

A TTFV–pyrene-based copolymer: synthesis, redox properties, and aggregation behaviour

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1. Experimental

1.1 General

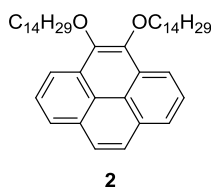
Chemicals and reagents were purchased from commercial suppliers and used without further purification. All reactions were performed in standard dry glassware under an inert atmosphere of N₂ unless otherwise noted. Evaporation and concentration was done at H₂O-aspirator pressure. Flash column chromatography was carried out with silica gel 60 (230-400 mesh) from VWR International. ¹H and ¹³C NMR spectra were measured on a Bruker AVANCE III 300 MHz spectrometer. Chemical shifts (δ) are reported in ppm downfield from the signal of the internal reference SiMe₄ or relative to the signals of residual solvents (CHCl₃: δ_H = 7.24 ppm, δ_C = 77.2 ppm). Coupling constants (*J*) are given in Hz. UV-Vis-NIR absorption spectra were recorded on a Cary 6000i spectrophotometer. Infrared spectra (IR) were recorded on a Bruker Tensor 27 spectrometer equipped with a ZnSe ATR module. Polymer molecular weight and polydispersity index (PDI) were estimated from gel permeation chromatography (GPC) using a Waters 2695 Separations Module equipped with a Waters 2996 photodiode array detector, a Waters 2414 refractive-index detector, and two Jordi Labs Jordi Gel DVB columns. Polystyrene standards were used for calibration, and THF was used as the eluent at a flow rate of 1.0 mL/min. Cyclic voltammetric (CV) analyses were carried out in a standard three-electrode setup controlled by a BASi Epsilon workstation. Delsa Nano S particle analyzer (Beckman Coulter, Inc.) were used for dynamic light scattering (DLS) measurements. Polymer solution were filtered through a 0.20 μm Millex-FG filter. The calculations of the particle size distributions were performed with the Delsa Nano software 2.30 (Beckman Coulter, Inc). Surface topography was obtained using a NewView 8000 3D optical surface profiler (Zygo Corp.). Pyrene precursors **1-3**¹ and TTFV **4**² were prepared according to literature procedures with suitable modifications.

¹ G. Venkataramana, P. Dongare, L. N. Dawe, D. W. Thompson, Y. Zhao and G. J. Bodwell, *Org. Lett.*, 2011, **13**, 2240.

² (a) G. Chen, I. Mahmud, L. N. Dawe, L. M. Daniels and Y. Zhao, *J. Org. Chem.*, 2011, **76**, 2701; (b) G. Chen, I. Mahmud, L. N. Dawe and Y. Zhao, *Org. Lett.*, 2010, **12**, 704.

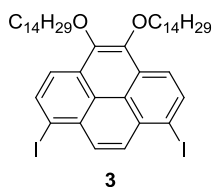
1.2 Synthetic procedures

4,5-Bis(tetradecyloxy)pyrene (2)



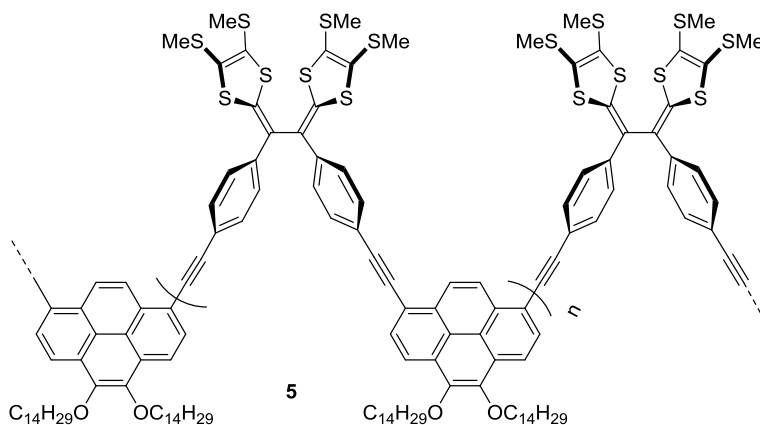
To a solution of pyrene-4,5-dione (**1**) (2.02 g, 9.98 mmol) in THF (100 mL) and H₂O (100 mL) were added TBAB (0.3 equiv.) and Na₂S₂O₄ (4.55 g, 26.1 mmol). The resulting clear orange solution was stirred at room temperature for 5 min. To the solution was added a solution of KOH (2.03 g, 3.62 mmol) in H₂O (100 mL). The resulting solution turned into a deep red colour, and the flask was immediately capped. To this solution was added the 1-bromododecane (9.98 g, 40.0 mmol). The flask was equipped with a capped condenser and was stirred at 100 °C for 6 h. The reaction mixture was cooled to room temperature and the layers were separated. The aqueous layer was extracted with ethyl acetate (3 × 15 mL) and the THF layer was washed with H₂O (15 mL) before being combined with the other organic extracts. The combined organic extracts were washed with H₂O (3 × 15 mL) to afford a clear yellow solution, which was then dried over anhydrous MgSO₄. The solvent was removed under reduced pressure and the residue was subjected to column chromatography (hexanes and then 10% CH₂Cl₂/hexanes) to afford 4,5-bis(dodecyloxy)pyrene (**2**) (2.08 g, 8.43 mmol, 85%) as a pale yellow solid. Mp: 53–54 °C; ¹H NMR (300 MHz, CDCl₃): δ 8.49 (dd, *J* = 1.1, 7.8 Hz, 2H), 8.13 (dd, *J* = 1.2, 7.6 Hz, 2H), 8.04 (s, 2H), 8.02 (t, *J* = 7.7 Hz, 2H), 4.33 (t, *J* = 6.7 Hz, 4H), 1.93–2.02 (m, 4H), 1.56–1.66 (m, 4H), 1.27–1.54 (m, 32H), 0.86–0.90 (m, 6H); ¹³C NMR (75 MHz, CDCl₃): δ 144.1, 131.1, 128.9, 127.3, 126.0, 124.3, 122.9, 119.4, 73.8, 32.0, 30.7, 29.8, 29.7, 29.6, 29.4, 26.4, 22.7, 14.2. MS (APCI-(+), CH₂Cl₂): *m/z* (%) 627.6 ([M+1]⁺); HRMS (ESI-(+), CH₂Cl₂): calcd for C₄₄H₆₆O₂ 626.5063, found 626.5045.

1,8-Diiodo-4,5-bis(tetradecyloxy)pyrene (3)



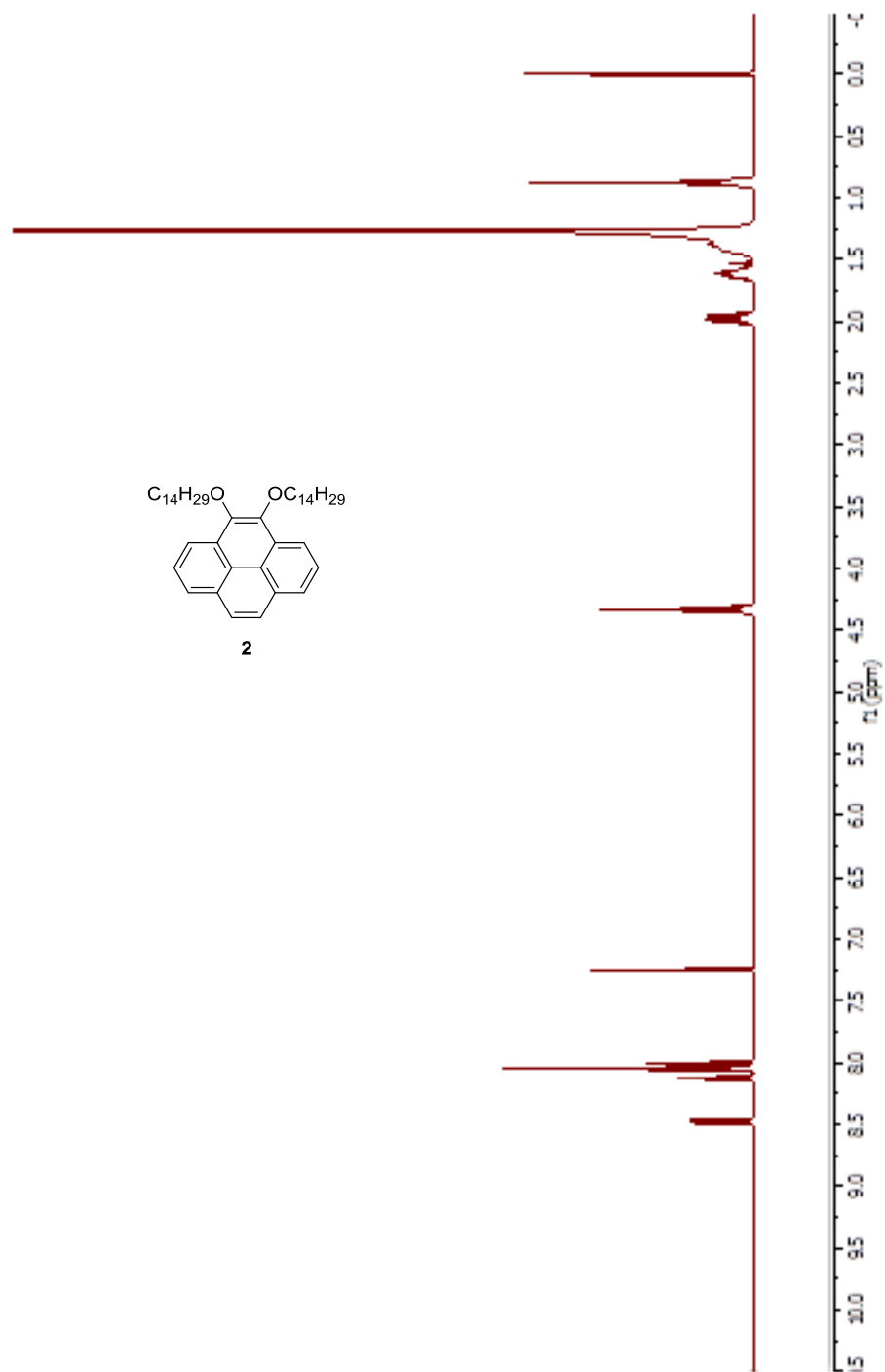
To a stirred solution of 4,5-bis(tetradecyloxy)pyrene (**2**) (1.50 g, 2.39 mmol) in CH_2Cl_2 (30 mL) was added mercuric acetate (1.68 g, 5.27 mmol). The reaction mixture was left to stir for 5 min. Iodine (1.34 g, 5.27 mmol) was then added and the resulting mixture was left to stir for 2.5 h at room temperature. The reaction mixture was filtered through a plug of Celite and extracted with CH_2Cl_2 (3×20 mL). The combined organic extractions were then washed with a saturated solution of sodium bisulfite (50 mL), 5% NaHCO_3 solution (50 mL), water (2×50 mL) and brine (50 mL). The resulting clear yellow solution was then dried over MgSO_4 and excess solvent was removed under reduced pressure. The residue was adsorbed onto silica gel and subjected to column chromatography (10% $\text{CH}_2\text{Cl}_2/\text{hexanes}$) to afford 1,8-diiodo-4,5-bis(tetradecyloxy)pyrene (**3**) (1.87 g, 2.13 mmol, 89%) as a white solid. Mp: 89.0–90.0 °C; ^1H NMR (300 MHz, CDCl_3): δ 8.54 (d, $J = 8.4$ Hz, 2H), 8.37 (s, 2H), 8.22 (d, $J = 8.4$ Hz, 2H), 4.31 (t, $J = 6.7$ Hz, 4H), 1.95 (quint, $J = 7.1$ Hz, 4H), 1.59–1.61 (m, 6H), 1.26–1.45 (m, 38H), 0.88 (t, $J = 6.2$ Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3): δ 181.3, 143.9, 137.5, 132.9, 132.4, 129.4, 123.1, 121.3, 96.2, 73.9, 34.1, 32.0, 30.5, 29.7, 29.7, 29.7, 29.6, 29.5, 29.4, 28.2, 26.3, 22.7, 14.2; MS (APCI, positive): m/z 879.8; HRMS (ESI, positive): calcd for $\text{C}_{44}\text{H}_{64}\text{O}_2\text{I}_2$, 878.7867, found 878.7868 (M^+).

TTFV-pyrene copolymer **5**



TTFV **4** (36 mg, 0.060 mmol) and 1,8-diiodopyrene **3** (52 mg, 0.060 mmol) were mixed with *i*-Pr₂NH (1 mL) in a mixed solvent of DMF (1.5 mL) and toluene (2.5 mL). The mixture was stirred with a magnetic bar at room temperature and to the mixture was added catalytic amounts of Pd(PPh₃)₄ (7.3 mg, 0.0060 mmol) and CuI (3.6 mg, 0.0020 mmol). The mixture was heated at 65 °C under N₂ for 24 h under stirring. The reaction mixture was then cooled to room temperature and poured into MeOH (200 mL) to give a brown colored precipitate, which was collected by vacuum filtration and washed with MeOH several times to afford copolymer **5** (65 mg, 87%) as a brown solid. IR (neat): 2916, 2846, 1592, 1463, 1373, 1297, 1214, 1086, 1007, 966, 873, 817, 718 cm⁻¹. ¹H NMR (300 MHz, CDCl₃): δ 8.72–8.18 (m, 6H), 7.72–7.33 (m, 8H), 4.36–4.27 (m, 4H), 2.47–2.38 (m, 12H), 2.01–1.89 (m, 4H), 1.56–1.36 (m, 44H), 0.91–0.83 (m, 6H); a meaningful ¹³C NMR spectrum could not be successfully obtained. GPC: $M_n = 4,562 \text{ g mol}^{-1}$, $M_w = 6,219 \text{ g mol}^{-1}$, PDI = 1.32.

2. NMR Spectra of New Compounds

**Fig. S-1** ^1H NMR (300 MHz, CDCl_3) spectrum of compound **2**.

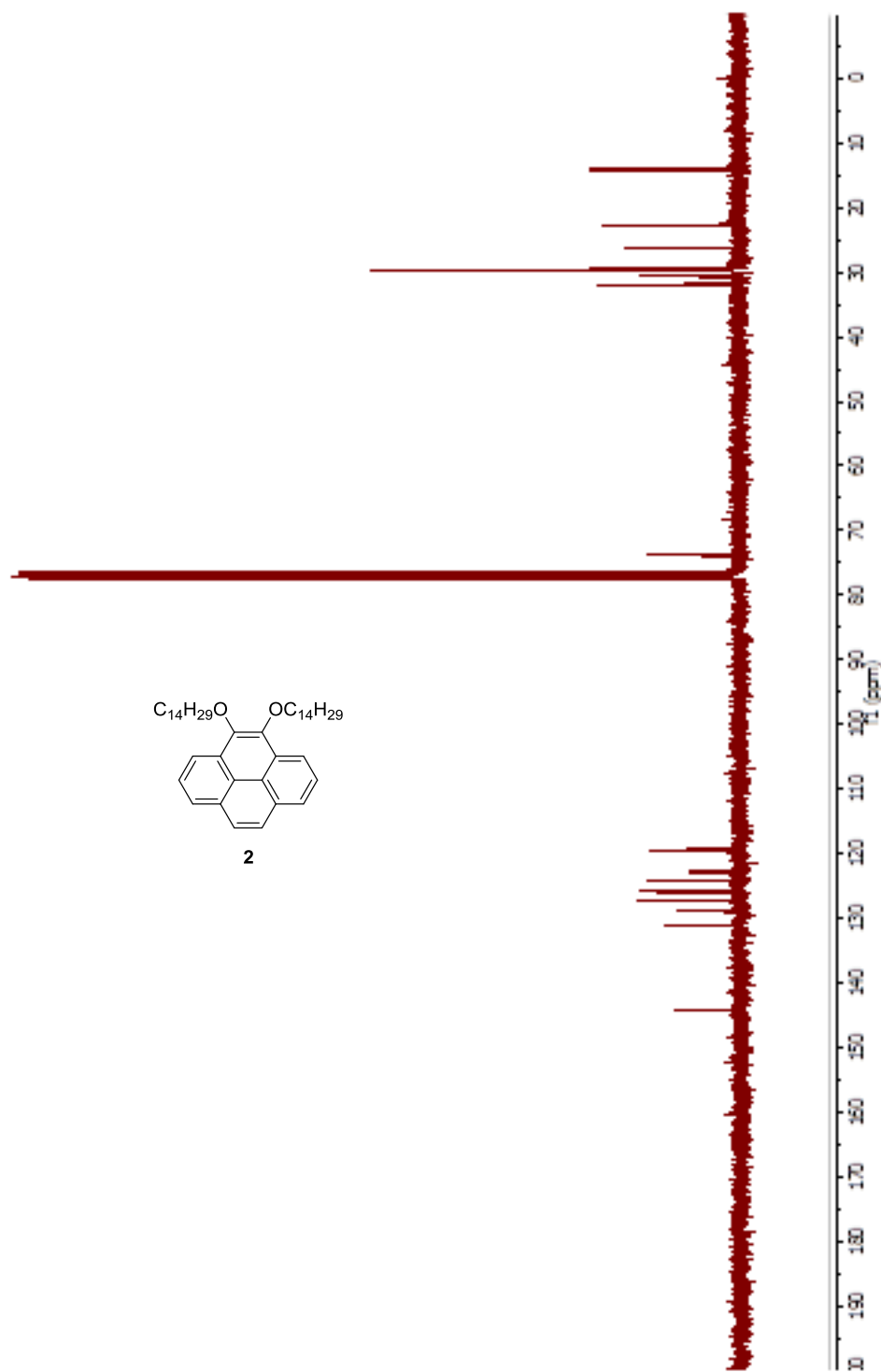


Fig. S-2 ^{13}C NMR (75 MHz, CDCl_3) spectrum of compound **2**.

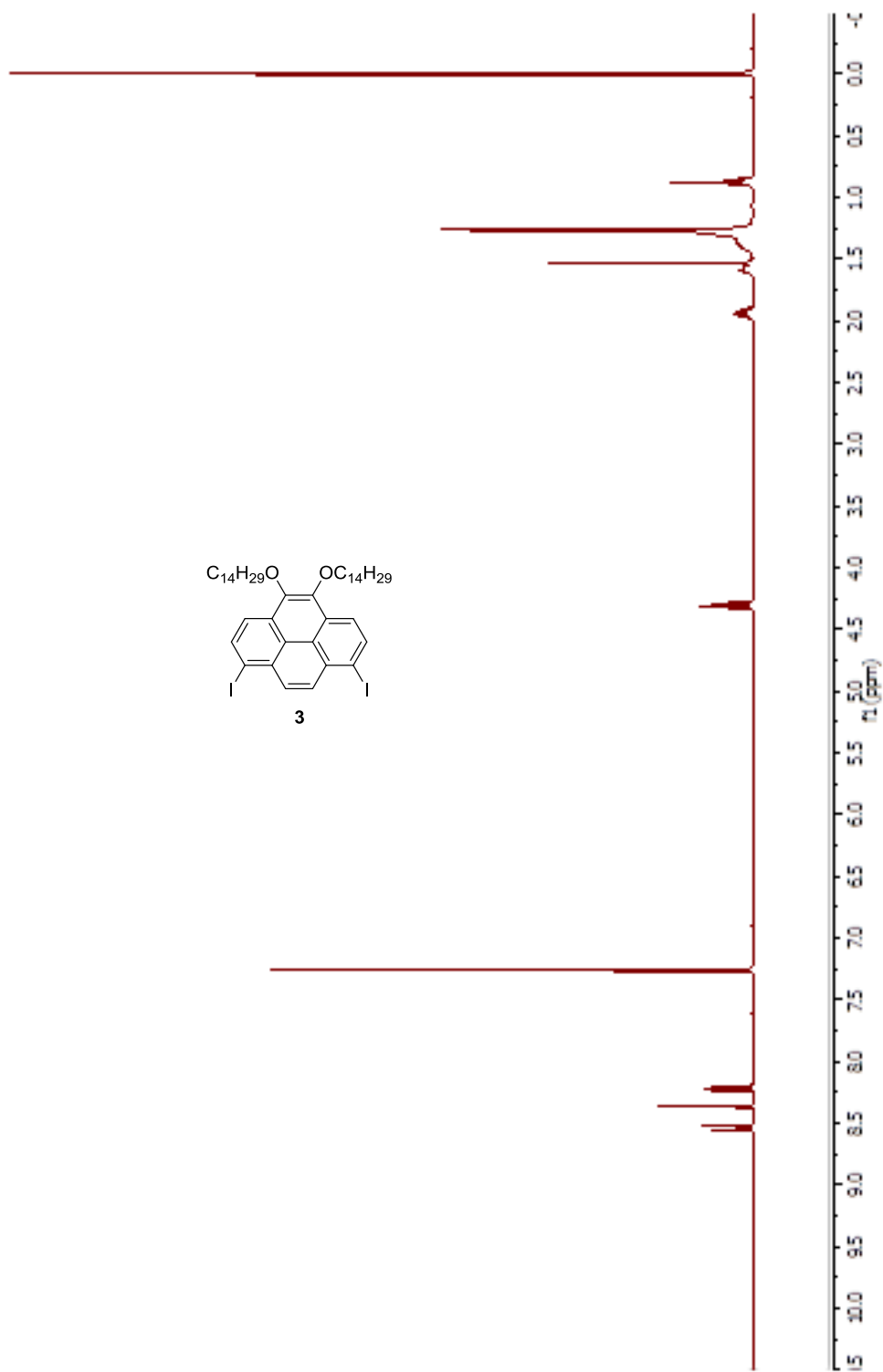


Fig. S-3 1H NMR (300 MHz, $CDCl_3$) spectrum of compound **3**.

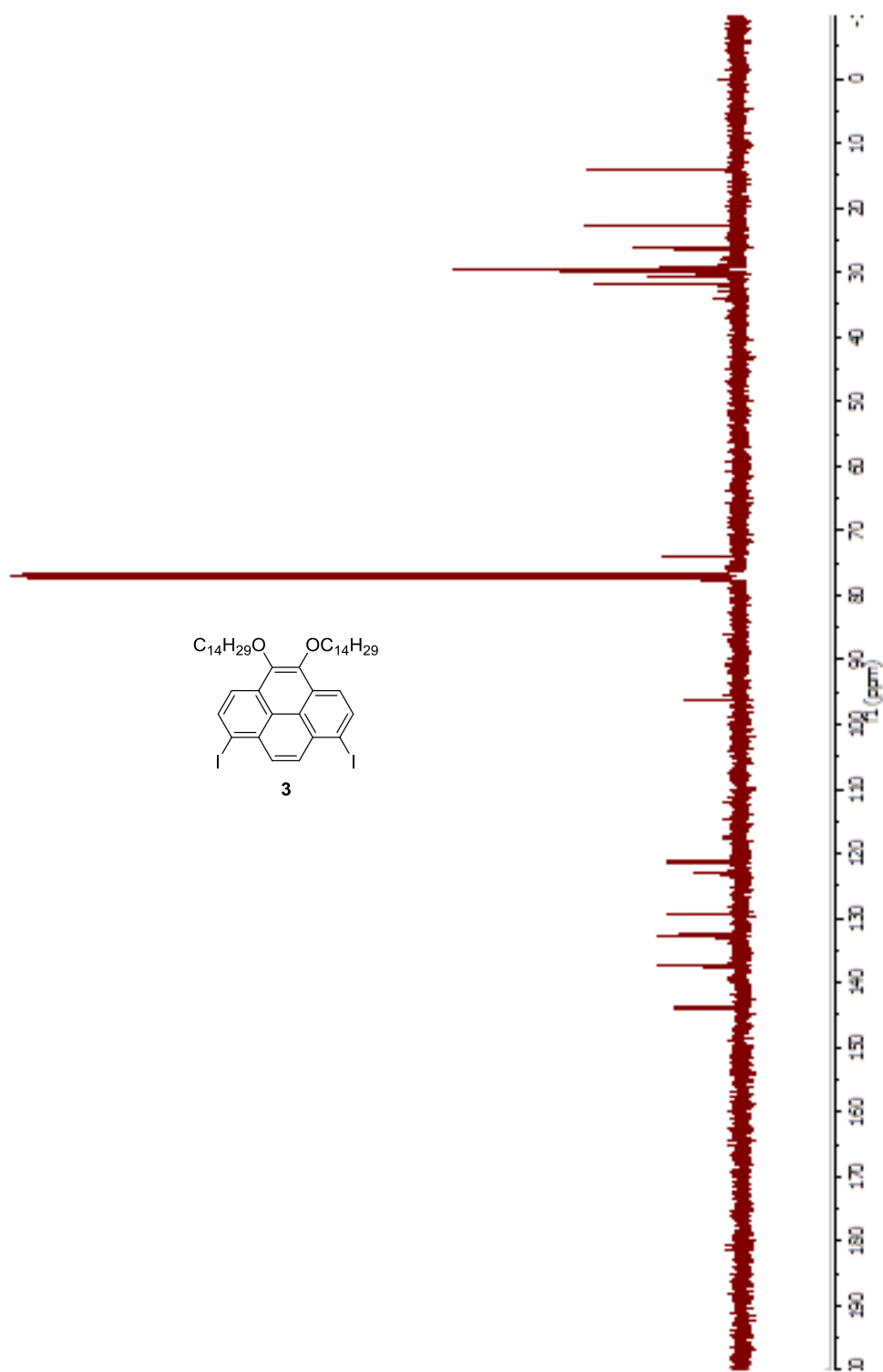


Fig. S-4 ^{13}C NMR (75 MHz, CDCl_3) spectrum of compound **3**.

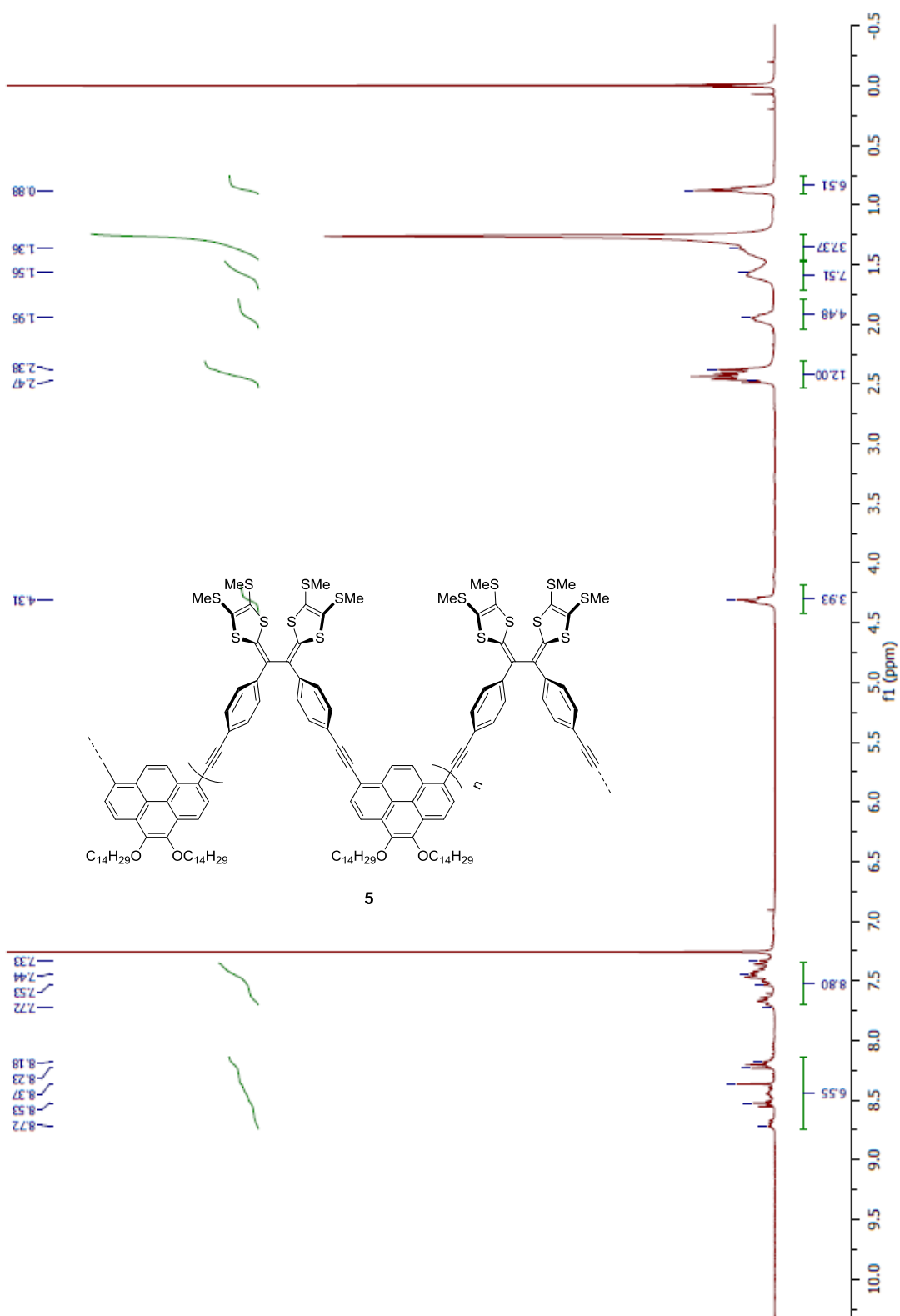


Fig. S-5 ^1H NMR (300 MHz, CDCl_3) spectrum of compound **5**.

3. GPC Analytical Result

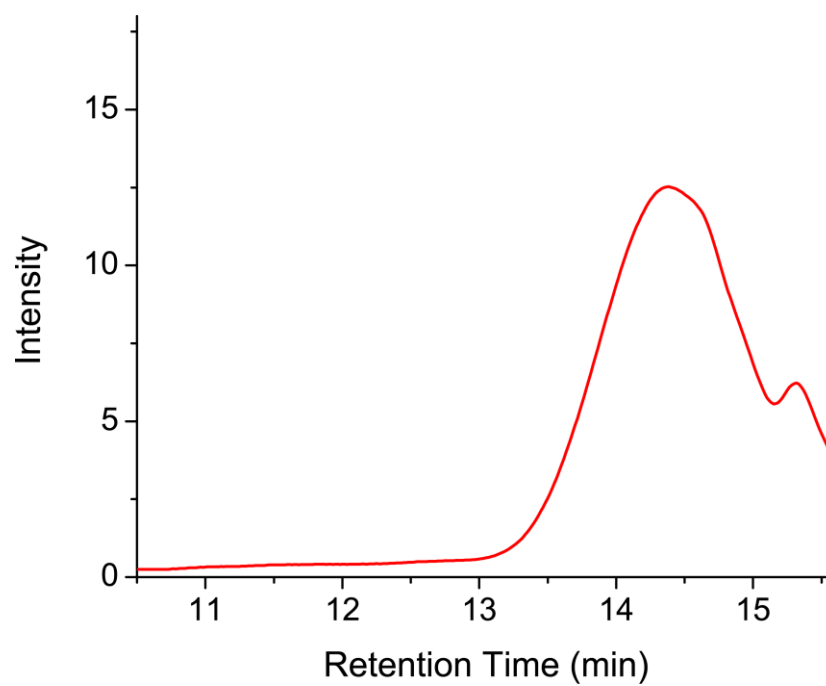


Fig. S-6 GPC profile of TTFV-pyrene copolymer **5**.

4. Diffusion NMR Data Analysis

Pulsed gradient spin echo (PGSE) NMR experiments were performed on copolymer **5** in CDCl₃, and the data extracted from these experiments enable the determination of a diffusion coefficient, from which a hydrodynamic radius can be calculated using the Stokes-Einstein equation:

$$D = \frac{k_B T}{6\pi\eta r_H}$$

where D is the diffusion coefficient, k_B is the Boltzmann constant ($1.3806448 \times 10^{-23}$ J K⁻¹), T is temperature (298 K), η is viscosity of chloroform (0.517 mPa S), and r_H is the hydrodynamic radius. This equation is for molecules which are spherical in shape. Using the average diffusion coefficient, 1.984×10^{-10} m²/s, obtained from the PGSE diffusion NMR experiments, the hydrodynamic radius r_H is calculated to be 2.13 nm.

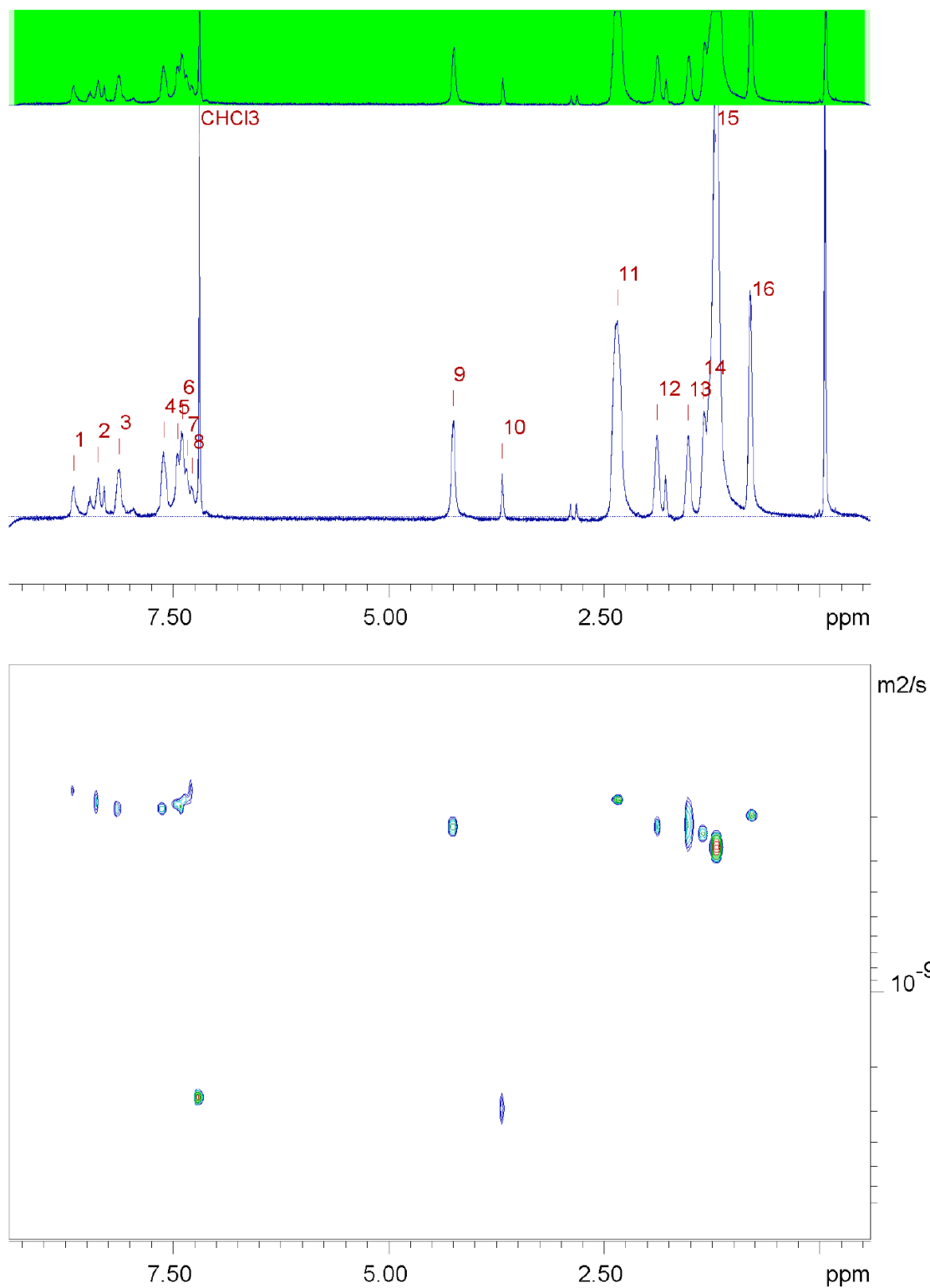
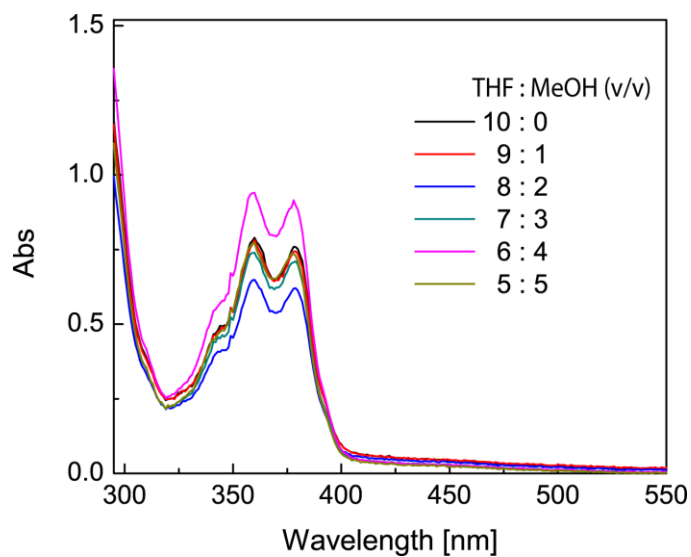
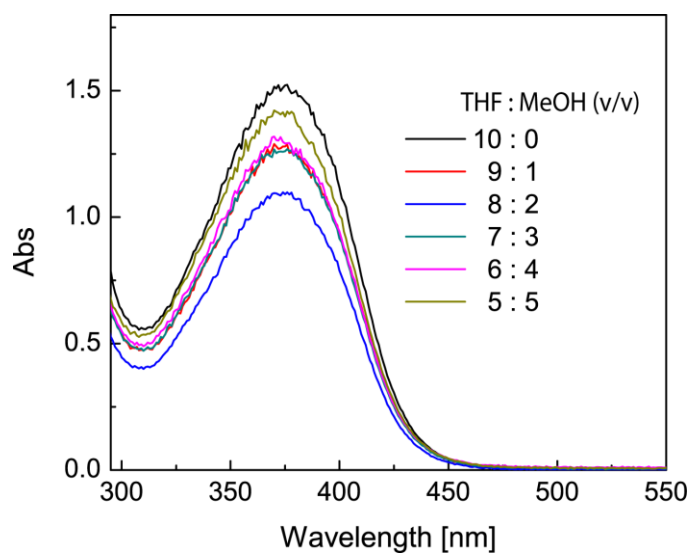


Fig. S-7 PGSE NMR (500 MHz, CDCl₃, 298 K) spectra of TTFV-pyrene copolymer **5**. The mean diffusion coefficient is $1.984 \times 10^{-10} \text{ m}^2/\text{s}$.

5. UV-Vis Absorption Properties of 3-5**Fig. S-8** UV-Vis spectra of pyrene precursor **3** in THF/MeOH.**Fig. S-9** UV-Vis spectra of TTFV precursor **4** in THF/MeOH.

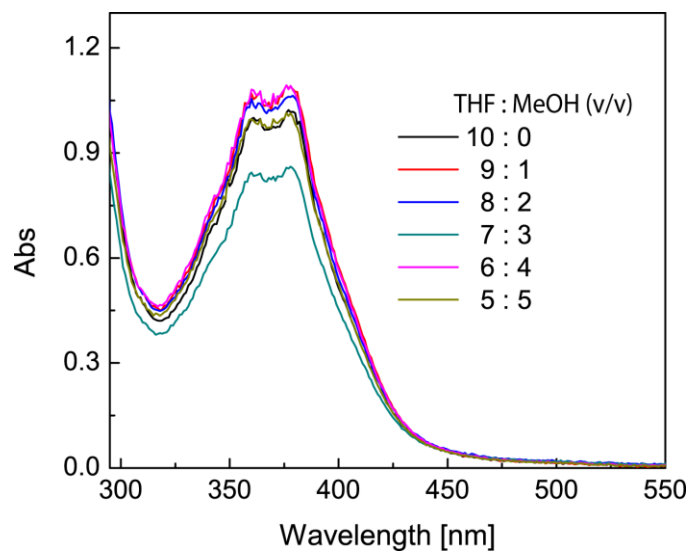


Fig. S-10 UV-Vis spectra of an equimolar mixture of **3** and **4** in THF/MeOH.

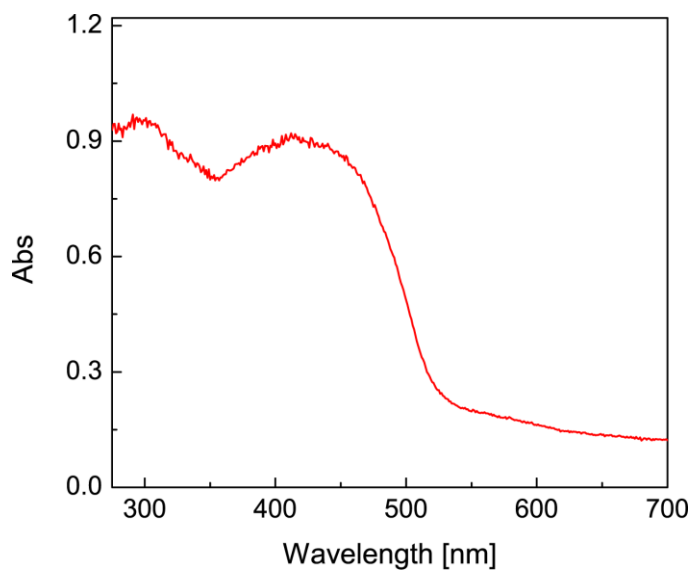


Fig. S-11 UV-Vis spectrum of the solid thin film of copolymer **5**.