Supporting Information For:

Nanoscale aryleneethynylene molecular wires with reversible fluorenone electrochemistry for self-assembly onto metal surfaces

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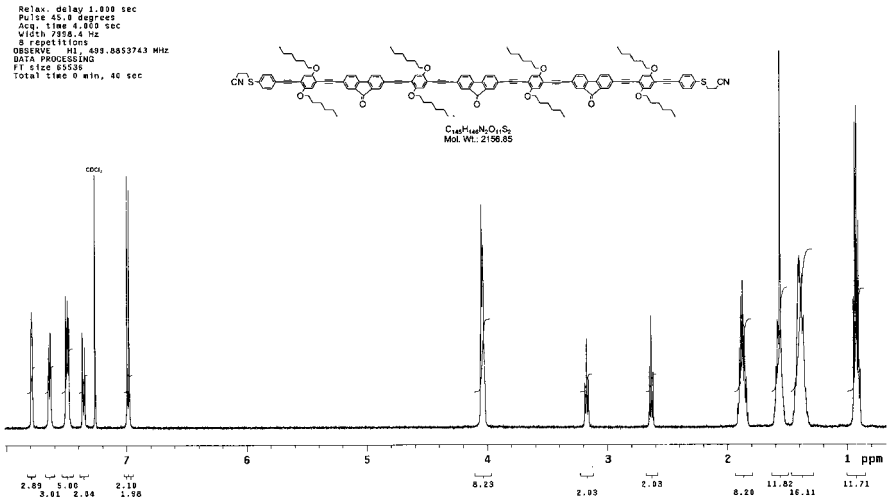
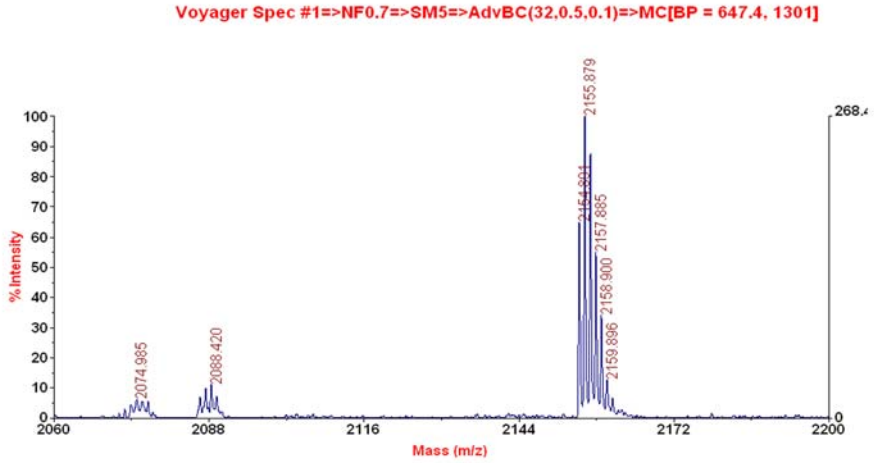
1 Characterisation data for compound 12.

Mp 258-260 °C; anal. calcd for $C_{145}H_{146}N_2O_{11}S_2$: C, 80.75; H, 6.82; N, 1.30; found: C, 80.37; H, 6.61; N, 1.16; ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.94 (m, 12H), 1.40 (m, 16H), 1.56 (m, 8H), 1.87 (m, 8H), 2.63 (t, J = 7.5 Hz, 2H), 3.17 (t, J = 7.5 Hz, 2H), 4.03 (m, 8H), 6.98 (s, 2H), 7.00 (s, 2H), 7.35 (d, J = 8.5 Hz, 2H), 7.48 (m, 5H), 7.62 (dd, J_{12} = 7.5 Hz, J_{13} = 1.5 Hz, 3H), 7.76 (s, 1H), 7.77 (s, 1H), 7.78 (s, 1H); ^{13}C NMR ($CDCl_3$, 500 MHz): δ 14.06, 14.08, 18.2, 22.65, 22.67, 22.69, 25.73, 25.76, 25.78, 29.3, 29.7, 31.59, 31.60, 69.5, 87.2, 88.2, 94.2, 94.3, 113.6, 113.7, 114.0, 116.65, 117.78, 120.5, 122.6, 124.7, 127.3, 130.3, 132.3, 133.8, 134.5, 137.7, 143.2, 153.63, 153.67, 192.2; MALDI-TOF MS: 2155.879 (M+, 100%).

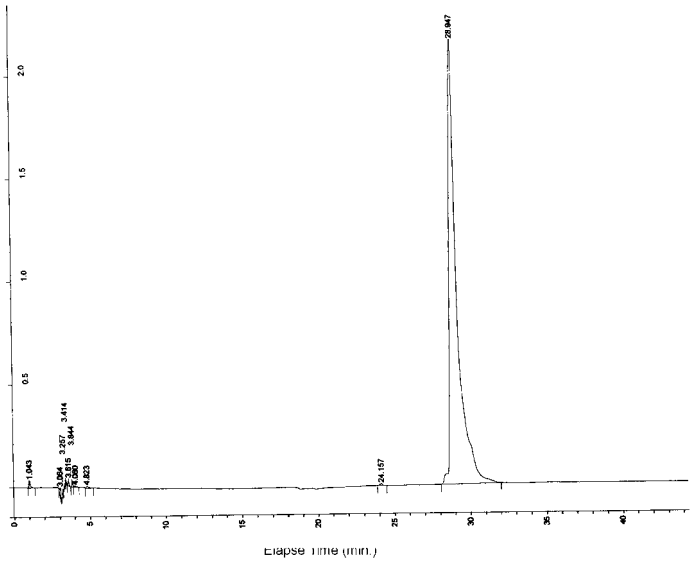
a) ^{1}H NMR ($CDCl_3$, 500 MHz) spectrum.



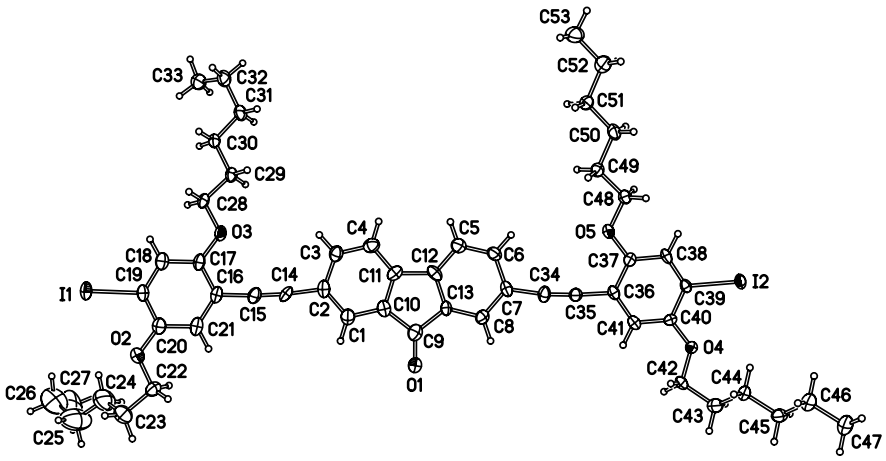
b) MALDI-TOF masss spectrum (dithranol matrix).



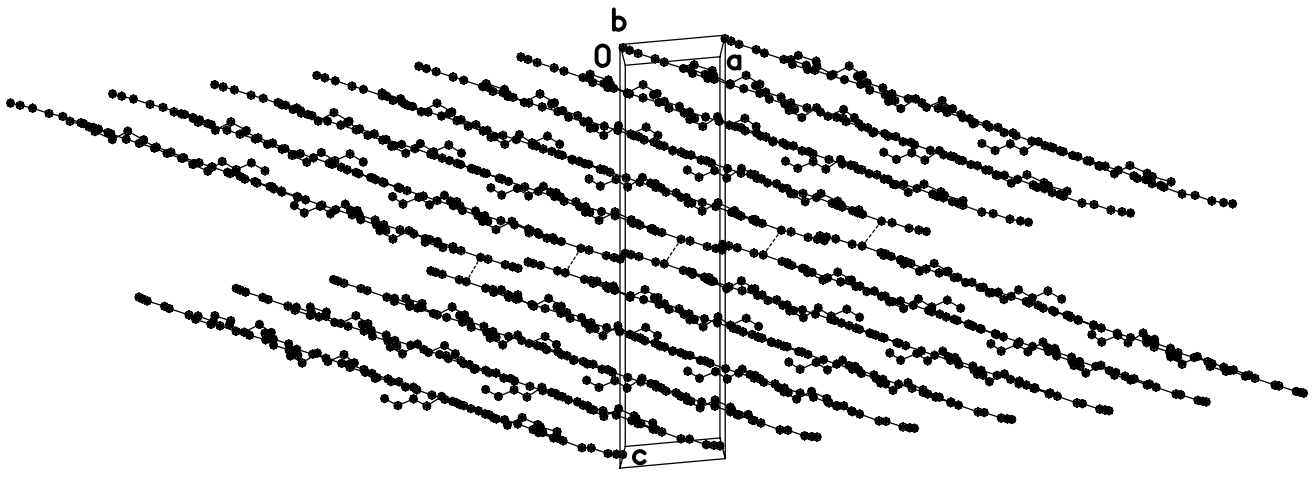
c) HPLC chromatogram (Hypersil C_{18} 5µ ODS reverse phase column, H_2O/THF gradient eluent, UV detector).



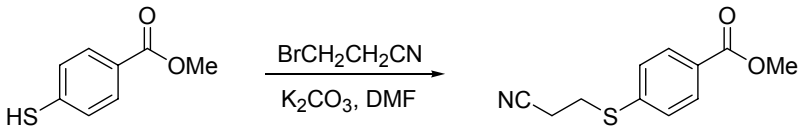
2 Molecular structure of compound 5, as determined by X-ray diffraction.



3 Packing diagram of molecules of compound 11 (viewed down the y axis).



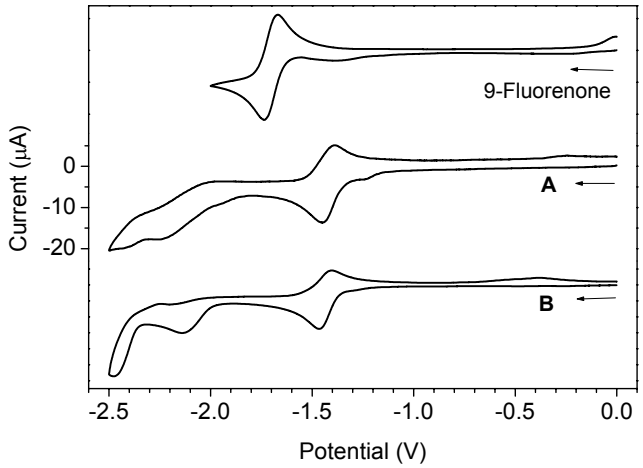
4 Synthesis of methyl 4-[2-cyanoethyl)thio]benzoate.

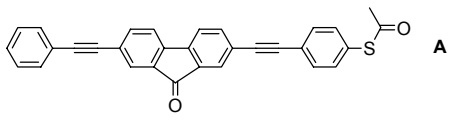


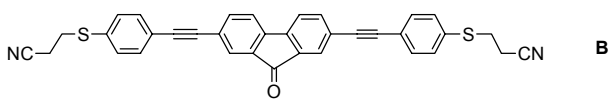
Methyl 4-mercaptobenzoate[1] (3.32 g, 19.7 mmol) was dissolved in anhydrous DMF (50 mL). The solution was degassed followed by the addtion of potassium carbonate powder (3.0 g, 21.7 mmol) and 3-bromopropionitrile (5.0 mL, 60 mmol). The mixture was stirred under argon at 100 ^{o}C for 12 h. The white solid was removed by suction filtration and the filtrate was vacuum evaporated to remove the solvent. The residue was column chromatographed on silica (dichloromethane eluent) then recrystallized from DCM-hexane mixture to yield the title compound as white crystals (3.74 g, 86%): mp 73.9 – 75.3 ^{o}C; Anal. Calcd for $C_{11}H_{11}NO_2S$: C, 59.71; H, 5.01; N, 6.33. Found: C, 59.77; H, 5.05; N, 6.38; ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.97 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.4 Hz, 2H), 3.90 (s, 3 H), 3.23 (t, J = 7.3 Hz, 2H), 2.66 (t, J = 7.3 Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 166.3, 140.1, 130.3, 128.4, 128.3, 117.6, 52.2, 28.5, 18.0; MS (EI) *m/z* 221 (M^+, 100%).

5 Cyclic voltammograms of 9-fluorenone and two model compounds of molecues 11 and 12.

Experimental conditions: supporting electrolyte: DMF containing 0.1 M $TBAPF_6$; electrodes: working, Pt disk (Φ = 1.8 mm); counter, Pt wire; reference, $Ag/AgNO_3$-acetonitrile. Scan rate: 100 mV/sec. The synthesis of A and B will be reported elsewhere.







[1] Wiley, P. F. *J. Org. Chem*. **1951**, *16*, 810-814.