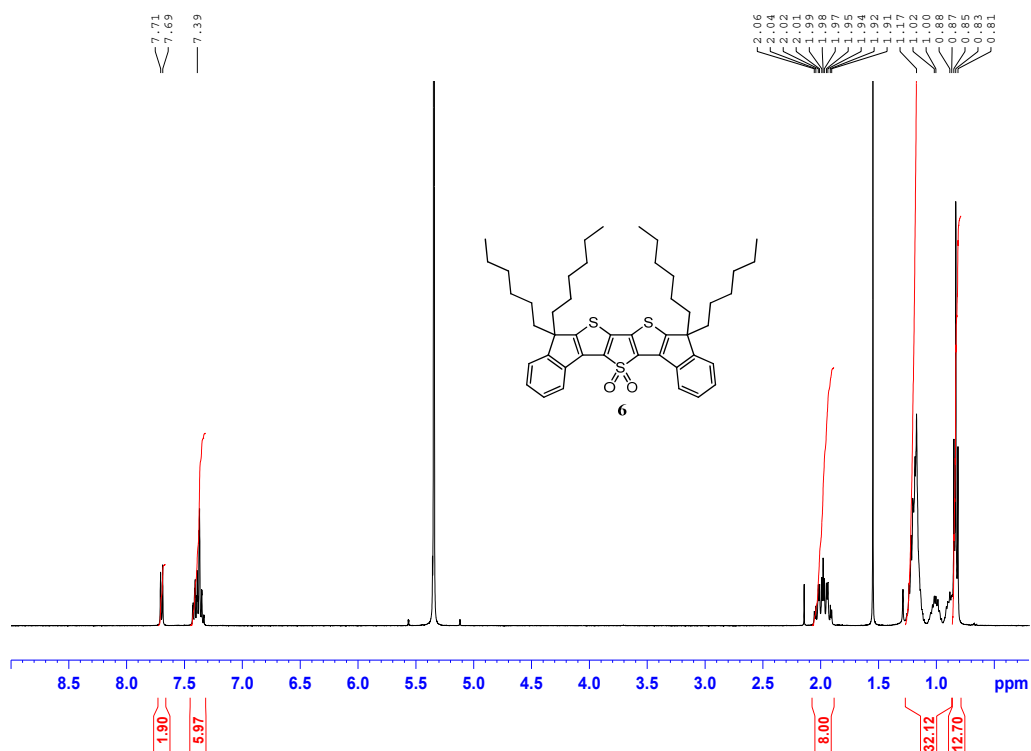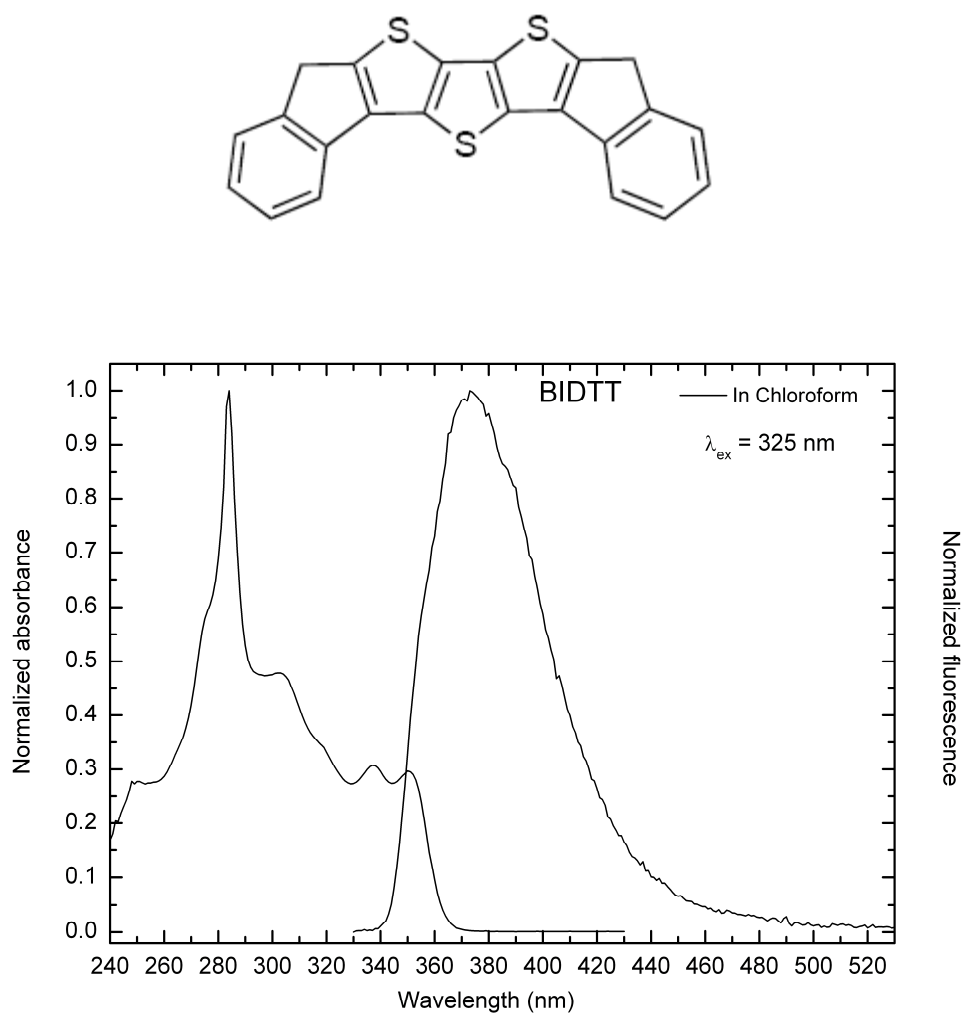# ^{1}H and ^{13}C NMR spectra
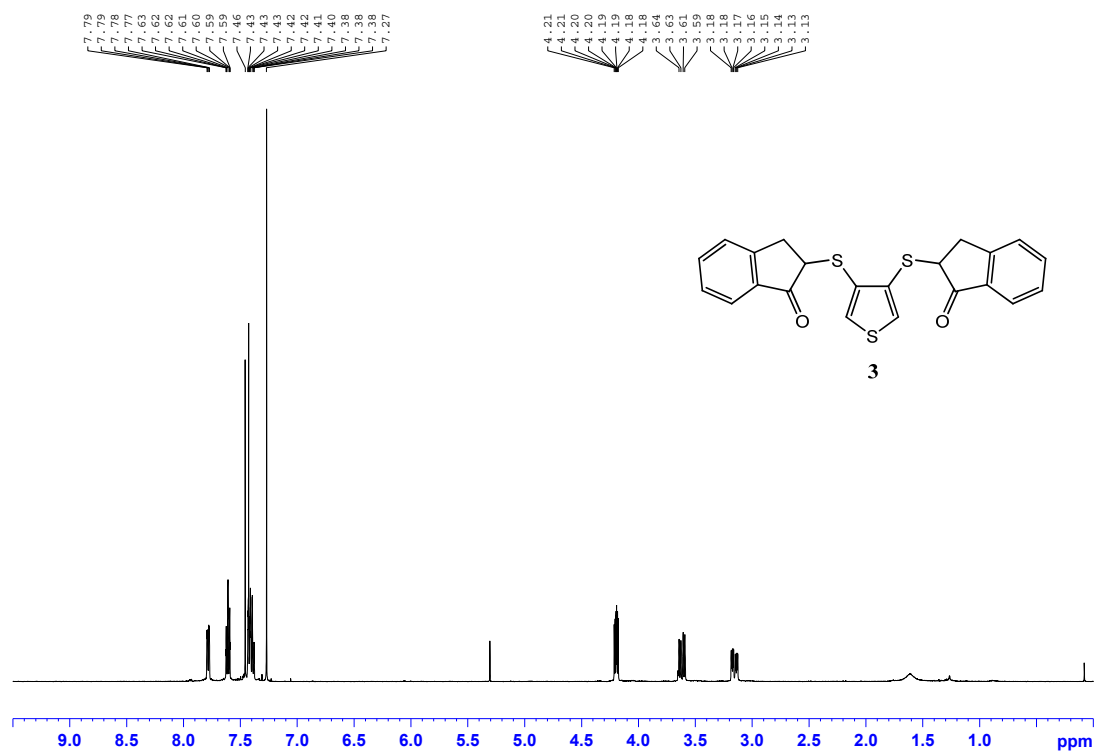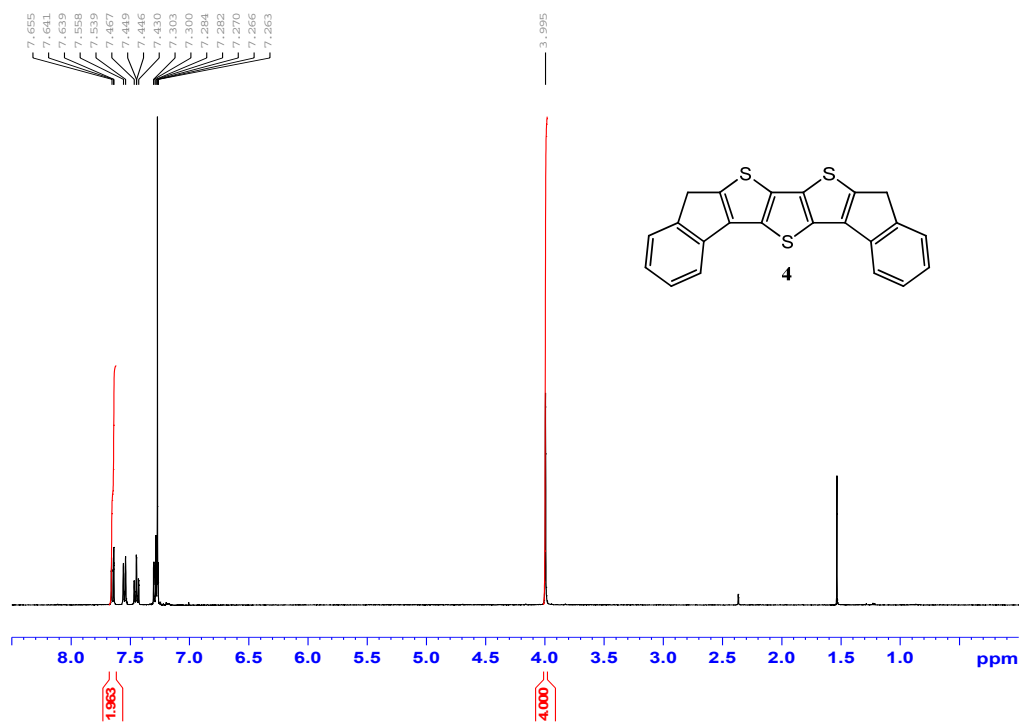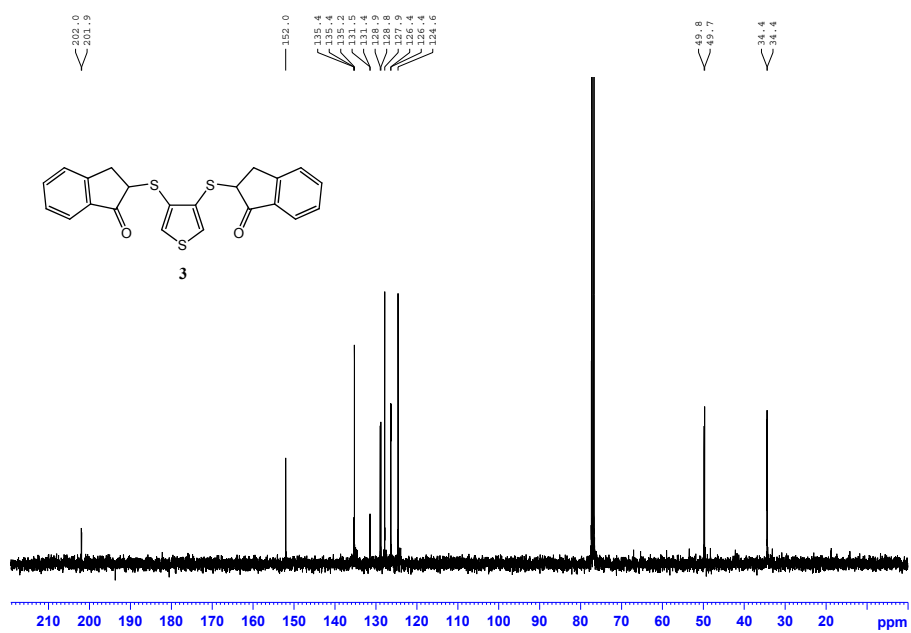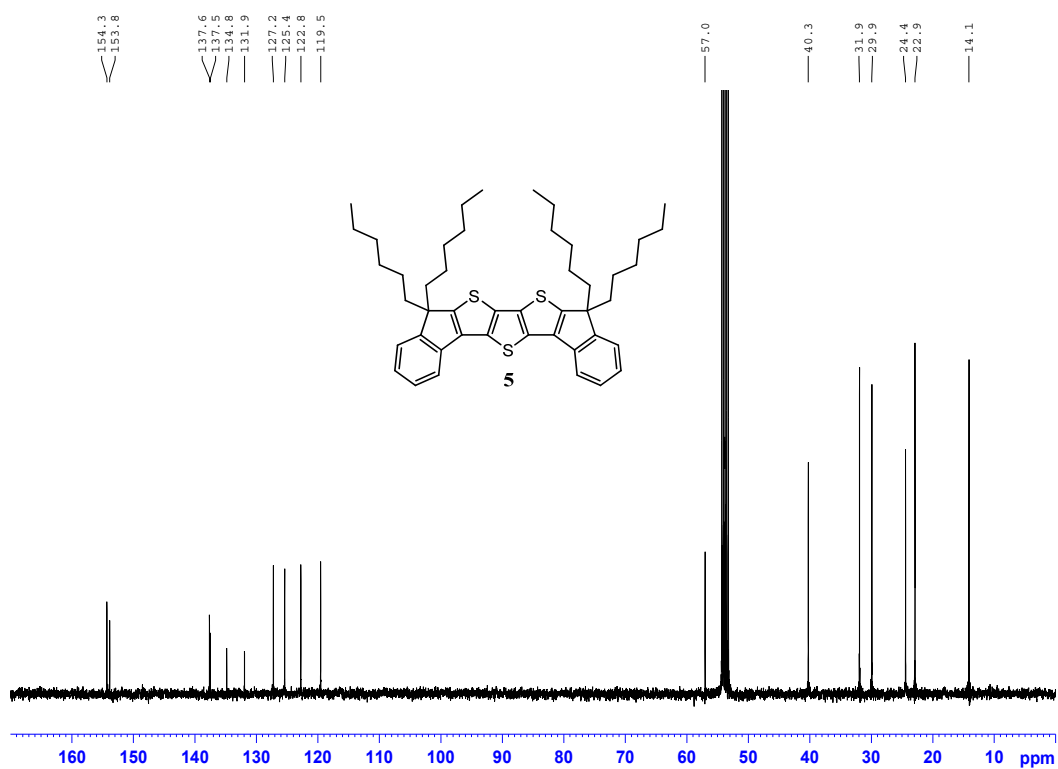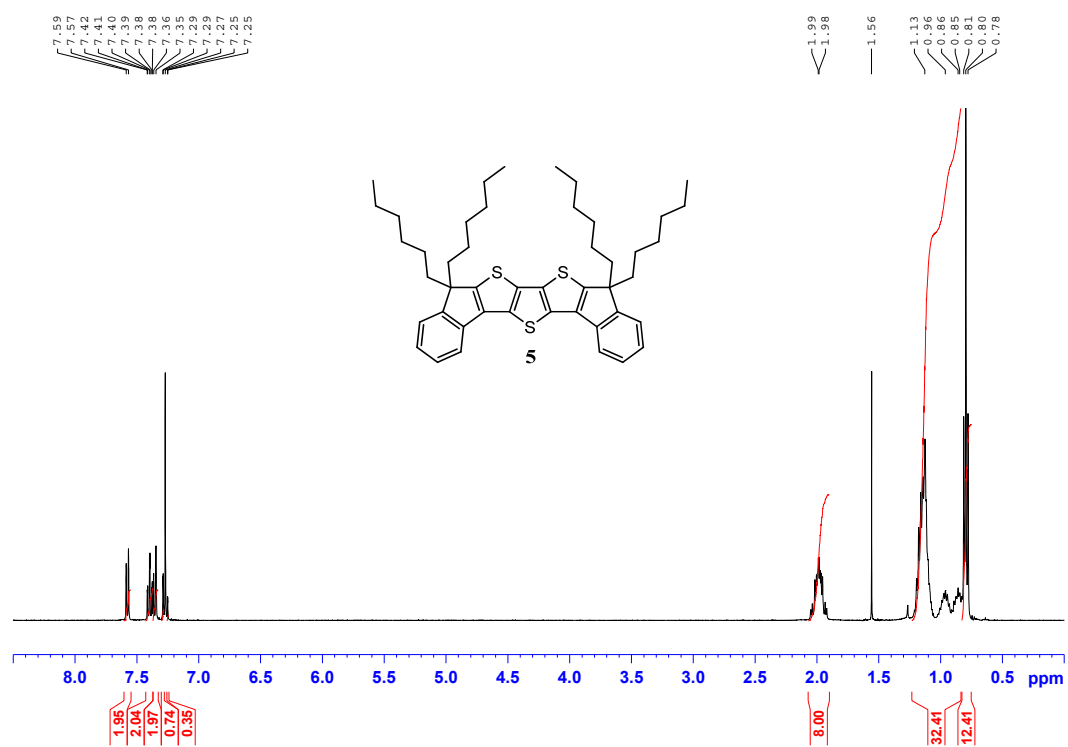
Figure S1 Normalised absorption and emission spectra for compounds **4**.

S1

A solvatochromic experiment was used to determine that the peak at 419 nm for compound **6** is an intramolecular charge transfer; five solvents of varying solvation character (hexane, diethyl ether, tetrahydrofuran, dichloromethane and dimethyl sulfoxide) were used to record absorption spectra. The table below shows that with increasing solvation character there is an increase in λ_{max}, indicating through positive solvatochromism that compound **6** undergoes intramolecular charge transfer.

Table S1. Solvatochromic data of compound **6** in selected solvents with π* values by Kamlet and Taft[1]

Solvent	π*	Peak max / nm
Hexane	-0.08	407
Diethyl Ether	0.27	411
Tetrahydrofuran	0.58	414
Dichloromethane	0.82	419
Dimethyl sulfoxide	1.00	423

Photoluminescence quantum yield:

Solutions (PLQY)

Solution photoluminescence quantum yields of the samples were measured by preparing a sample in chloroform solvent with the same absorption at 360 nm as a standard solution of quinine sulphate in 0.5 M sulphuric acid.

The emission spectrum was then measured in a JY Horiba Fluoromax spectrometer with the samples excited at 360 nm.

Table S2

Samples	$\lambda_{abs, max}$ (nm)	$\lambda_{em, max}$ (nm)	PLQY	Absorbance @360 nm	Comments
					$\lambda_{ex} = 360$ nm
4	284	373	0.01±0.004	0.102	Solvent Chloroform
5	273	376	0.004±0.002	0.0975	Solvent Chloroform
6	419	524	0.72±0.07	0.105	Solvent Chloroform

Films (PLQY)

The photoluminescence quantum yield of the films were determined using a He-Cd laser operating at 325nm to excite the sample and an integrating sphere to collect the resulting emission following the method of Greenham *et. al.*[2] The integrating sphere containing the sample was purged with nitrogen

Table S3

Samples	Conc.	Spin speed	Thickness	$\lambda_{abs, max}$ (nm)	$\lambda_{em, max}$ (nm)	PLQY@ 325 nm
5	25 mg/ml	1500	140±5 nm	273	376	-
6	20 mg/ml	1500	85±3 nm	414	508	0.14±0.02

Time resolved spectroscopy of DITT derivatives

Fluorescence lifetime measurements:

The lifetime of a fluorescent molecule is determined by the rate of radiative and non-radiative decay processes dissipating the excited state energy. The PLQY is equal to the ratio of the radiative rate to the sum of radiative and non-radiative rates. By combining measurements of PLQY and fluorescence lifetime in solutions and thin films it is possible to obtain more information about the impact of molecular interactions.

Time-resolved fluorescence measurements were made by the time correlated single photon counting (TCSPC) technique. A pulsed nitride laser diode at 393 nm was used to excite the sample and the resulting emission passed through a monochromator to a microchannel plate-photomultiplier.

The time delay between the excitation pulse and the photon detection was determined by a time to amplitude converter and a histogram of the measured time delays accumulated. Decay curves were fitted by iterative reconvolution of the instrument response function with one or two exponential decay functions, as described below. The instrument response function was recorded by scattering from Ludox solution.

For the compounds in solutions with emission collected at the peak of the fluorescence signal ie at 376 nm and at longer wavelengths i.e. at 600 nm the fluorescence signal decays were described by a mono exponential decay function:
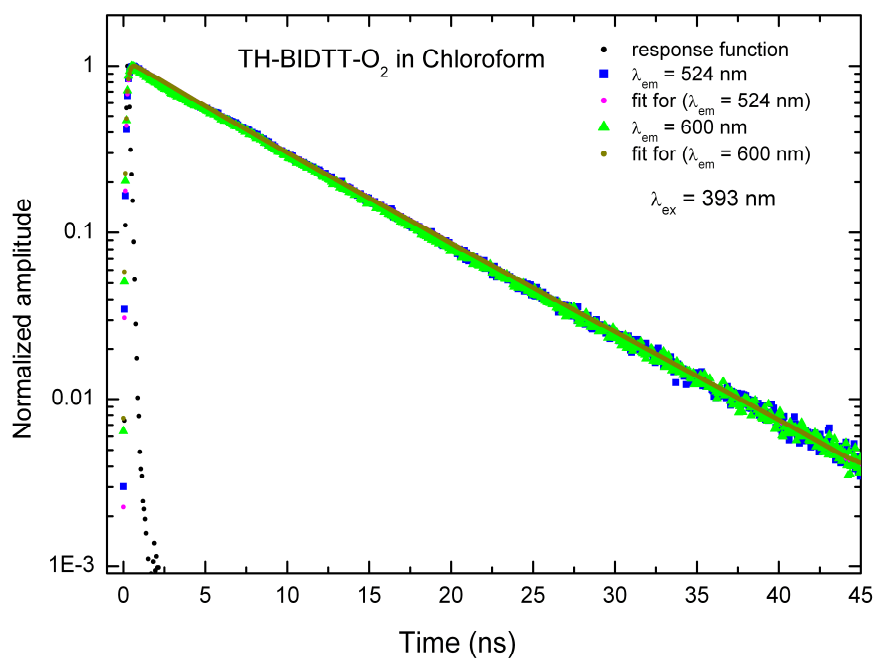
$$S_F(t) = A_1 \exp(-t/\tau) + B$$

Where τ is the fluorescence lifetime and B is a constant.

For the films with emission collected at the peak at 524 nm and at longer wavelength i.e. at 600 nm the fluorescence signal decays were described by a bi-exponential decay function.
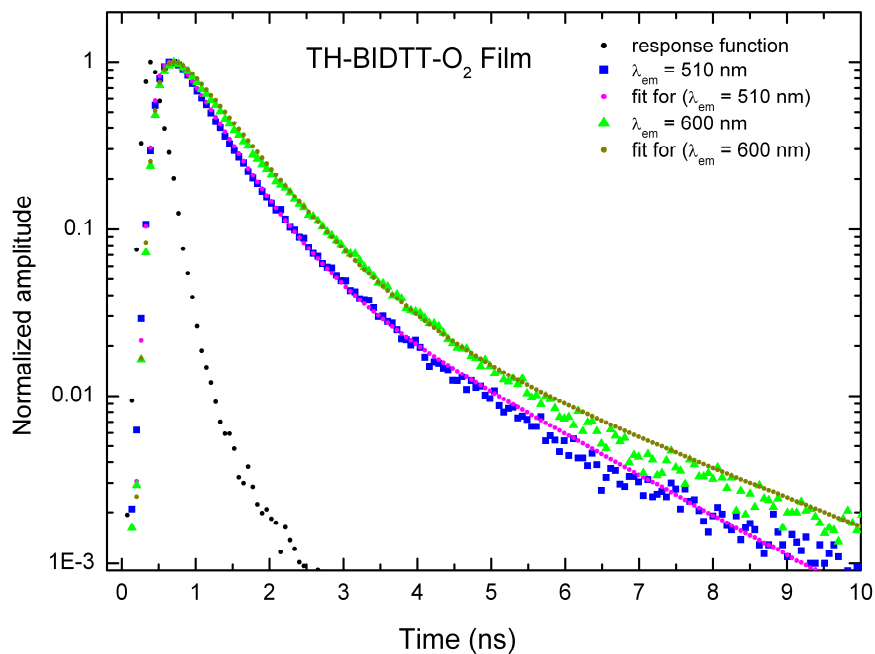
$$S_F(t) = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) + B$$

TCSPC of compound 6 in solution

Emission collected	A_1	τ_1	χ^2
λ_{em} = 524 nm	1	7.89	1.16
λ_{em} = 600 nm	1	7.90	1.42

TCSPC of compound 6 as a film

Emission collected	A_1	τ_1	A_2	τ_2	χ^2
λ_{em} = 510 nm	0.79	0.497	0.21	1.77	0.82
λ_{em} = 600 nm	0.85	0.689	0.15	2.41	0.92

References

1. M. J. Kamlet, J. L. M. Abboud, M. H. Abraham and R. W. Taft, *J. Org. Chem.*, 1983, 48, 2877.
2. N. C. Greenham, I. D. W. Samuel, G. R. Hayes, R. T. Phillips, Y. Kessener, S. C. Moratti, A. B. Holmes and R. H. Friend, *Chem. Phys. Lett.*, 1995, 241, 89.