

Fluorenone Core Donor-Acceptor-Donor π -Conjugated Molecules End-Capped with Dendritic Oligo(thiophene)s: Synthesis, Liquid Crystalline behaviour, and Photovoltaic Applications.

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S1. Synthetic procedures

General

All reagents and chemicals were purchased from Aldrich or Acros and used as received, except for THF which was distilled over sodium-benzophenone prior to use. Thin layer chromatography was performed on silica gel-coated aluminium plates with a particle size of 2-25 μm and a pore size of 60 Å. Merck 60 (70-230 mesh) silica was used for flash chromatography. All synthesised products were identified by ^1H and ^{13}C NMR spectroscopy, as well as by elemental analysis. NMR spectra were recorded in chloroform-*d*, containing tetramethylsilane (TMS) as internal standard, on a Bruker AC200 spectrometer. Elemental analyses (C, H, N, and S) were carried out by the Analytical Service of CNRS Vernaison (France) or by CRMPO at the university of Rennes 1.

2-trimethyltin-5-octylthiophene (2).

n-BuLi (8.54 mL of 2.5M solution in hexane, 21.36 mmol) was added dropwise to a solution of 2-octylthiophene **1** (3.5 g, 17.8 mmol) in dry THF (35 mL) at -78°C under argon. After stirring the mixture for 1 h at -40°C , the resulting greenish solution was again cooled to -78°C and trimethyltinchloride (3.72 g, 18.7 mmol) in THF (15 mL) was added. The reaction mixture turned yellow and it was then allowed to warm to room temperature and stirred for 2h. Saturated aqueous solution of NH_4Cl (10 mL) was added and the resulting mixture was extracted three times with diethyl ether (50 mL). The combined organic layers were washed with saturated aqueous solution of NH_4Cl (50 mL), twice with water (50 mL), dried over MgSO_4 and concentrated. The crude compound **2** was titrated by ^1H NMR spectroscopy at 60% and used directly for coupling reaction. ^1H NMR (200 MHz, CDCl_3) δ (ppm): 7.01 (d, $^3\text{J}=2.9$ Hz, 1H), 6.90 (d, $^3\text{J}=2.9$ Hz, 1H), 2.85 (t, $^3\text{J}=7.8$ Hz, 2H) 1.79 (m, 2 H), 1.14 (m, 10 H), 0.84 (t, $^3\text{J}=6.8$ Hz, 3H), 0.34 (s, $\text{J}=28.7$ Hz, 9H).

5,5''-dioctyl-2,2':3',2''-terthiophene (3-G1).

2,3-dibromothiophene (1.22 g, 5.17 mmol) and the crude stannylated compound **2** (6.2 g, 11.37 mmol) were placed in anhydrous DMF (30 mL). The mixture was stirred under argon for 10 min and then 358 mg of Pd(P(Ph)₃)₄ (0.31 mmol) were added. The mixture was kept for an additional period of 15 h at 100°C with constant stirring and then allowed to cool to room temperature. The crude product was extracted with diethyl ether, washed with HCl 1M aqueous solution, and filtered through celite. After usual work-up, the crude product was purified by column chromatography (silica gel, hexane) to afford 2.15 g (88%) of light yellow oil (blue luminescent). ¹H NMR (200 MHz, CDCl₃) δ(ppm): 7.21 (d, ³J=5.3 Hz, 1H), 7.11 (d, ³J=5.3 Hz, 1H), 6.93 (d, ³J=3.5 Hz, 1H), 6.86 (d, ³J=3.5 Hz, 1H), 6.67 (dm, ³J=3.5 Hz, 1H), 6.65 (dm, ³J=3.5 Hz, 1H), 2.77 (t, ³J=7.7 Hz, 4H), 1.66 (m, ³J=6.5 Hz, 4H), 1.39-1.17 (m, 20H), 0.92-0.85 (t, ³J=6.5 Hz, 6H). ¹³C NMR (CDCl₃, 50 MHz): δ (ppm): 147.97 (1C), 146.47 (1C), 135.41 (1C), 132.72 (1C), 132.55 (1C), 131.76 (1C), 130.06 (1C), 128.07 (1C), 126.37 (1C), 124.58 (1C), 124.44 (1C), 124.42 (1C), 32.34 (2C), 32.09 (1C), 32.05 (1C), 30.63 (1C), 30.57 (1C), 29.80 (2C), 29.72 (2C), 29.59 (1C), 29.57 (1C), 23.14 (2C), 14.60 (2C). Anal. Found (calcd): C, 71.14 (71.13); H, 8.51 (8.53); S, 20.32 (20.34).

Trimethyl-(5,5''-dioctyl-2,2':3',2''-terthiophen-5'-yl) stannane (4).

n-BuLi (3.9 mL of 2.5 M solution in hexane, 7.02 mmol) was added dropwise to a solution of **3-G1** (2.97 g, 6.28 mmol) in dry THF (20 mL) at -78°C under argon. After stirring the mixture for 1h30 at -40°C, the resulting greenish solution was again cooled to -78°C and trimethyltinchloride (1.13 g, 6.59 mmol) in THF (15 mL) was added. The reaction mixture turned yellow and it was then allowed to warm to room temperature and stirred for 2 h. Saturated aqueous solution of NH₄Cl (10 mL) was added and the resulting mixture was extracted three times with diethyl ether (50 mL). The combined organic layers were washed with saturated aqueous solution of NH₄Cl (50 mL), twice with water (50 mL), dried over MgSO₄ and concentrated. The crude compound was titrated by ¹H NMR spectroscopy at 80% and used directly for coupling reaction. ¹H NMR (200 MHz, CDCl₃) δ(ppm): 7.14 (s, 1H), 6.90 (d, ³J=3.5 Hz, 1H), 6.86 (d, ³J=3.5 Hz, 1H), 6.65 (d, ³J=3.5 Hz, 2H), 2.76 (t, ³J=7.1 Hz, 4H), 1.70-1.55 (m, 4H), 1.40-1.20 (m, 20H), 0.92-0.82 (t, br, 6H), 0.38 (s, J=28.8 Hz, 9H).

2,3-(5',5''-dioctyl-2',2'':3'',2''''-terthiophen-5''-yl)-thiophene (5-G2).

A suspension of triphenylphosphine (210 mg, 0.80 mmol) and Pd(OAc)₂ (45 mg, 0.20 mmol) in THF (1.5 mL) was stirred at 60°C under argon for 15 min. The resulting yellow precipitate was added to a solution of 2,3-dibromothiophene (504 mg, 2.08 mmol) and the stannylated compound **4** (5 mmol) in anhydrous DMF (30 mL). The mixture was kept for an additional period of 16 h at 100°C with constant stirring and then allowed to cool to RT. The crude product was extracted with diethyl ether, washed with HCl 1M aqueous solution, and filtered through celite. After usual work-up, the crude product was purified by column chromatography (silica gel, hexane-chloroform 95/5) to afford 1.80 g (85%) of yellow-orange oil. ¹H NMR (200 MHz, CDCl₃) δ(ppm): 7.28 (d, ³J=5.3 Hz, 1H), 7.21 (s,

1H), 7.17 (s, 1H), 7.16 (d, $^3J=5.3$ Hz, 1H), 6.94 (d, $^3J=3.5$ Hz, 1H), 6.94 (d, $^3J=3.6$ Hz, 1H), 6.87 (t, $^3J=3.7$ Hz, 2H), 6.66 (d, $^3J=3.5$ Hz, 4H), 2.76 (t, $^3J=7.7$ Hz, 8H), 1.69-1.60 (m, $^3J=7.3$ Hz, 8H), 1.45-1.20 (m, 40H), 0.88 (t, $^3J=6.6$ Hz, 12H). ^{13}C NMR (CDCl_3 , 50 MHz): δ (ppm): 148.11 (1C), 147.90 (1C), 146.73 (1C), 146.57 (1C), 135.53 (1C), 135.27 (1C), 134.96 (1C), 133.39 (1C), 133.03 (1C), 132.67 (1C), 132.40 (1C), 132.35 (1C), 132.30 (1C), 132.15 (1C), 131.91 (1C), 131.58 (1C), 130.93 (1C), 130.13 (1C), 129.77 (1C), 128.03 (1C), 127.89 (1C), 126.78 (1C), 126.60 (1C), 125.31 (1C), 124.60 (1C), 124.57 (1C), 124.45 (1C), 124.43 (1C), 32.33 (4C), 32.10 (2C), 32.02 (2C), 30.63 (2C), 30.59 (2C), 29.81 (2C), 29.78 (2C), 29.72 (2C), 29.70 (2C), 29.59 (2C), 29.57 (2C), 23.13 (4C), 14.57 (4C). Anal. Found (calcd): C, 70.30 (70.26); H, 7.88 (7.86); S, 21.78 (21.88).

Trimethyl- [2,3-(5',5'''-dioctyl-2',2'':3'',2''''-terthiophen-5''-yl)thiophen-5-yl]stannane (6).

n-BuLi (0.4 mL of 2.5 M solution in hexane, 1.6 mmol) was added dropwise to a solution of **5-G2** (1020 mg, 1.0 mmol) in dry THF (25 mL) at -78°C under argon. After stirring the mixture for 90 min at -50°C , the resulting red solution was again cooled to -78°C and trimethyltinchloride (215 mg, 1.08 mmol) in THF (10 mL) was added. The reaction mixture was then allowed to warm to room temperature and stirred for 2h. Saturated aqueous solution of NH_4Cl (10 mL) was added and the resulting mixture was extracted three times with diethyl ether (50 mL). The combined organic layers were washed with saturated aqueous solution of NH_4Cl (50 mL), twice with water (50 mL), dried over MgSO_4 and concentrated. The crude compound was titrated by ^1H NMR spectroscopy at 80% and used directly for coupling reaction. ^1H NMR (200 MHz, CDCl_3) δ (ppm): 7.20 (s, 1H) 7.19 (s, 1H), 7.17 (s, 1H), 6.93 (d, $^3J=3.5$ Hz, 2H), 6.87 (d, $^3J=3.4$ Hz, 2H), 6.66 (m, 4H), 2.76 (t, $^3J=7.4$ Hz, 8H), 1.70-1.50 (m, 8H), 1.45-1.15 (m, 40H), 0.95-0.80 (t, br, 12H), 0.41 (s, $J=28.8$ Hz, 9H).

2,7-Bis(5'-bromo-4-octyl-5,2'-bithien-2-yl)-fluorenone (8).

2,7-Bis(4-octyl-5,2'-bithien-2-yl)-fluorenone (7) (290 mg, 0.395 mmol) was dissolved in chloroform (20 mL) at room temperature. The resulting solution was stirred at room temperature for 10 min. N-bromosuccinimide (150 mg, 0.843 mmol) dissolved in chloroform (20 mL) was added dropwise to this solution over a period of 10 min. The mixture was kept for an additional period of 12 h at room temperature with constant stirring. The crude product was extracted with chloroform, washed three times with water and then concentrated under vacuum. The product was purified by column chromatography using mixtures of solvent of increasing polarity (hexane-dichloromethane, 100/0 to 70/30 v/v). **8** was obtained as a red-purple powder in 63% yield (248 mg). ^1H NMR (200 MHz, CDCl_3) δ (ppm): 7.80 (d, $^5J=1.7$ Hz, 2H), 7.60 (dd, $^3J=7.8$ Hz and $^5J=1.7$ Hz, 2H), 7.41 (d, $^3J=7.8$ Hz, 2H), 7.17 (s, 2H), 7.01 (d, $^3J=3.8$ Hz, 2H), 6.87 (d, $^3J=3.8$ Hz, 2H), 2.68 (t, $^3J=7.4$ Hz, 4H), 1.67-1.56 (m, $^3J=7.6$ Hz, 4H), 1.44-1.17 (m, 20H), 0.89 (t, $^3J=6.8$ Hz, 6H). ^{13}C NMR (CDCl_3 , 50 MHz): δ (ppm): 193.15 (C=O), 142.64 (2C), 141.13 (2C), 140.75 (2C), 137.49 (2C), 134.99 (2C), 134.74 (2C), 131.21 (2C), 130.25 (2C), 129.84 (2C), 126.51 (2C), 126.03 (2C), 120.96 (2C), 120.77 (2C), 112.02 (2 C-Br), 31.88 (2C), 30.54 (2C), 29.55 (2C), 29.41 (2C), 29.25 (4C), 22.69 (2C), 14.14 (2C). Found (calcd): C,

61.83 (60.67); H, 5.38 (5.20); S, 14.54 (14.40).

2,7-bis(5'-iodo-4-octyl-5,2'-bithien-2-yl)-fluoren-9-one (9).

7 (2130 mg, 2.90 mmol) was dissolved in a mixture of chloroform (50 mL) and acetic acid (50 mL) at room temperature. The resulting solution was stirred at RT for 10 min. N-iodosuccinimide (1438 mg, 6.39 mmol) dissolved in a mixture of chloroform (25 mL) and acetic acid (25 mL) was added dropwise to this solution over a period of 15 min. The mixture was kept for an additional period of 12 h at room temperature with constant stirring. The crude product was extracted with chloroform, washed three times with water and then concentrated under vacuum. The product was precipitated from methanol and washed abundantly with methanol and hexane. The product was dissolved in THF and precipitated from acetone, filtered and dried to afford 2110 mg (74%) of a red-purple powder. ¹H NMR (200 MHz, CDCl₃) δ(ppm): 7.86 (d, ⁵J=1.3 Hz, 2H), 7.65 (dd, ³J=7.9 Hz and ⁵J=1.5 Hz, 2H), 7.47 (d, ³J=7.9 Hz, 2H), 7.22 (d, ³J=3.6 Hz, 2H), 7.21 (s, 2H), 6.82 (d, ³J=3.9 Hz, 2H), 2.71 (t, ³J=7.7 Hz, 4H), 1.69-1.56 (m, ³J=7.6 Hz, 4H), 1.45-1.22 (m, 20H), 0.91 (t, ³J=6.8 Hz, 6H). ¹³C NMR (CDCl₃, 50 MHz): δ (ppm): 193.41 (C=O), 142.97 (2C), 142.17 (2C), 141.42 (2C), 141.01 (2C), 137.55 (2C), 135.26 (2C), 134.99 (2C), 131.46 (2C), 130.07 (2C), 127.47 (2C), 126.75 (2C), 121.21 (2C), 121.03 (2C), 73.41 (2 C-I), 32.17 (2C), 30.78 (2C), 29.83 (2C), 29.73 (2C), 29.69 (2C), 29.53 (2C), 22.97 (2C), 14.43 (2C).

S2. Physicochemical Characterisations

UV-vis absorption spectra were recorded in solution on a Perkin-Elmer Lambda 2 spectrometer (wavelength range: 180-820 nm; resolution: 2 nm) and were confirmed during the SEC analyses using a diode array UV-vis spectrometer. The fluorescence spectra were recorded on a HITACHI F4500 spectrophotometer.

Electrochemical studies of the synthesized molecules were carried out in a one compartment, three-electrode electrochemical cell equipped with a flat platinum working electrode (7 mm²), a Pt wire counter electrode, and a Ag wire pseudo-reference electrode, whose potential was checked using the Fc/Fc⁺ couple as an internal standard. The electrolyte consisted of 0.1 M tetrabutylammonium hexafluorophosphate (Bu₄NPF₆) solution in dichloromethane containing 1.2 to 2 × 10⁻³ M macromonomer (depending on the solubility). The electrolytic solution was purged with argon for 300 s before each experiment.

The optical textures of the mesophases were studied with a Leica DMLM polarizing optical microscope equipped with a Linkam LTS350 hot stage and its associated Linkam CI94 temperature controller. The transition temperatures and enthalpies were measured by differential scanning calorimetry with a TA Instruments DSC-Q1000 instrument operated at a scanning rate of 10°C min⁻¹ on heating. The apparatus was calibrated with indium (156.6 °C; 28.4 J g⁻¹) and gallium (29.8°C) as the standards. The TGA measurements were carried out on a SDTQ 600 apparatus at scanning rate of 10°C min⁻¹. The XRD patterns were obtained with two different experimental set-ups. In all cases, a linear

monochromatic Cu-K α 1 beam ($\lambda = 1.5405 \text{ \AA}$) was obtained using a sealed-tube generator (900 W) equipped with a bent quartz monochromator. In the first set, the transmission Guinier geometry was used, whereas a Debye-Scherrer-like geometry was used in the second experimental set-up. In all cases, the crude powder was filled in Lindemann capillaries of 1 mm diameter. The initial set of diffraction patterns was recorded on an image plate; periodicities up to 80 \AA can be measured, and the sample temperature controlled to within $\pm 0.3^\circ\text{C}$ in the 20 to 350 $^\circ\text{C}$ temperature range. The second set of diffraction patterns was recorded with a curved Inel CPS120 counter gas-filled detector linked to a data acquisition computer (periodicities up to 60 \AA) or can be measured on image plates (periodicities up to 100 \AA); the sample temperature controlled to within $\pm 0.05^\circ\text{C}$ in the 20 to 200 $^\circ\text{C}$ temperature range. In each case, exposure times were varied from 1 to 24 h.

HRMS was performed using VARIAN MAT 311 (Inverted NIER-JOHNSON) in Centre Régional de Mesures Physiques de l'Ouest (CRMPO). The mass spectra were obtained under electronic impact (EI = 70 eV). The ion acceleration was 3000 V. The molecules were dissolved in dichloromethane.

Size-Exclusion Chromatography (SEC) analyses were performed on a Hewlett-Packard 1100 Chemstation equipped with a 300*7.5 mm Polymer labs PLgel Mixed-D 5 $\mu\text{m}/104\text{\AA}$ column, a DAD detector and a refractive index (RI) detector. The column temperature and the flow rate were fixed to 40 $^\circ\text{C}$ and 1 mL.min $^{-1}$, respectively. The calibration curve was built using 10 polystyrene (PS) narrow standards (SM2-10* kit from Polymer Labs). Two runs of 20 μL injection of *ca.* 0.2 mg mL $^{-1}$ HPLC grade THF solutions were typically analyzed for each sample with an UV-vis detection located at 385 nm.

AFM investigations were carried out under ambient conditions in the amplitude-modulation mode (AM-AFM) using a Cervantès AFM head controlled by a Dulcinea unit from Nanotec Electronica (Spain), and Si cantilevers (NCHR from Nanosensors, resonant frequency in the range 260-300kHz). A non-disturbing imaging was achieved, by applying amplitude set-points not far from the free resonance of the cantilevers (lower than 5% of amplitude reduction for all images). Last, Nanotec's WsXM software ^[Horcas] was used to drive the scanning probe microscopy (SPM) unit and for data processing. [Horcas] I. Horcas, R. Fernández, J. M. Gómez-Rodríguez, J. Colchero, J. Gómez-Herrero, A. M. Baro, *Rev. Sci. Instr.* **2007**, 78, 013705.

S3. Devices fabrication and characterisation

Bulk-heterojunction solar cells were fabricated on a glass substrate covered by a transparent conductive oxide, ITO, according to the procedure and layout described in ref. [14]. The ITO was covered with a 40 nm thick interfacial PEDOT/PSS layer (Baytron-P), onto which the active layer was spin-coated from chlorobenzene solutions containing the donor/PCBM mixture. Finally, a 0.6 nm thick layer of LiF was evaporated on top of the active layer and covered by the aluminium electrode (100 nm). The active surface of the devices was 0.28 cm 2 . Current-voltage, $I-V$, characteristics and PCEs of the solar cells, illuminated through the ITO, were measured in inert atmosphere via a

computer controlled Keithley 1 SMU 2400 unit using 100 mW cm^{-2} air-mass (1.5)-simulated white light generated by a Steuernagel Solar Constant 575 simulator. These simulated conditions are consistent with most published work to date. A monocrystalline silicon solar cell, calibrated at the Fraunhofer Institut Solare Energiesysteme (Freiburg, Germany), was used as a reference cell to confirm stabilization of the 100 mW cm^{-2} illumination. The used apparatus was a standard system that is widely used and gives mismatch factors of around 4% in the 300 to 1100 nm range. The mismatch factors were obtained by comparison of simulated light with outdoor tests. The temperature of the polymer heterojunction, measured using a thermocouple (Pt100) mounted on the ITO substrate, reached 30°C during the first I - V characterization.

S4. Crystal data and structure refinement for compound 8

Identification code	fl156
Empirical formula	C ₄₅ H ₄₆ Br ₂ O ₄ S ₄
Formula weight	890.88
Temperature	571(2) K
Wavelength	0.71073 Å
Crystal system	Triclinic
Space group	P -1
Unit cell dimensions	a = 10.490(2) Å alpha = 82.290(20) deg. b = 12.677(4) Å beta = 86.545(17) deg. c = 15.721(3) Å gamma = 78.64(2) deg.
Volume, Z	2029.9(8) Å ³ , 2
Density (calculated)	1.458 Mg/m ³
Absorption coefficient	2.237 mm ⁻¹
F(000)	916
Crystal size	0.22 x 0.06 x 0.01 mm
Theta range for data collection	3.30 to 23.25 deg.
Limiting indices	-11 ≤ h ≤ 11, -14 ≤ k ≤ 14, -17 ≤ l ≤ 15
Reflections collected	9188
Independent reflections	5318 [R(int) = 0.0731]
Max. and min. transmission	0.9780 and 0.6341
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5318 / 0 / 471
Goodness-of-fit on F ²	0.709
Final R indices [I > 2σ(I)]	R1 = 0.0537, wR2 = 0.0835
R indices (all data)	R1 = 0.1783, wR2 = 0.1017
Largest diff. peak and hole	0.268 and -0.438 e.Å ⁻³

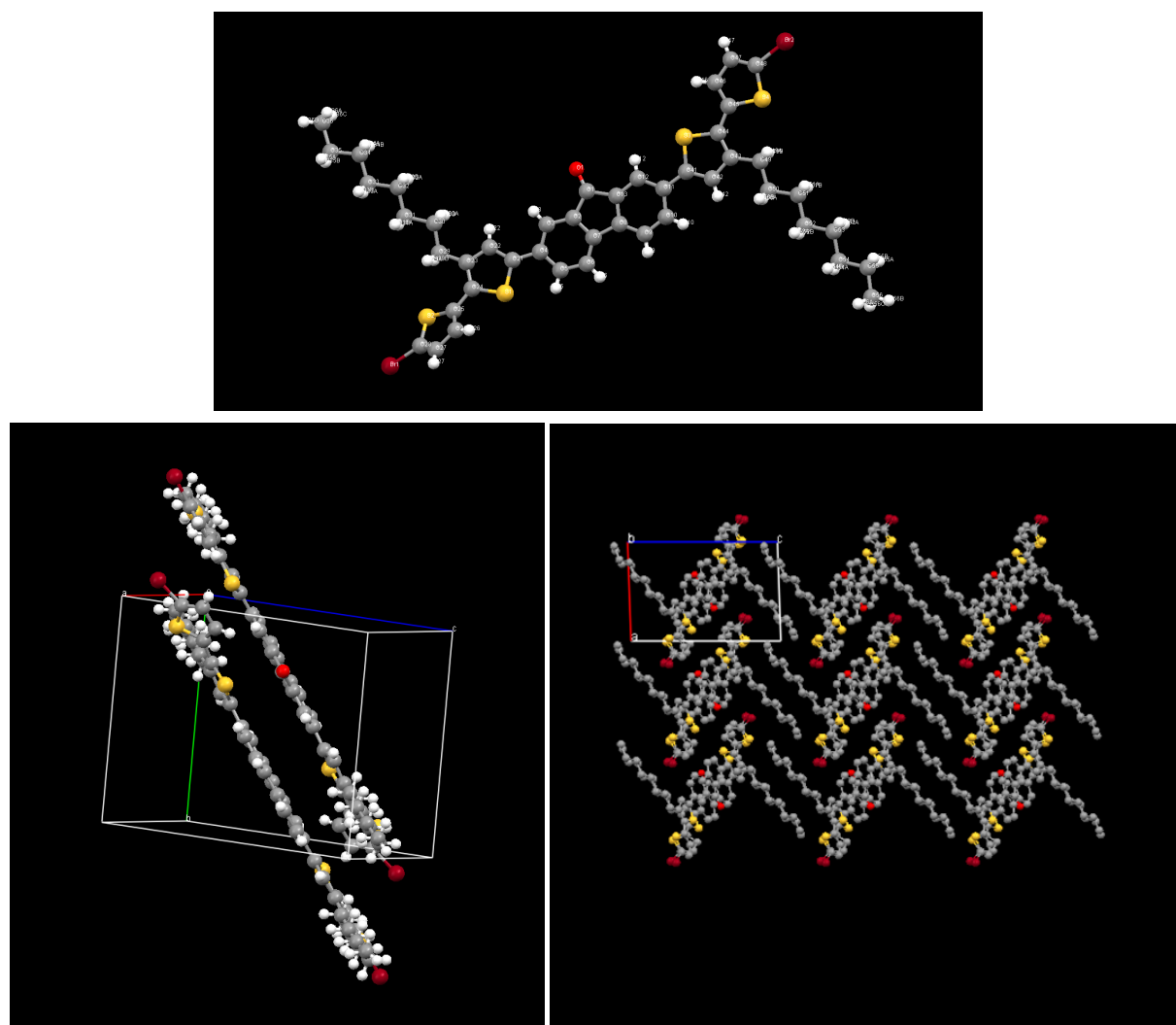


Fig S4: Mercury diagrams of the structure of compound 8

S5. XRD patterns in the small angles region for compound FG1

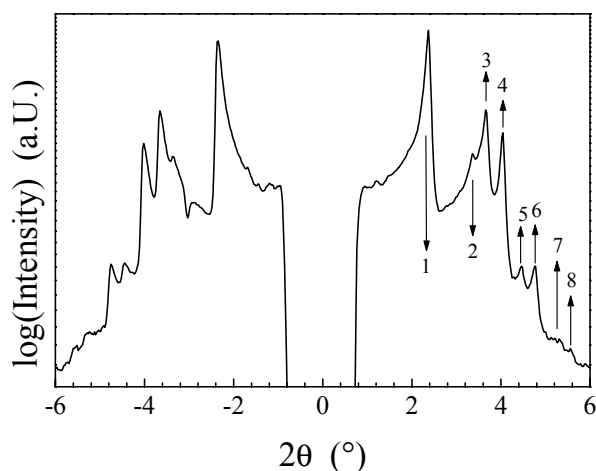


Fig S5 : XR patterns in the small angles region for compound **FG1**

N ^a	2θ _{obs} [°]	d _{obs} [Å]	I ^a	hkl ^a	2θ _{cal} [°]	d _{cal} [Å] ^b
1	2.372±0.017	37.21±0.27	VS	001	2.372	37.21
2	3.357±0.023	26.29±0.18	W	200	3.358	26.29
3	3.655±0.017	24.15±0.11	S	1-10	3.643	24.23
4	4.034±0.017	21.89±0.09	S	110	4.044	21.83
5	4.446±0.023	19.86±0.10	M	201	4.435	19.91
6	4.756±0.023	18.57±0.09	M	002	4.746	18.61
7	5.340±0.046	16.53±0.14	VW	11-2	5.331	16.56
8	5.546±0.046	15.92±0.13	VW	1-12	5.556	15.89

^a N^o: Numbering of the reflections; I: Intensity of the reflections; hkl: Miller indices. ^b θ_{obs}, θ_{cal}, d_{obs} and d_{cal} are the observed and calculated diffraction angles and spacings; d_{cal} (d_{hkl}) was calculated according to the following triclinic direct and reciprocal cell relationships: $1/d_{hkl}^2 = h^2 a^{*2} + k^2 b^{*2} + l^2 c^{*2} + 2hka^*b^* \cos \gamma^* + 2hla^*c^* \cos \beta^* + 2klb^*c^* \cos \alpha^*$, with $a^* = b \sin \alpha / V$, $b^* = a \sin \beta / V$, $c^* = a \sin \gamma / V$, $\cos \alpha^* = (\cos \beta \cos \gamma - \cos \alpha) / \sin \beta \sin \gamma$, $\cos \beta^* = (\cos \alpha \cos \gamma - \cos \beta) / \sin \alpha \sin \gamma$, $\cos \gamma^* = (\cos \alpha \cos \beta - \cos \gamma) / \sin \alpha \sin \beta$ and $V = abc \sqrt{(1 - \cos^2 \alpha - \cos^2 \beta - \cos^2 \gamma + 2 \cos \alpha \cos \beta \cos \gamma)}$

Table S5: Reflections in the small angles region for compound **FG1**

S7. Size Exclusion Chromatography Analysis

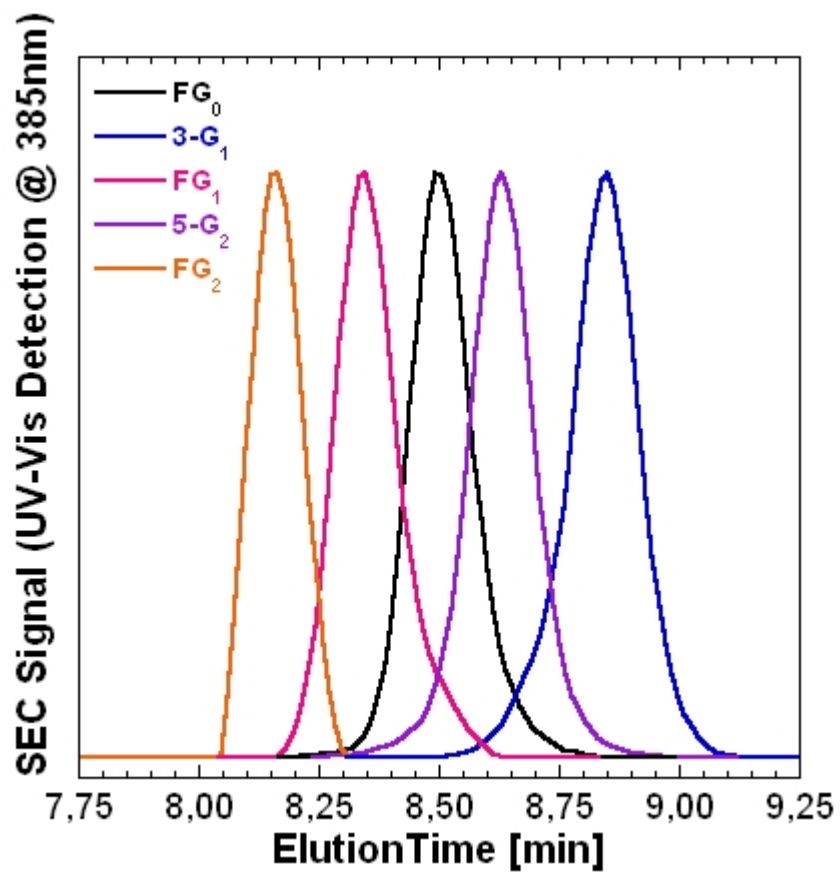


Fig S7: SEC Elugrams of FG_x, 3-G₁ and 5-G₂.