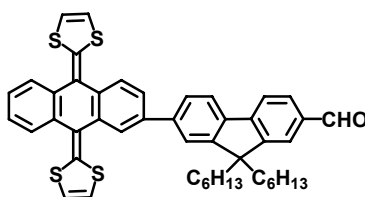


Electronic Supplementary Information for Chemical Communications

Experimental Section

^{13}C and ^1H NMR spectra were recorded with either a 300, or 500 MHz spectrometer for ^1H -NMR and either a 75 or 125 MHz spectrometer for ^{13}C -NMR. Chemical shifts are given as δ values (internal standard: TMS). Cyclic voltammograms were recorded on a potentiostat/galvanostat equipped with a software GPES for Windows version 4.8. The electrochemical analyses were carried out using a GCE (glassy carbon) as working electrode, SCE (standard calomel) as reference electrode, Bu_4NClO_4 as supporting electrolyte, and *o*-dichlorobenzene/acetonitrile (ratio 4:1 v/v) as solvent at a scan rate of 100 mV/s. The purity of compounds **2a,b** and **3a,b** has been proven by HPLC chromatography (column: Cosmosil Buckyprep, 4.6 I. D x 250 mm; solvent: toluene/acetonitrile 8/2 v/v; flow rate: 0.5 ml min^{-1}).

7-(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-6-yl)-9,9-dihexyl-9H-fluorene-2-carbaldehyde (**2a**).

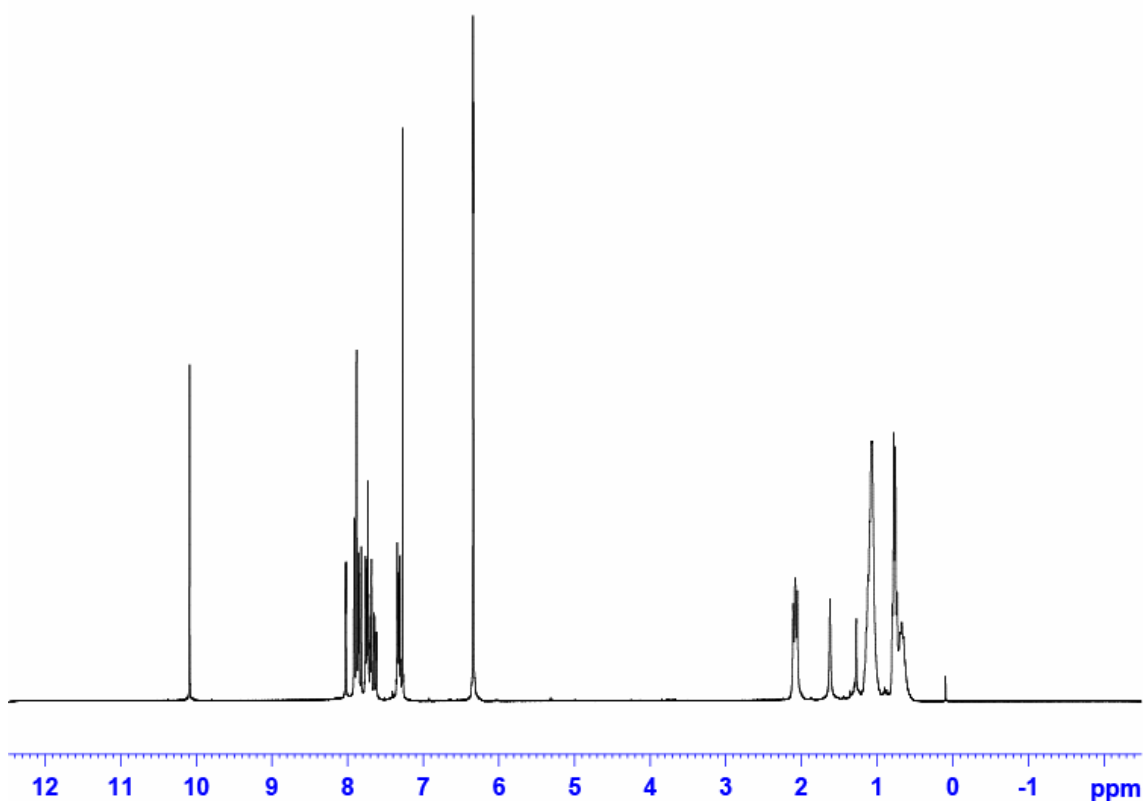


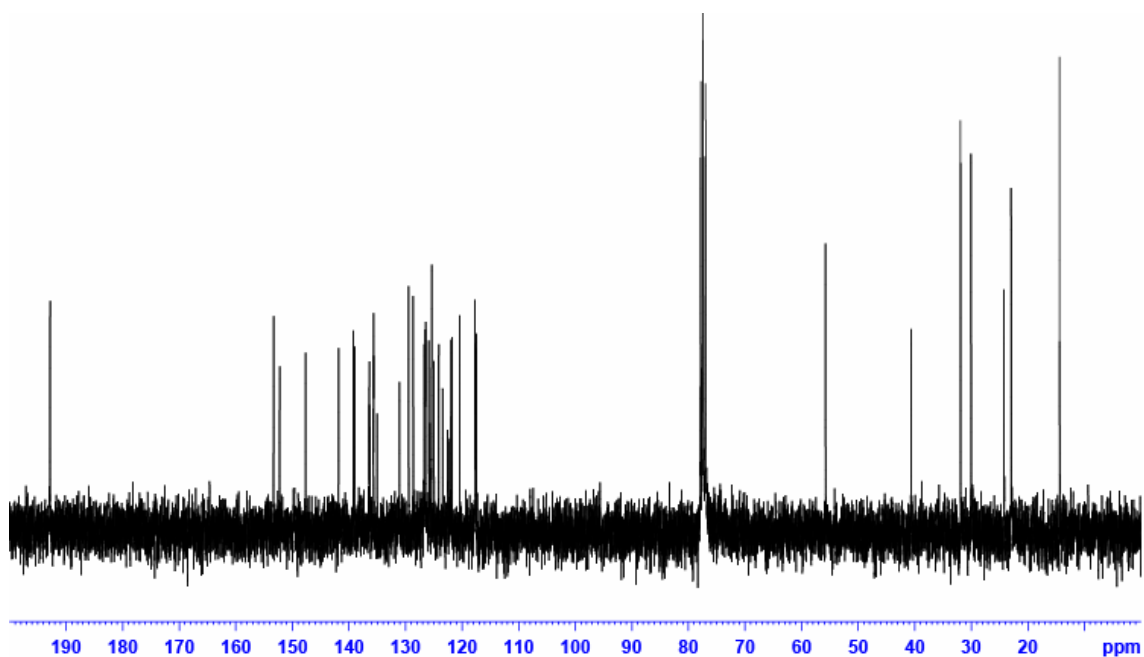
2-Iodo-*ex*TTF (112 mg, 1.1 equiv., 0.22 mmol), K_2CO_3 (210 mg, 1.6 mmol, 8.0 equiv.), $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (10 mg) and 7-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dihexylfluorene-2-carbaldehyde **1a** (98 mg, 1 equiv., 0.2 mmol) were reacted via standard Suzuki-Miyaura coupling and purified using toluene/hexane as eluent to yield **2a** (77 mg, 52%) as an orange solid.

^1H -NMR (300 MHz, CDCl_3), δ : 10.08 (s, 1H, CHO), 8.02 (d, 1H, $J=1.8$ Hz, ArH), 7.91-7.82 (m, 5H, ArH), 7.77- 7.68 (m 4H, ArH), 7.65-7.61 (dd 1H, $J=1.8$ Hz, $J= 8.2$ Hz,

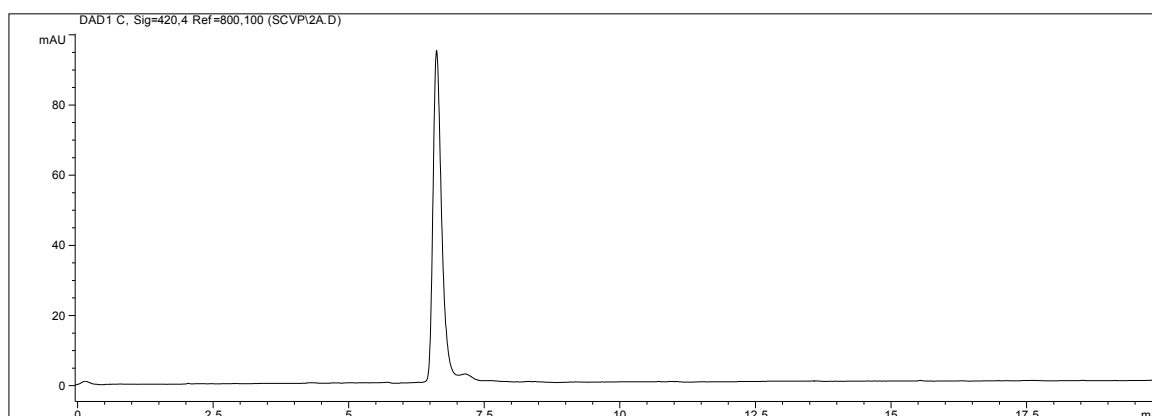
$\text{Ar}_{\text{extff}}\text{H}$), 7.33-7.29 (m, 2H, $\text{Ar}_{\text{extff}}\text{H}$), 6.34 (s, 2H, CH_{extff}), 6.33 (s, 2H, CH_{extff}), 2.08 (dd 4H, $J=7.3\text{Hz}$, $J=9.0\text{Hz}$, $\text{CH}_2_{\text{aliph}}$) 1.14- 1.06 (m, 12H), 0.78-0.65 (m, 10H).

^{13}C -NMR (300 MHz, CDCl_3), δ : 192.82, 153.33, 147.67, 141.84, 139.20, 139.01, 136.41, 136.37, 136.31, 135.04, 131.07, 126.71, 126.50, 126.46, 125.90, 125.38, 124.96, 124.12, 123.45, 122.59, 122.25, 121.96, 121.77, 120.42, 117.76, 117.71, 117.63, 117.48, 55.77, 40.66, 31.90, 30.12, 30.04, 24.24, 22.98, 14.41. ESI-MS, m/z : 763 $[\text{M}+\text{Na}]^+$.

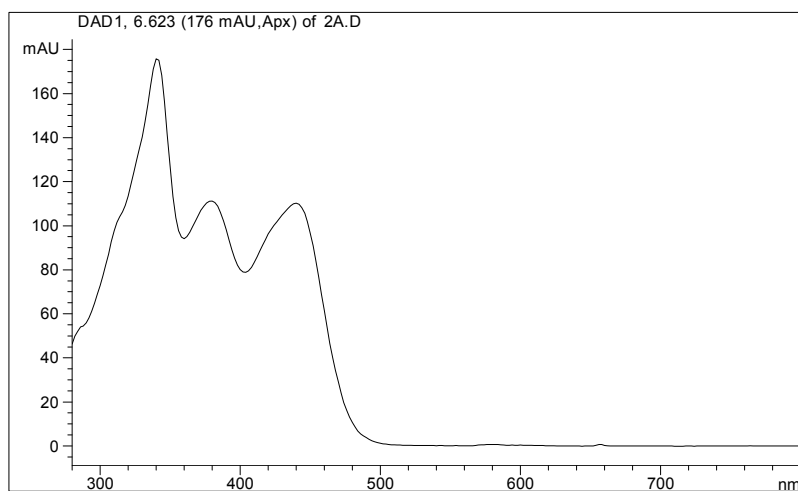




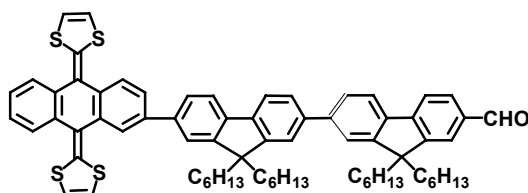
HPLC diagram



UV spectrum



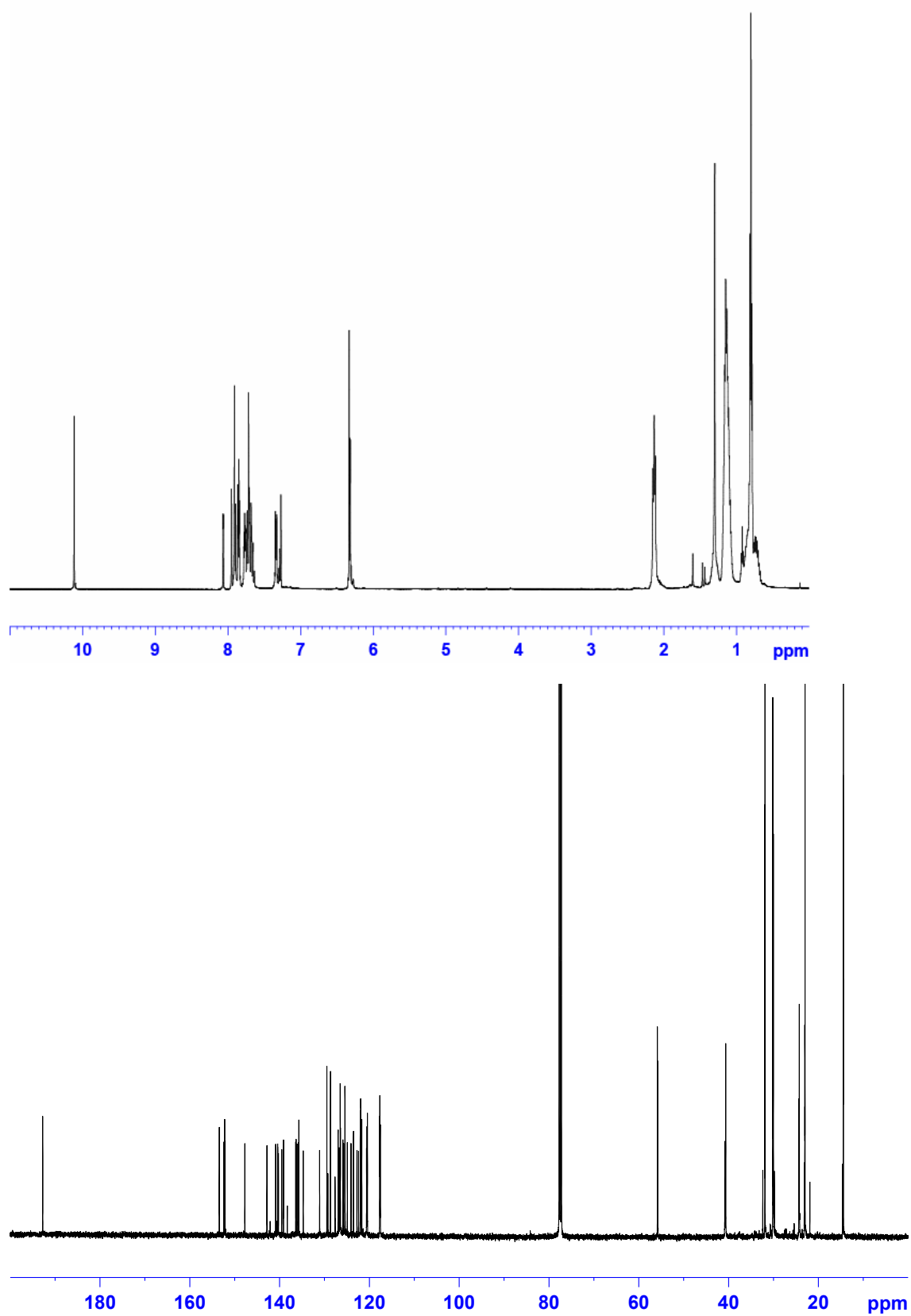
7'-(2-(9,10-di(1,3-dithiol-2-ylidene)-9,10-dihydroanthracen-6-yl)-9,9-dihexyl-9H-fluoren-7-yl)-9',9'-dihexyl-9'H-fluorene-2'-carbaldehyde (2b).



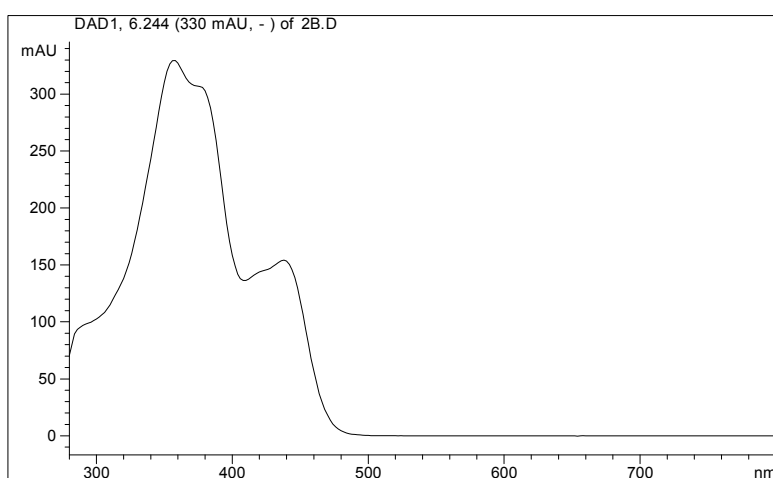
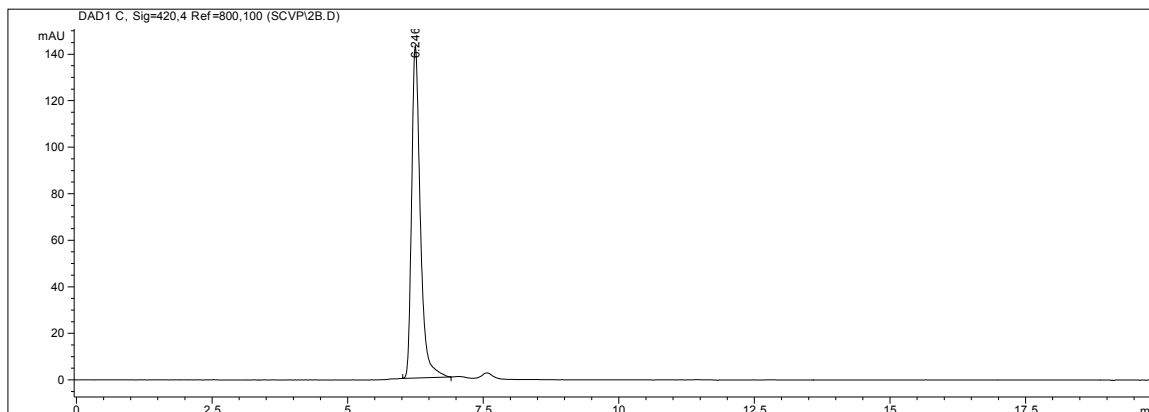
2-Iodo-*ex*TTF (112 mg, 1.5 equiv., 0.22 mmol), K₂CO₃ (210 mg, 1.6 mmol, 8.0 equiv.), Pd(PPh₃)₂Cl₂ (10 mg) and **1b** (126 mg, 1 equiv., 0.15 mmol) were reacted via Suzuki coupling and purified using toluene/hexane as eluent to yield **2b** (66%).

¹H-NMR (500 MHz, CDCl₃), δ: 10.12 (s, 1H, CHO), 8.06 (d, 1H, *J*=1.7 Hz, ArH), 7.96-7.83 (m, 6H, ArH), 7.79- 7.68 (m, 8H, ArH), 7.67-7.65 (dd, 1H, *J*=1.9 Hz, *J*= 8.0 Hz, Ar_{extttf}H), 7.35-7.31 (m, 3H, Ar_{extttf}H), 6.33 (s, 2H), 6.31 (d, 2H, *J*= 2.1 Hz), 2.13 (bt, 8H, *J*= 8.2 Hz, CH₂ aliph), 1.18- 1.06 (m, 22H), 0.85-0.60 (m, 22H).

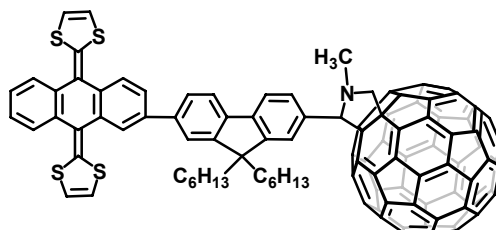
¹³C-NMR (125 MHz, CDCl₃), δ: 192.75; 153.4; 152.4; 152.3; 152.2; 147.7; 142.8; 140.9; 140.5; 140.4; 140.2; 139.5; 139.1; 139.1; 136.4; 136.3; 136.1; 135.8; 135.7; 135.6; 134.3; 131.1 ; 129.5; 129.2; 128.7; 127.6; 127.0; 126.7; 126.5; 126.4; 125.9; 125.7; 125.4; 124.9; 124.1; 123.5; 122.8; 122.4; 122.0; 121.9; 121.7; 120.6; 120.5; 120.4; 117.7; 117.6; 117.5; 55.8; 55.7; 40.8; 40.6; 31.9; 31.8; 30.2; 30.1; 30.0; 24.3; 24.2; 23.1; 23.0; 22.9; 14.5; 14.4. ESI-MS, *m/z*: 1096 [M+Na]⁺.



HPLC diagrams



exTTF-Fl-C₆₀ (3a).

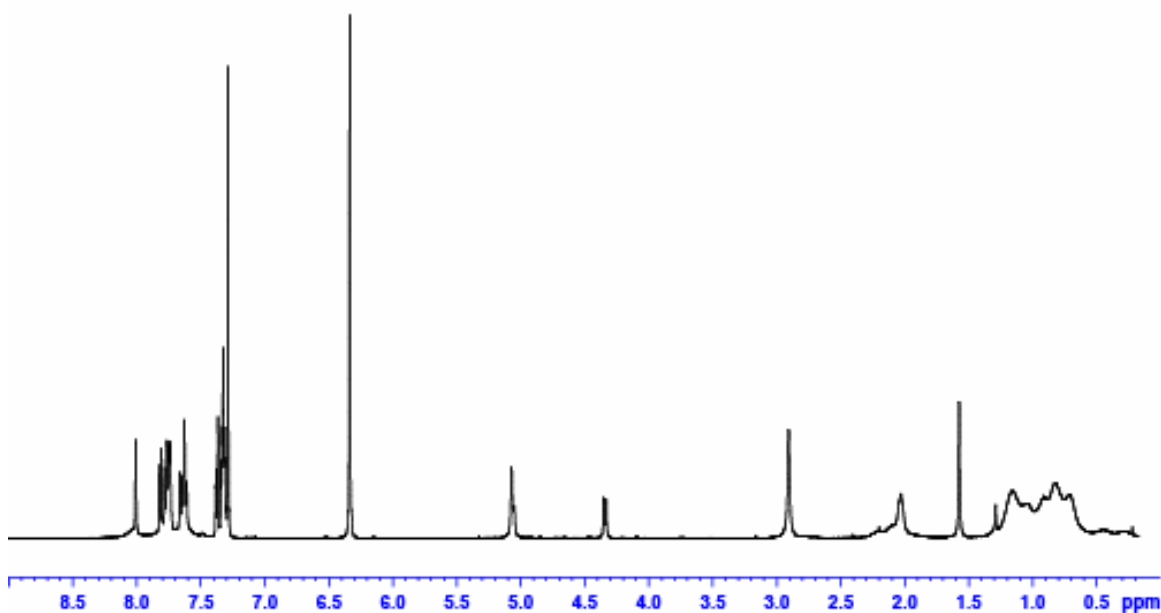


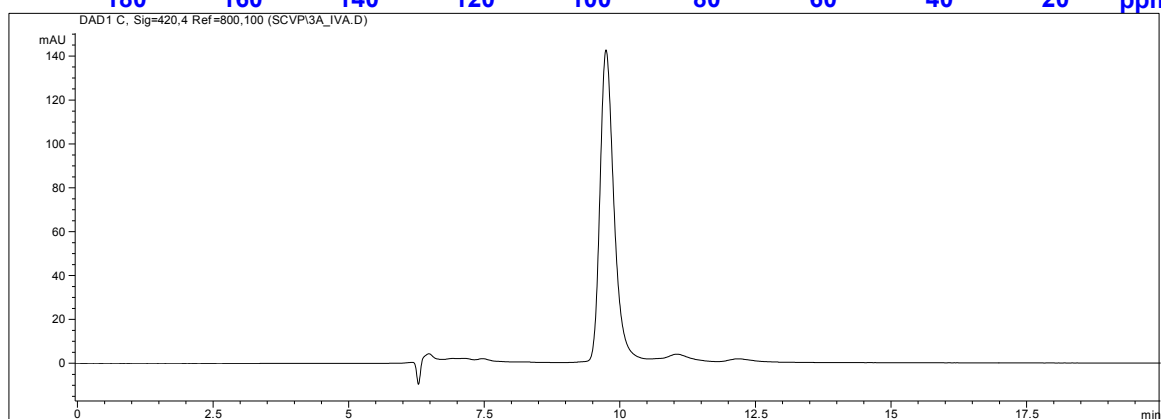
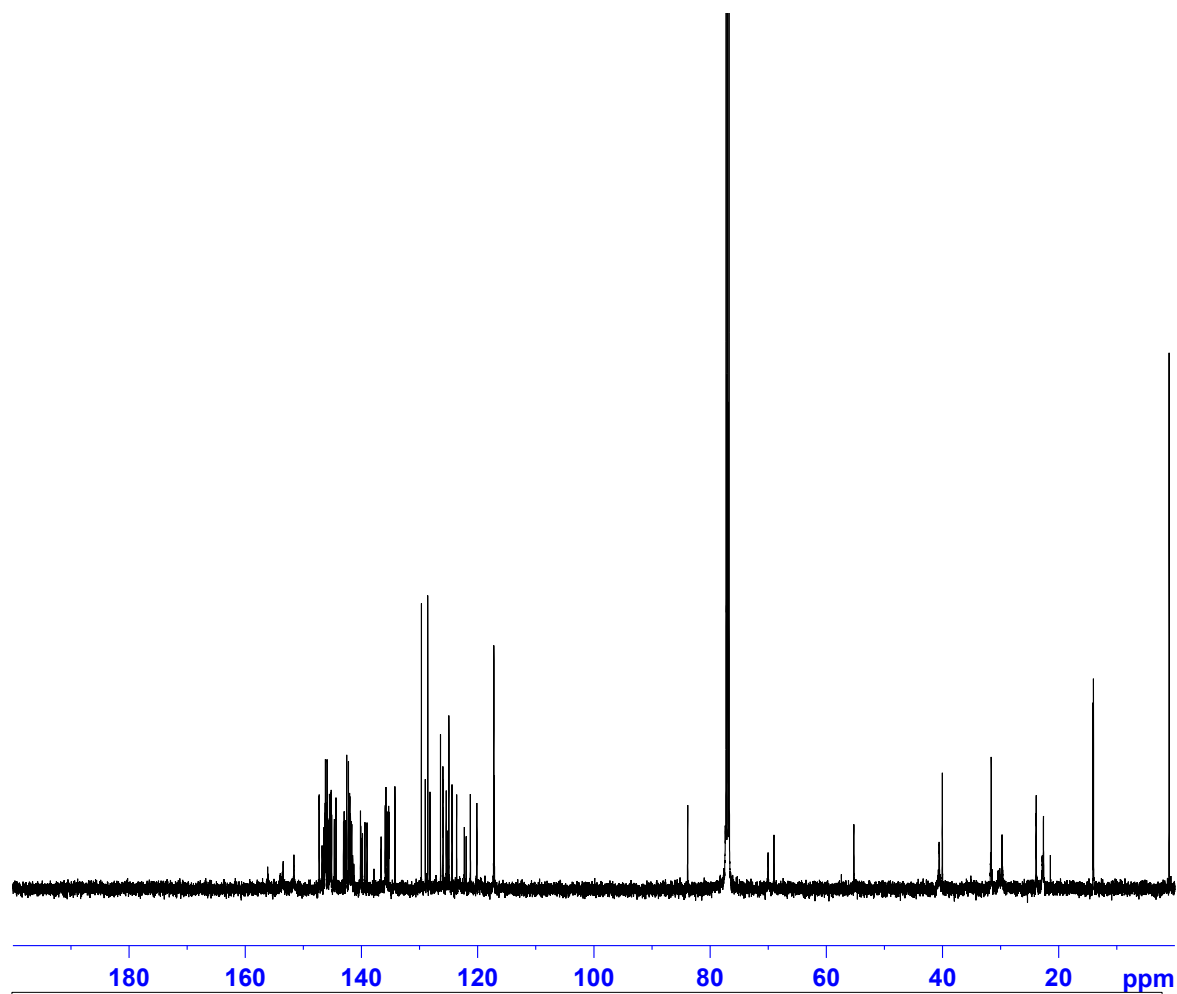
Sarcosine (90 mg), C₆₀ (400 mg) and exTTF-fluorene aldehyde **2a** (100mg) were refluxed in chlorobenzene under argon and without light for 2 h. The solvent was removed *in vacuo*

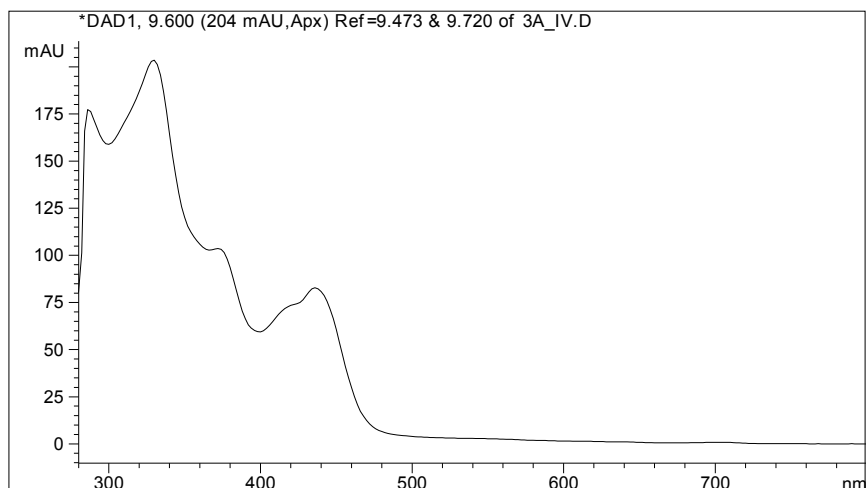
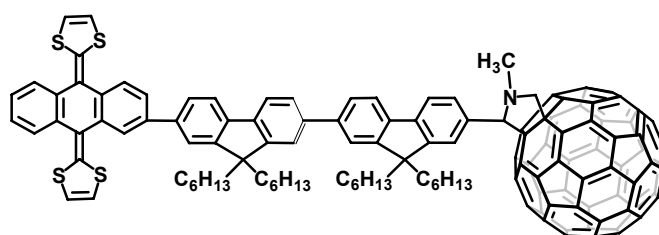
in the dark. The purification was carried out, in the dark, on a silica gel column (eluent CS₂ then toluene). Yield: 27%.

¹H-NMR (500 MHz, CDCl₃), δ: 8.02 (bs, 2H, ArH), 7.81 (d, 1H, *J*=8.1Hz), 7.77 (d, 1H, *J*=7.9Hz), 7.75 (dd, 2H, *J*=3.1Hz, *J*=5.6Hz), 7.65 (d, 1H, *J*=8.1Hz), 7.62 (m, 2H), 7.37 (m, 1H), 7.32 (m, 3H), 6.34 (bs, 4H), 5.06 (bd, 2H, *J*=10.0Hz), 4.34 (d, 1H, *J*=9.4Hz), 2.91 (s, 3H), 2.03 (bs, 4H), 1.3-0.5 (bm, 22H).

¹³C-NMR (125 MHz, CDCl₃), δ: 156.15; 153.48; 151.63; 147.27; 146.78; 146.47; 146.30; 146.23; 146.20; 146.14; 146.11; 146.08; 145.91; 145.72; 145.55; 145.51; 145.49; 145.44; 145.34; 145.29; 145.25; 145.21; 145.13; 144.67; 144.37; 143.09; 142.97; 142.67; 142.54; 142.24; 142.14; 142.13; 142.05; 142.01; 141.89; 141.75; 141.67; 141.51; 141.31; 140.17; 140.12; 140.01; 139.83; 139.41; 139.04; 136.62; 135.91; 135.85; 135.78; 135.53; 135.32; 135.29; 134.24; 129.68; 128.59; 126.01; 125.98; 125.93; 125.41; 124.96; 124.41; 123.62; 122.30; 121.98; 121.26; 120.14; 117.22; 117.13; 83.85; 70.01; 69.01; 55.26; 40.598; 40.03; 31.72; 31.62; 29.76; 23.87; 22.82; 22.63; 14.10. ESI-MS, *m/z*: 1488 [M]⁺.



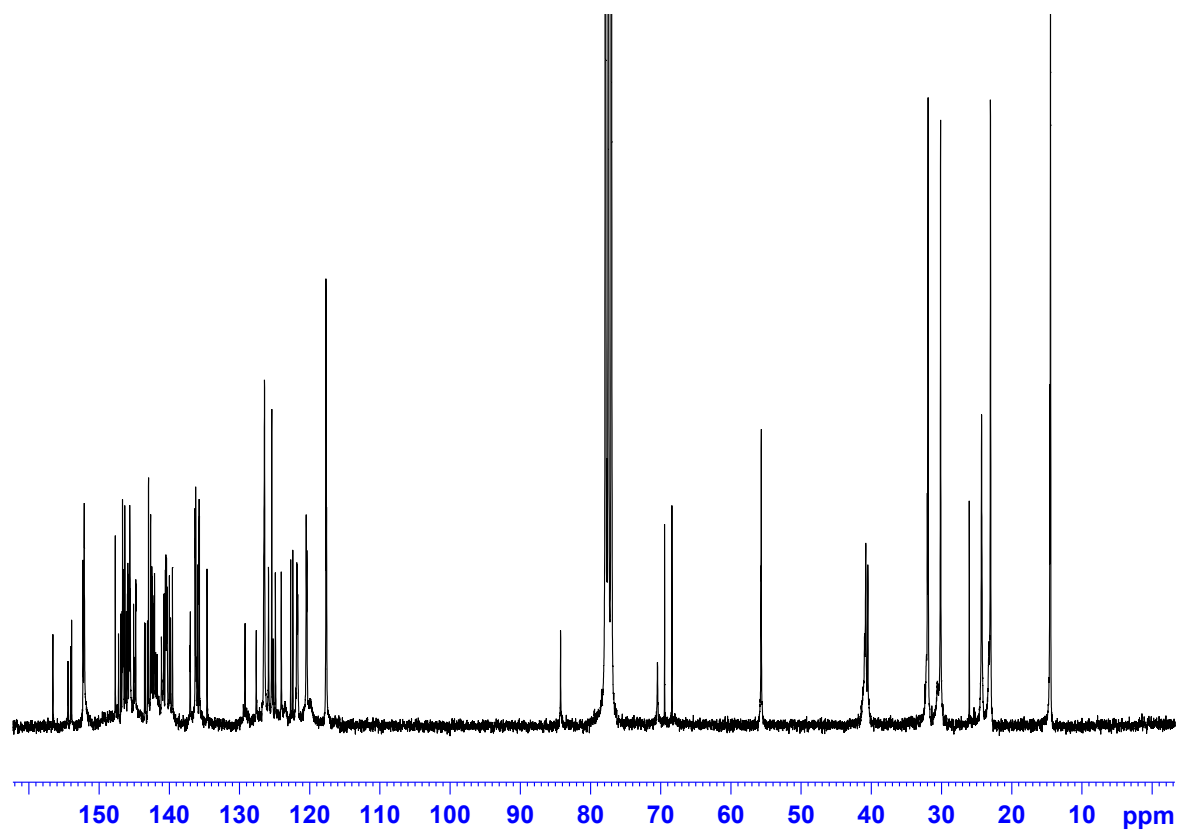
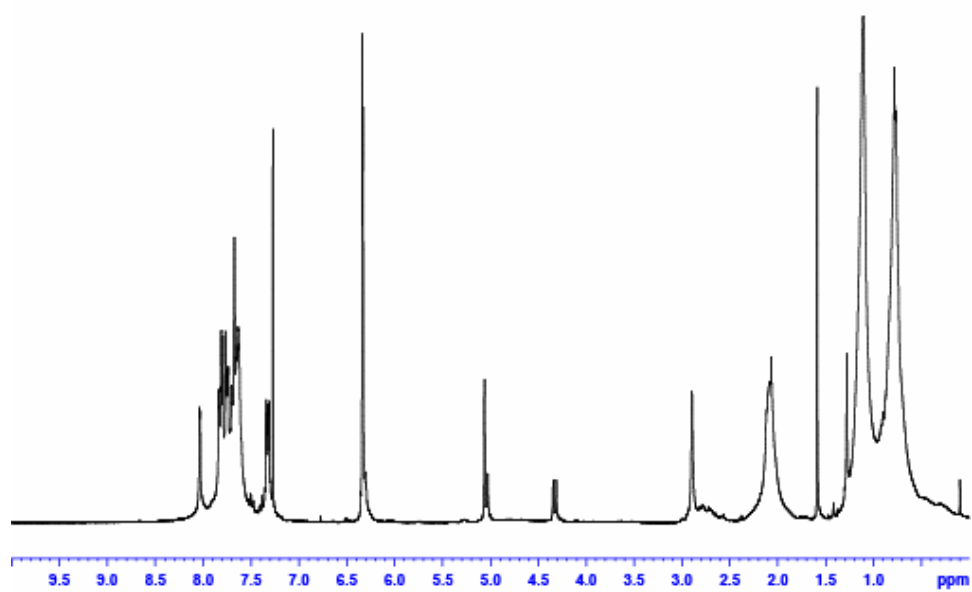


**exTTF-Fl₂-C₆₀ (3b).**

C₆₀ (280 mg, 0.4 mmol), *ex*TTF-Fl₂-CHO **2b** (107 mg, 0.1 mmol) and sarcosine (40 mg, 0.5 mmol) were reacted via the 1,3-dipolar cycloaddition procedure (under argon and protected against light) for 4 h. Purification in the dark using CS₂, followed by toluene as eluent yielded **3b** (44 mg, 24%) as a black solid.

¹H-NMR (500 MHz, CDCl₃), δ: 8.03 (d, 2H, *J*=1.7 Hz, ArH); 7.91-7.52 (bm, 15H, ArH); 7.35-7.29 (m, 2H, Ar_{extif}H); 6.33 (m, 4H); 5.06 (s, 1H, CHN); 5.04 (d, *J*=10.5 Hz, 1H, CH₂N); 4.33 (d, *J*=10.5 Hz, 1H, CH₂N); 2.90 (bs, 3H, NCH₃); 2.08 (bs, 8H, CH₂ aliph); 1.25-0.98 (bm, 22H), 0.95-0.60 (bm, 22H).

¹³C-NMR (125 MHz, CDCl₃), δ: 154.43; 154.06; 153.89; 152.29; 152.13; 152.09; 147.70; 147.23; 146.92; 146.73; 146.67; 146.63; 146.57; 146.53; 146.50; 146.34; 146.15; 145.97; 145.94; 145.91; 145.88; 145.77; 145.72; 145.68; 145.64; 145.55; 145.10; 144.87; 144.81; 144.78; 143.52; 143.40; 143.11; 142.97; 142.67; 142.57; 142.55; 142.49; 142.44; 142.31; 142.16; 142.10; 141.95; 141.73; 141.12; 140.80; 140.60; 140.56; 140.50; 140.40; 140.33; 140.28; 140.00; 139.84; 139.55; 137.06; 137.02; 136.33; 136.31; 136.25; 136.14; 135.98; 135.75; 135.72; 134.63; 129.22; 127.62; 126.55; 126.51; 126.47; 126.44; 125.87; 125.41; 125.22; 124.89; 124.05; 122.72; 122.41; 121.98; 121.85; 121.81; 121.72; 120.51; 120.41; 117.68; 117.61; 84.26; 70.46; 69.45; 68.41; 55.73; 55.68; 40.97; 40.80; 40.50; 32.13; 32.02; 31.92; 30.15; 26.05; 24.30. ESI-MS, *m/z*: 1843 [M+Na]⁺;



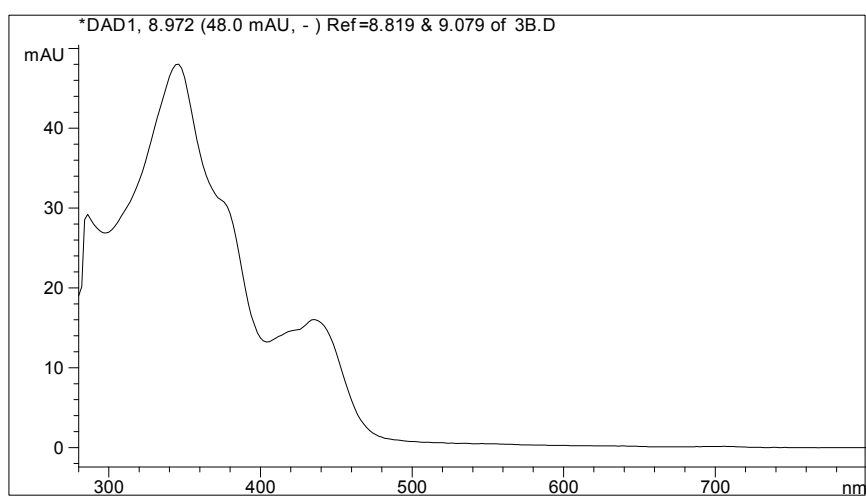
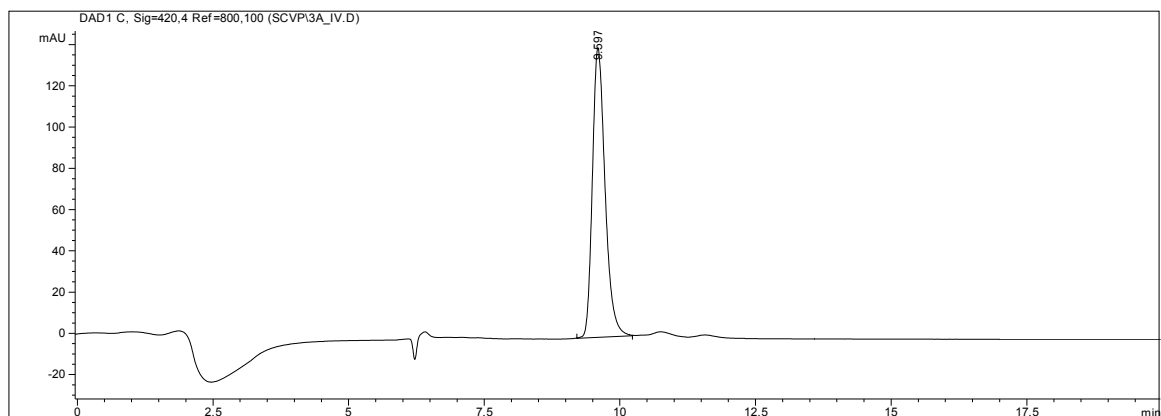


Table 1. Redox potential values of triads **3a,b**.^a

| Compound | E^1_{red} | E^2_{red} | E^3_{red} | E^4 | E^1_{ox} | E^2_{ox} | E^3_{ox} |
|---|--------------------|--------------------|--------------------|--------------------|-------------------|-------------------|-------------------|
| C₆₀ | -761 ^b | -1171 ^b | -1632 ^b | -2098 ^b | | | |
| N-methyl fulleropyrrolidine | -863 ^b | -1263 ^b | -1802 ^b | | 1140 | 1710 | |
| I-exTTF | | | | | 232 | 1643 | |
| 1a (BE-FL-CHO) | -1848 | | | | 1380 | | |
| 1b (BE-FI-FI-CHO) | | | | | 1250 | | |
| 2a (exTTF-FI-CHO) | -1978 | | | | 234 | 1458 | |
| 2b (exTTF-FI-FI-CHO) | | | | | 259 | 1280 | |
| Fl₂-CHO^c | -2029 | | | | 1295 | 1608 | 1873 |
| 3a (exTTF-FI-C ₆₀) | -874 ^b | -1291 ^b | -1834 ^b | / | 215 | 1091 | 1665 |
| 3b (exTTF-FI-FI-C ₆₀) | -889 ^b | -1287 ^b | -1787 ^b | / | 281 | 1277 | 1682 |

a) Potentials in mV; scan rate 100 mVs⁻¹; glassy carbon working electrode, Ag/AgNO₃ reference electrode, Pt counter electrode; 0.1 M Bu₄NClO₄ in *o*-DCB / CH₃CN (4:1 v/v); b) half wave potential values ($E_{1/2}$); c) ref. C. Van der Pol, M. R. Bryce, M. Wielopolski, C. Atienza-Castellanos, D. M. Guldi, S. Filippone, N. Martín *J. Org. Chem.* in press.

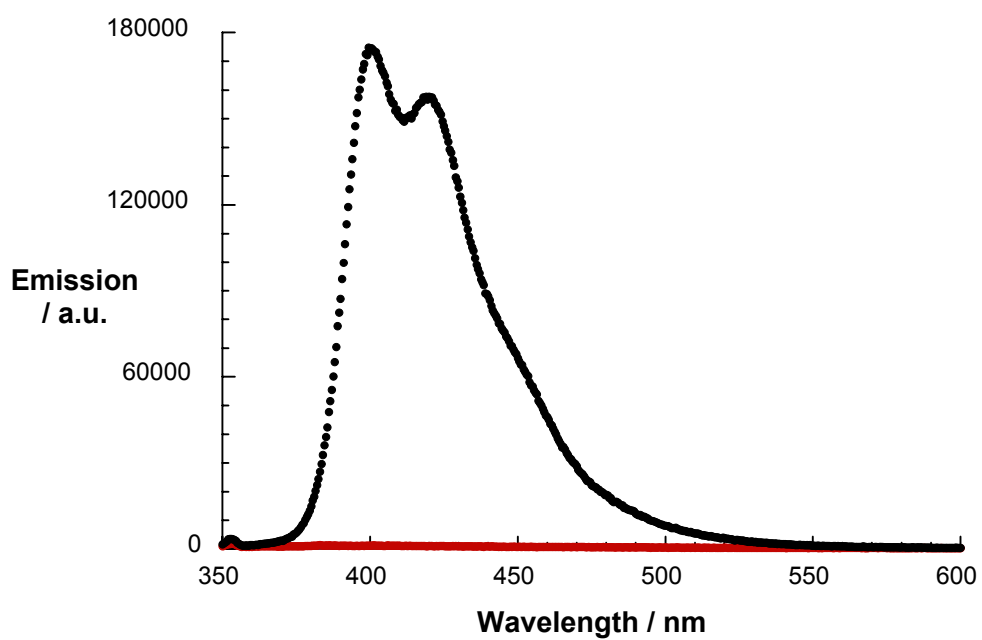


Figure S1: Room temperature fluorescence spectra of oFl₂ (black) and C₆₀-oFl₂-exTTF (brown) in THF recorded with solutions that exhibit optical absorptions at the 360 nm excitation wavelength of 0.45.

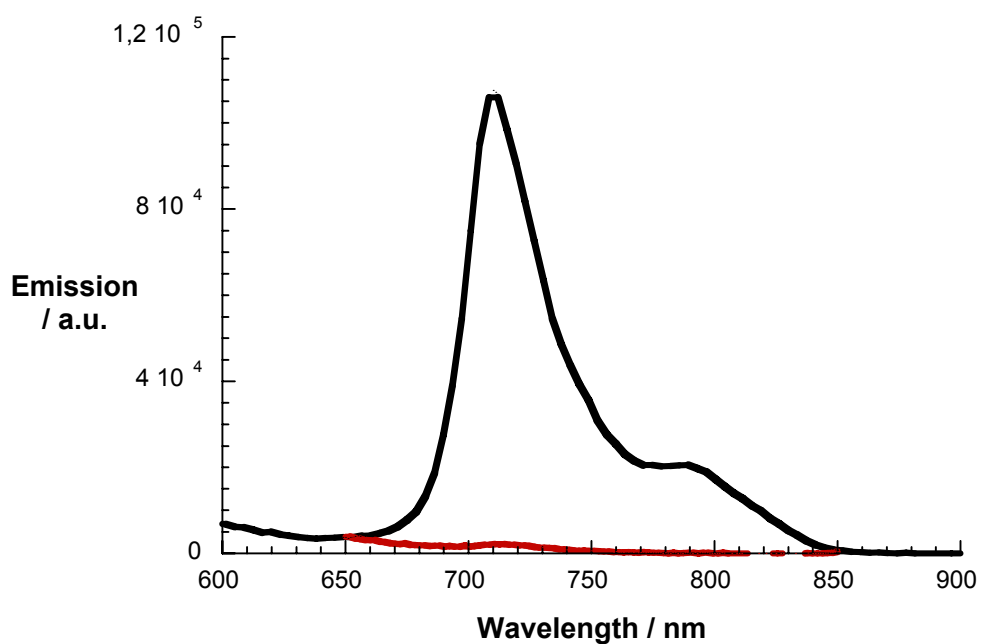


Figure S2: Room temperature fluorescence spectra of C₆₀ (black) and C₆₀-oFl₁-exTTF (brown) in THF recorded with solutions that exhibit optical absorptions at the 435 nm excitation wavelength of 0.22.

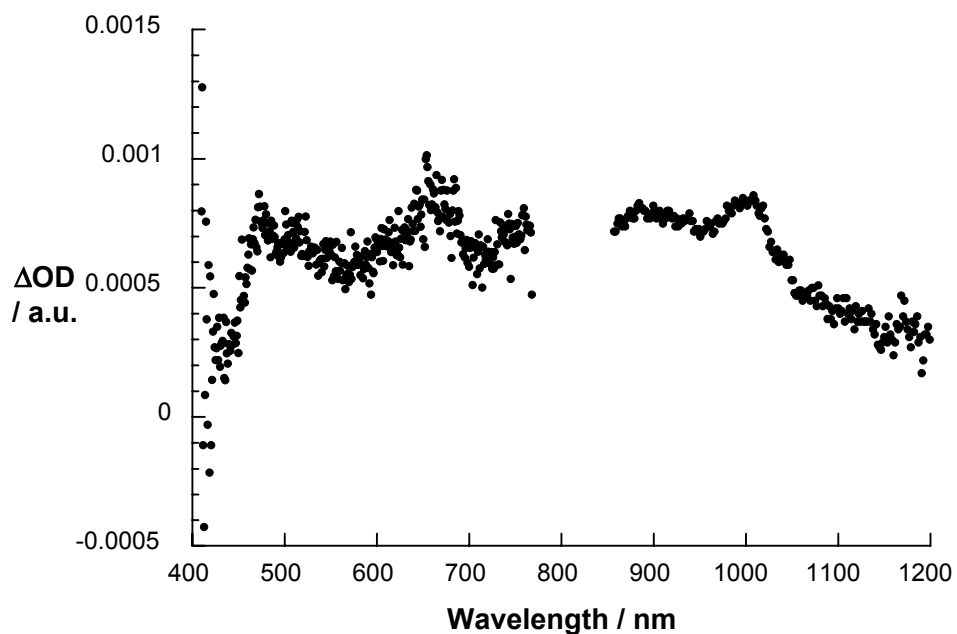


Figure S3: Differential absorption spectrum (visible and near-infrared) obtained upon femtosecond flash photolysis (387 nm) of C_{60} -oFl₂-exTTF in nitrogen saturated THF (1.0×10^{-5} M) with a time delay of 155 ps at room temperature.

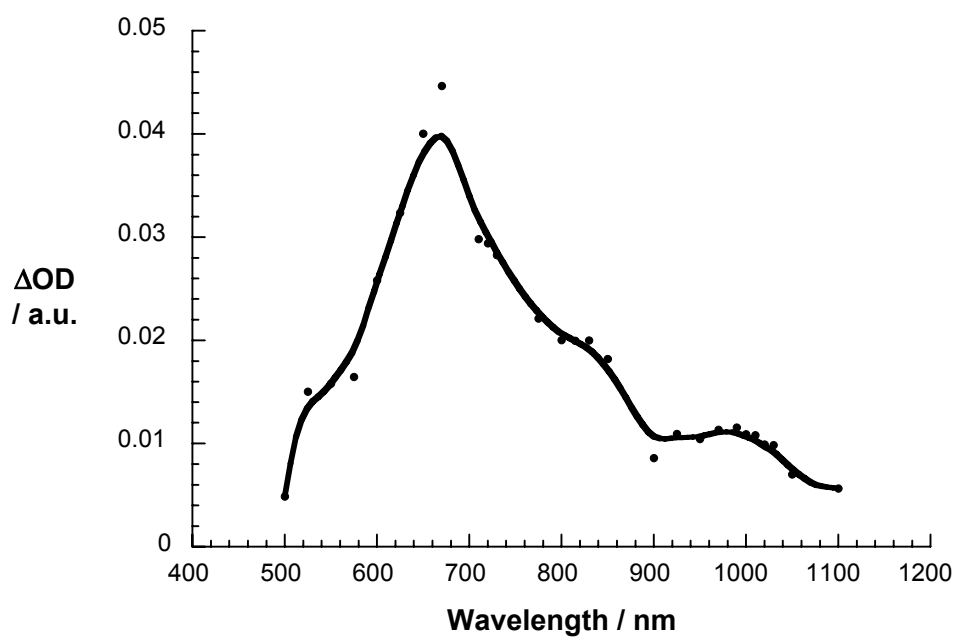


Figure S4: Differential absorption spectrum (visible and near-infrared) obtained upon nanosecond flash photolysis (355 nm) of C_{60} -oFl₂-exTTF in nitrogen saturated THF (1.0×10^{-5} M) with a time delay of 100 ns at room temperature.