

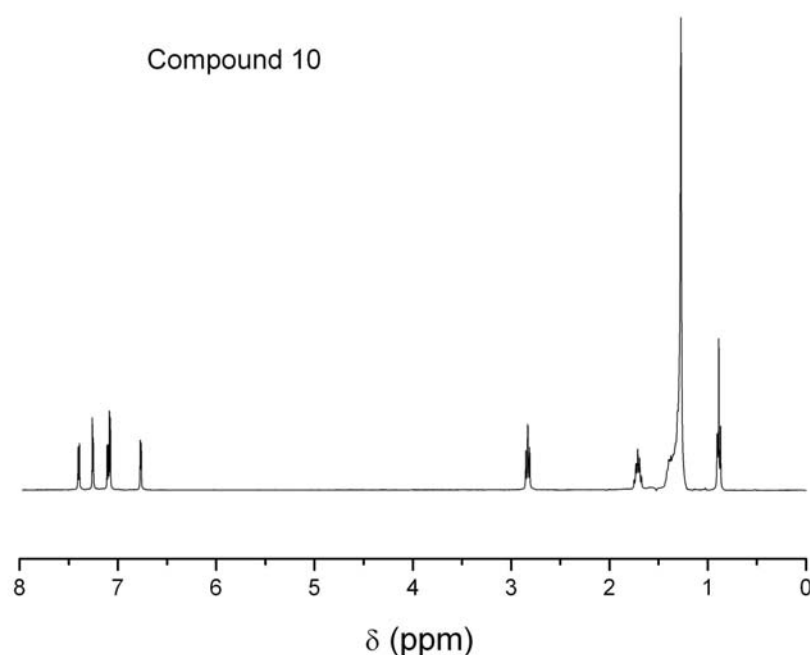
## The synthesis of an end-capped sexithiophene bearing fused TTF units

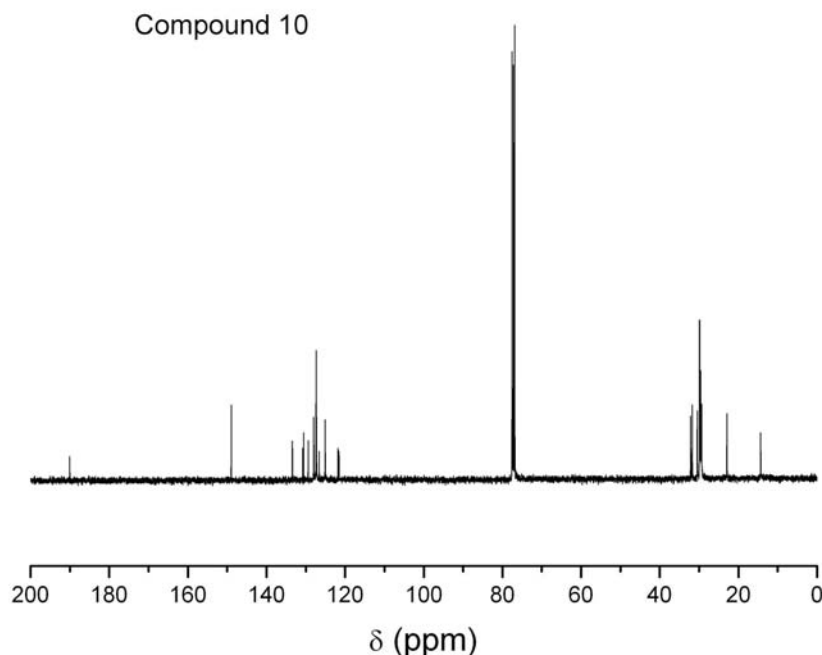
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### Supporting Information Section

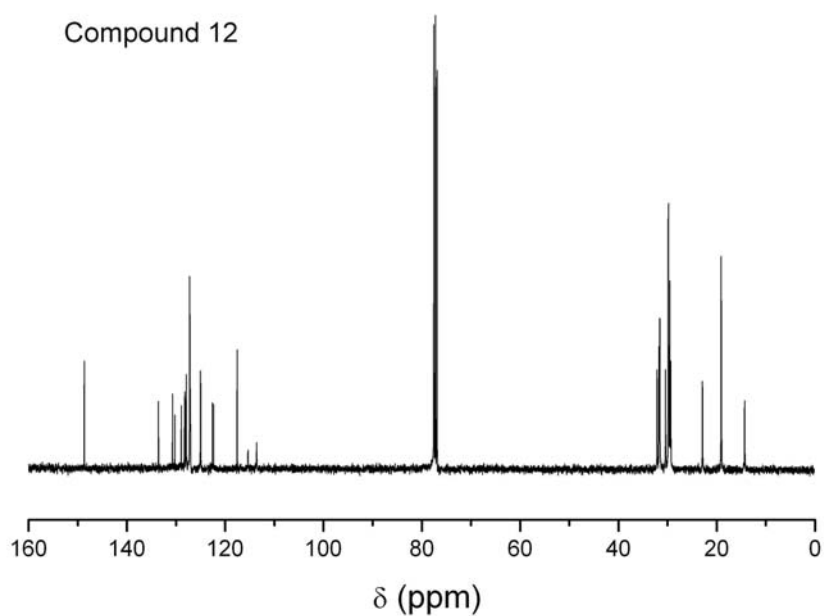
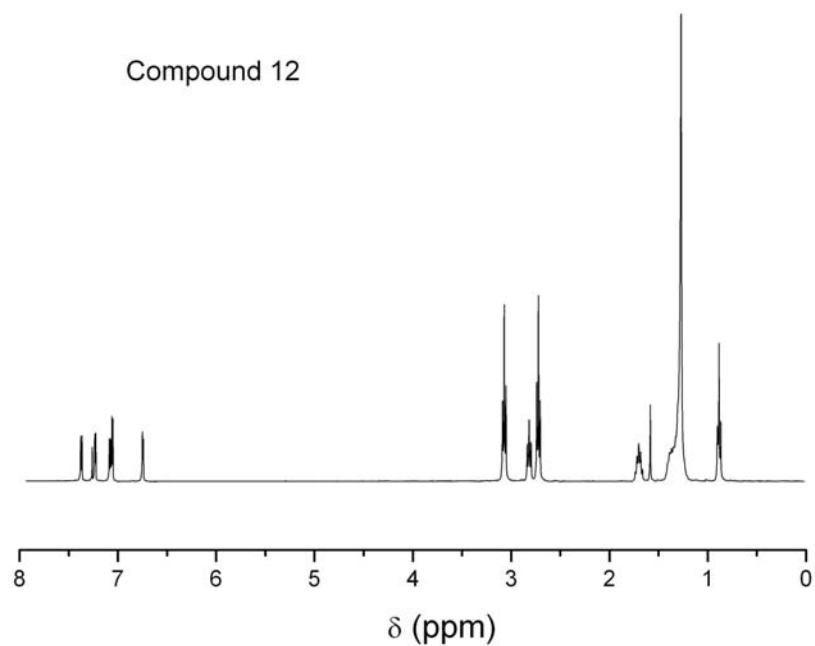
#### [1] Synthesis

**5-(5-Dodecyl-thiophen-2-yl)-7-thiophen-2-yl-1,3,4,6,8-pentathia-s-indacen-2-one (10).** A solution of 5-(5-methyl-thiophene-2-carbonyl)-6-(thiophene-2-carbonyl)-5,6-dihydro-[1,3]dithiolo[4,5-b][1,4]dithiin-2-one (9) (3.93 g, 6.58mmol) was stirred with P<sub>4</sub>S<sub>10</sub> (14.3 g, 32.2 mM) and NaHCO<sub>3</sub> (4.57 g, 54.4mmol) at 90 °C for 2 hours. After cooling, water (150ml) was added to destroy excess phosphorus pentasulfide and the mixture stirred at 70 °C for half an hour. After pouring the mixture onto 300 ml ice water the precipitate was filtered and washed with water. The crude product was dried, dissolved in toluene and filtered through a plug of silica. After evaporation of toluene the residue was recrystallized from DCM:petroleum ether to afford 3.02 g (5.08mmol, 77.1%) of light yellow powder (M.p. 91-92. °C) (Found: C, 54.29, H, 4.94; C<sub>27</sub>H<sub>30</sub>N<sub>2</sub>OS<sub>7</sub> requires C, 54.51, H, 5.08),  $\delta_{\text{H}}$  (CDCl<sub>3</sub>) 7.40 (1H, dd, *J* 5.1, 1.0), 7.25 (1H, dd, *J* 3.7, 1.0), 7.10 (1H, dd, *J* 5.1, 3.7), 7.08 (1H, dd, *J* 3.6), 6.77 (1H, d, *J* 3.6), 2.83 (2H, t, 7.6), 1.71 (2H, m), 1.27 (18H, m), 0.89 (3H, t, 6.8),  $\delta_{\text{C}}$  (CDCl<sub>3</sub>) 190.047, 148.946, 133.425, 130.751, 130.568, 129.387, 128.008, 127.789, 127.422, 127.380, 127.301, 126.592, 125.086, 121.806, 121.556, 32.139, 31.750, 30.429, 29.855, 29.755, 29.548, 29.351, 22.906, 14.330. MS (electrospray) *M*<sup>+</sup>=595.



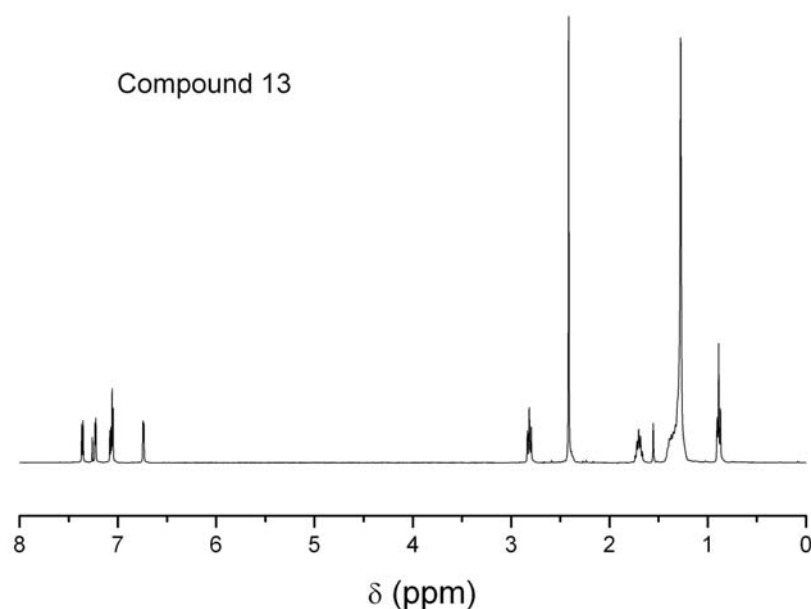


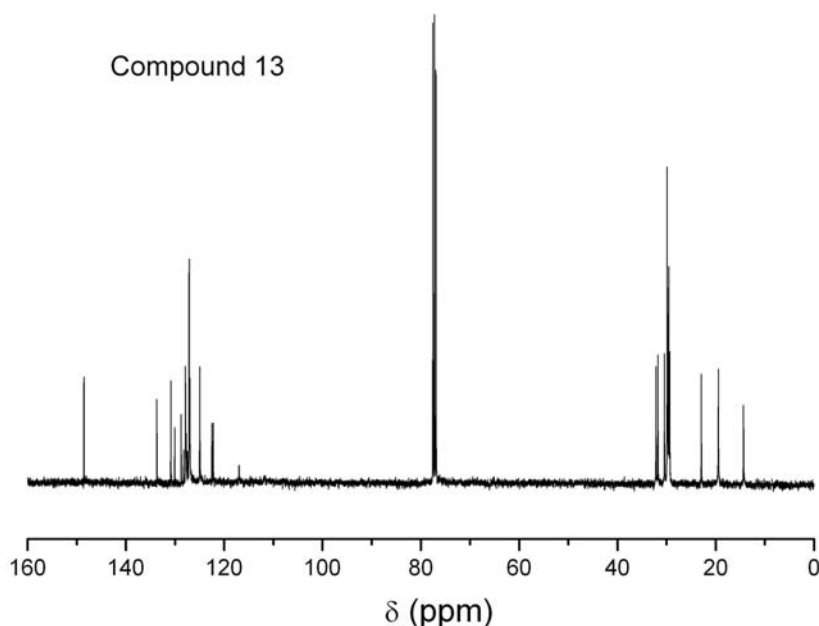
**3-{5-(2-Cyano-ethylsulfanyl)-2-[5-(5-dodecyl-thiophen-2-yl)-7-thiophen-2-yl-1,3,4,6,8-pentathia-s-indacen-2-ylidene]-[1,3]dithiol-4-ylsulfanyl}-propionitrile (12).** A mixture of compound **10** (1.911g, 3.212mmol) and thione **11** (1.205g, 3.957mmol) in freshly distilled triethyl phosphite (~56 ml) was allowed to stir at 120 °C for 2 hour. After cooling to room temperature the reaction mixture was diluted with methanol and filtered. The precipitate was dissolved in DCM, filtered and dried. Further product was isolated by evaporating the filtrate and subjecting the residue to flash column chromatography on silica gel using DCM as the eluent. The middle fraction was collected and reprecipitated from DCM : methanol to afford **12** as an orange powder (M.p. 34-37 °C) Yield 1.933g (70.7) %. (Found: C, 51.06, H, 4.50, N, 2.99, S, 41.67; C<sub>36</sub>H<sub>38</sub>N<sub>2</sub>S<sub>11</sub> requires C, 50.79, H, 4.50, N, 3.29, S, 41.43 %), δ<sub>H</sub> (CDCl<sub>3</sub>) 7.38 (1H, d, *J* 5.0), 7.24 (1H, d, *J* 3.4), 7.09 (1H, dd, *J* 5.0, 3.7), 7.07 (1H, d, *J* 3.6), 6.76 (1H, d, *J* 3.6), 3.08 (4H, t, *J* 7.0), 2.83 (2H, t, 7.6), 2.73 (4H, t, *J* 7.0), 1.71 (2H, m), 1.27 (18H, m), 0.88 (3H, t, 6.8); δ<sub>C</sub> (CDCl<sub>3</sub>) 148.650, 133.563, 130.716, 130.237, 128.921, 128.243, 128.187, 127.979, 127.918, 127.199, 127.150, 127.080, 124.995, 122.611, 122.345, 117.546, 115.348, 113.598, 32.109, 31.721, 31.579, 30.394, 29.829, 29.731, 29.530, 29.335, 22.877, 19.074, 14.314. MS (electrospray) (M+Na)<sup>+</sup>=873, (M – dimer + Na)<sup>+</sup> = 1724, (M-(CH<sub>2</sub>-CH<sub>2</sub>CN))<sup>-</sup>=796).



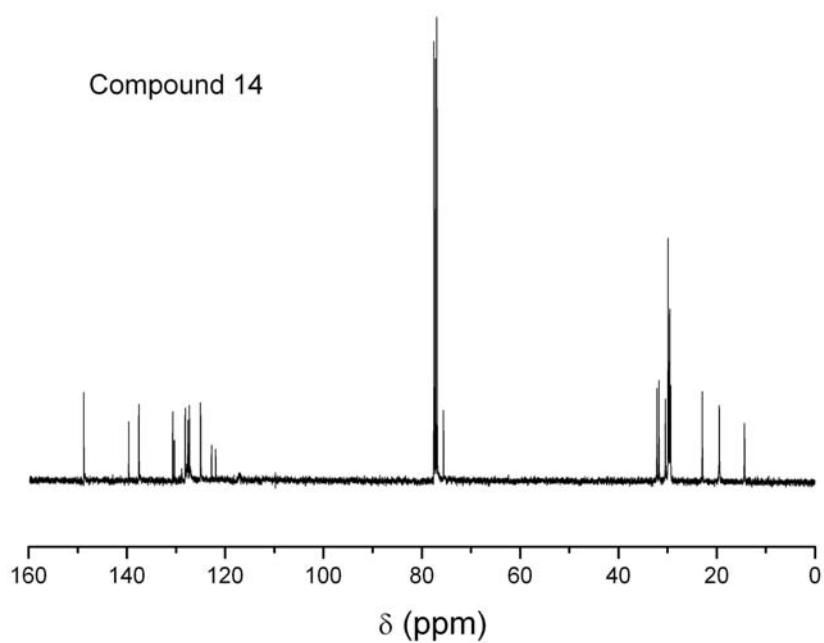
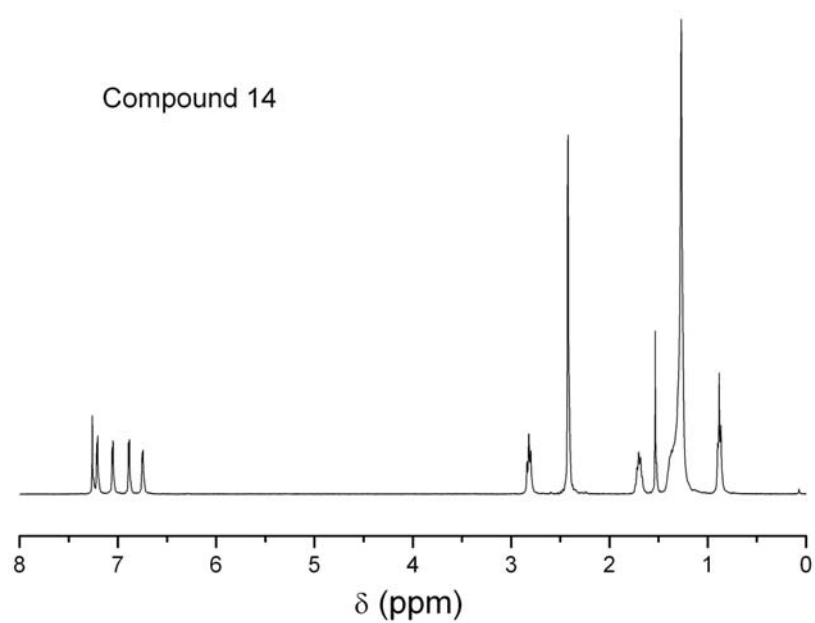
**2-(4,5-Bis-methylsulfanyl-[1,3]dithiol-2-ylidene)-5-(5-dodecyl-thiophen-2-yl)-7-thiophen-2-yl-1,3,4,6,8-pentathia-s-indacene (13).** A solution of compound **12** (504.2 mg, 592.2 $\mu$ mol) in 20 ml of THF was cooled in an ice bath and sodium methoxide, was added (ca. 25 wt.% solution in methanol, 0.41ml, 1.8mmol). The solution was stirred at 0 °C for 1 hour and 0.18 ml (2.89mmol) of iodomethane was

added. The reaction mixture was stirred at room temperature overnight. The solvent was removed under vacuum. The residue was dissolved in DCM, filtered and after evaporation of the solvent, recrystallized from DCM:methanol to afford an orange powder (M.p.39-42 °C). Yield 443 mg 96.7 %.(Found: C, 49.77, H, 4.65, S, 45.36;  $C_{36}H_{38}N_2S_{11}$  requires C, 49.70, H, 4.69, S, 45.61 %),  $\delta_H$  ( $CDCl_3$ ) 7.38 (1H, dd,  $J$  5.1, 1.0), 7.24 (1H, dd,  $J$  3.6, 1.0), 7.09 (1H, dd,  $J$  5.1, 3.7), 7.06 (1H, d,  $J$  3.6), 6.75 (1H, d,  $J$  3.6), 2.82 (2H, t, 7.6), 2.42 (6H, s), 1.71 (2H, m), 1.27 (18H, m), 0.88 (3H, t, 6.8);  $\delta_C$  ( $CDCl_3$ ) 148.522, 133.689, 130.846, 130.059, 128.743, 128.255, 127.869, 127.759, 127.680, 127.422, 127.127, 126.973, 124.995, 122.499, 122.237, 32.129, 31.734, 30.407, 29.851, 29.752, 29.552, 29.352, 22.897, 19.451, 14.330. MS (MALDI-TOF)  $M^+=772$ .





**2-(4,5-Bis-methylsulfanyl-[1,3]dithiol-2-ylidene)-5-(5-dodecyl-thiophen-2-yl)-7-(5-iodo-thiophen-2-yl)-1,3,4,6,8-pentathia-s-indacene (14).** To a solution of **13** (151 mg, 195.4  $\mu$ mol) in THF (10 ml) at 78 °C, was added LDA (1.5 M in cyclohexane) (150  $\mu$ l, 225  $\mu$ mol). The reaction mixture was stirred at this temperature for 1 hour before adding perfluorohexyl iodide (85  $\mu$ l, 393  $\mu$ mol) and allowing the reaction mixture to reach room temperature overnight. The reaction mixture was diluted with  $\text{NH}_4\text{Cl}$  solution and extracted with DCM. The combined extracts were washed with  $\text{NH}_4\text{Cl}$  solution and dried over  $\text{MgSO}_4$ . After evaporating the solvent, the residue was columned on silica with DCM: petroleum ether 1:5 as the eluent. The first fraction was recrystallized from DCM: methanol mixture to afford a yellow – orange powder. (M.p. 54-57 °C). Yield 129.2 mg 73.54%. (Found: C, 43.12, H, 3.60;  $\text{C}_{36}\text{H}_{38}\text{N}_2\text{S}_{11}$  requires C, 42.74, H, 3.92%),  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 7.21 (1H, d,  $J$  3.8), 7.05 (1H, d,  $J$  3.6), 6.89 (1H, d,  $J$  3.8), 6.75 (1H, d,  $J$  3.6) 2.82 (2H, t, 7.6), 2.424 (3H, s), 2.420 (3H, s), 1.72 (2H, m), 1.27 (18H, m), 0.88 (3H, t, 6.8);  $\delta_{\text{C}}$  ( $\text{CDCl}_3$ ) 148.741, 139.619, 137.550, 130.663, 130.332, 128.838, 128.131, 127.611, 127.545, 127.269, 124.996, 122.775, 121.920, 75.580, 32.135, 31.725, 30.425, 29.858, 29.763, 29.559, 29.369, 22.904, 19.469, 14.336. (MALDI-TOF)  $\text{M}^+$ =898,  $(\text{M}-125)^+$ =773 (the intensity of this peak enlarges with increasing laser power).



**Oxidative dimerization of 13 in the presence of FeCl<sub>3</sub>.**

To a solution of compound **13** (32.9mg, 42.54  $\mu$ mol) in dry nitrobenzene (3.0ml) was added FeCl<sub>3</sub> (0.487M in nitrobenzene)(0.79 ml, 0.38 mmol) and the reaction mixture stirred at room temperature for 1 hour. The reaction was diluted with methanol (75ml) and water (3ml) and the precipitate was filtered and washed with methanol. The

product was treated with  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$  and  $\text{CHCl}_3$ . After washing off excess  $\text{N}_2\text{H}_4\cdot\text{H}_2\text{O}$ , a solution of the crude product in 50 ml of  $\text{CHCl}_3$  was treated with  $\text{EDTA}\cdot\text{Na}_2$  solution (0.1 M, 100 ml) at 70 °C for 2 hours. Washing, drying ( $\text{MgSO}_4$ ) and evaporating the solvent afforded 36 mg of a red solid, poorly soluble in  $\text{CHCl}_3$ . Similar treatment with a solution of  $\text{NaCN}$  (0.5g) in 100 ml of water at 70 °C for 3 hours did not improve the solubility.

The crude product was subjected to column chromatography on silica gel using  $\text{CS}_2$  as the eluent to afford the dimer **1** (8mg, 24%).

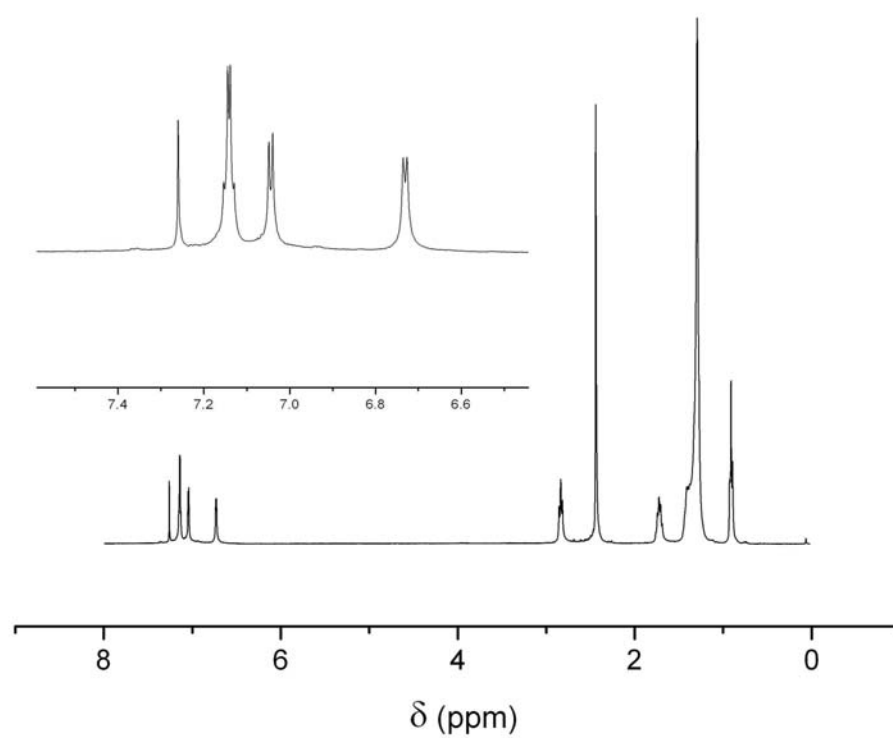
#### **Dimerization of 14 by the Ullmann reaction.**

A mixture of compound **14** (85 mg, 94.5  $\mu\text{mol}$ ), copper powder (85 mg) and DMF (5 ml) was heated under reflux at 160 °C for 3 hours. After cooling to room temperature, the reaction was diluted with methanol (~150 ml) and water (~5 ml). The precipitate was filtered, washed with methanol and dissolved in hot toluene. After filtering off residual Cu, the solvent was evaporated and the crude product was subjected to column chromatography on silica gel, firstly eluting with DCM : petroleum ether to remove the product of deiodination (**13**, ~12 mg, 16.4%) and then continuing with chloroform to afford 70 mg of red solid. The latter was dissolved in 50 ml of  $\text{CHCl}_3$  and stirred with 50 ml of 0.1M solution of  $\text{EDTA}\cdot 2\text{NH}_3$  for 8 hours at 70 °C. The organic layer was separated dried with  $\text{Na}_2\text{SO}_4$  and after evaporation of the solvent (68 mg) subjected to another column on silica gel with  $\text{CS}_2$  as eluent to afford the dimer **1** (32 mg, 43.8 %) as a red solid.

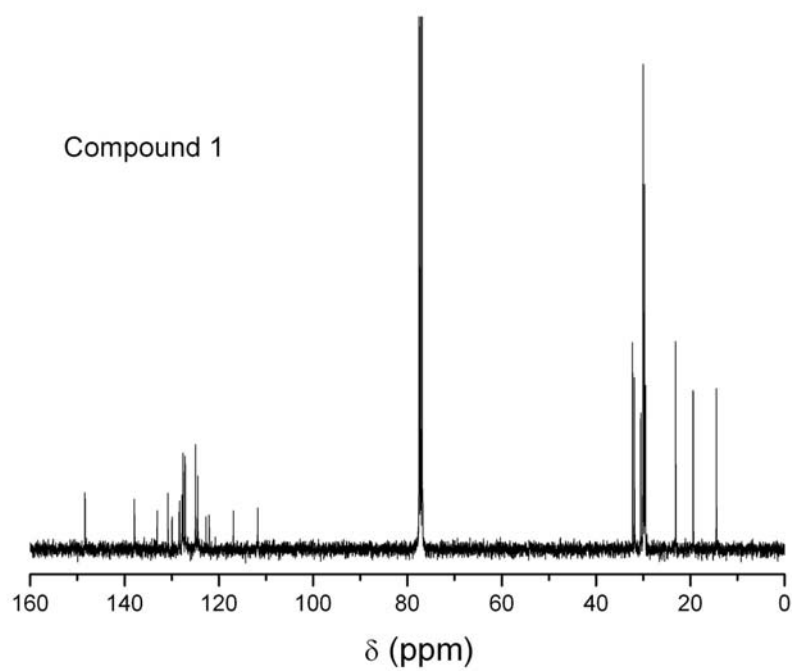
#### **Dimerization of 14 by the Yamamoto route.**

To a mixture of  $\text{Ni}(\text{COD})_2$  (22 mg, 80 $\mu\text{mol}$ ), COD (10  $\mu\text{l}$ , 82 $\mu\text{mol}$ ) and 2,2'-bipyridine (13 mg, 83  $\mu\text{mol}$ ) in 3 ml of DMF was added a solution of compound **14** (120 mg, 133  $\mu\text{mol}$ ) in 0.5 ml of toluene. The reaction was stirred under nitrogen at 60 °C for 20 hours. After cooling to room temperature, the reaction mixture was diluted with methanol. The precipitate was filtered, washed with methanol and then dissolved from the filter paper using hot toluene. After evaporation of the solvent the crude product was subjected to column chromatography on silica gel using  $\text{CS}_2$  as the eluent to afford the starting compound **14** (12 mg, 10%) as the first fraction, followed by the dimer **1** (10 mg, 9.7%).

(Found: C, 50.10, H, 4.64;  $\text{C}_{36}\text{H}_{38}\text{N}_2\text{S}_{11}$  requires C, 49.77, H, 4.57%),  $\delta_{\text{H}}$  ( $\text{CS}_2\text{-CDCl}_3$ ) 7.149 (1H, d, *J* 3.8), 7.134 (1H, d, *J* 3.8), 7.044 (1H, d, *J* 3.5), 6.731 (1H, d, *J* 3.5) 2.836 (2H, t, 7.5), 2.442 (3H, s), 2.439 (3H, s), 1.73 (2H, m), 1.29 (18H, m), 0.911 (3H, t, 6.5);  $\delta_{\text{C}}$  ( $\text{CS}_2\text{-CDCl}_3$ ) 148.376, 137.910, 133.055, 130.793, 129.925, 128.433, 128.320, 127.812, 127.735, 127.570, 127.137, 124.927, 124.460, 122.693, 122.040, 116.918, 111.738, 77.542, 77.225, 76.909, 32.243, 31.843, 30.493, 29.994, 29.919, 29.708, 29.514, 23.107, 19.380 and 14.448. (MALDI-TOF)  $\text{M}^+=1543$ .

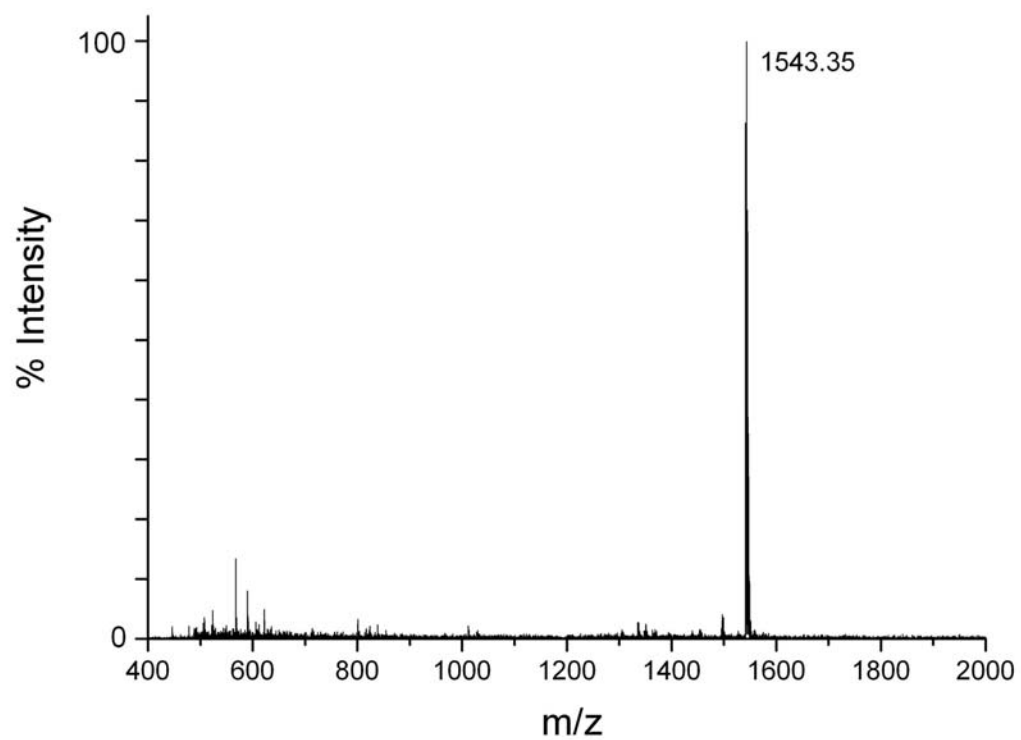


$^1\text{H}$  NMR spectrum of **1** in  $\text{CS}_2\text{-CDCl}_3$ .



$^{13}\text{C}$  NMR spectrum of **1** in  $\text{CS}_2\text{-CDCl}_3$ .

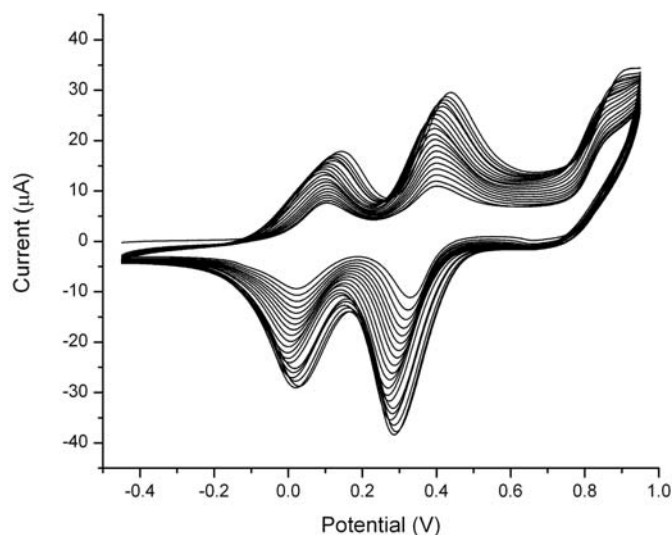




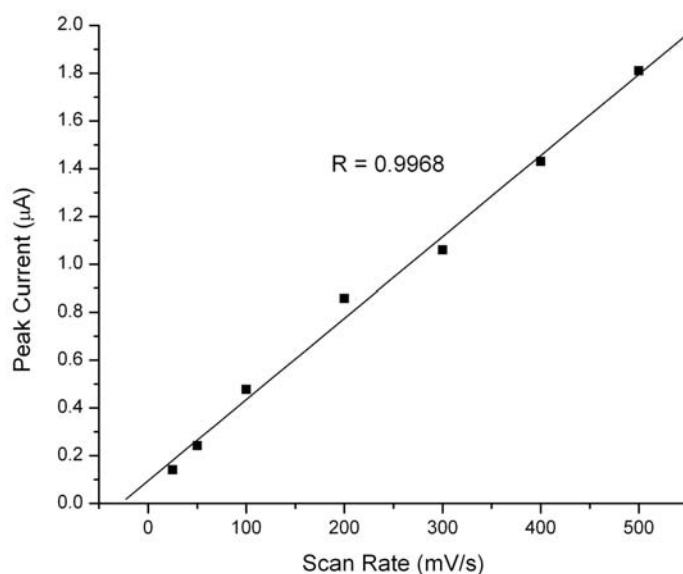
MALDI-TOF mass spectrum of compound **1**. The matrix was  $\alpha$ -cyano-4-hydroxycinnamic acid.

## [2] Growth of **1** by cyclic voltammetry

Although **1** was made routinely by potentiostatic growth on the working electrode, the following graph shows the dimerization process and deposition of the product by cyclic voltammetry under similar conditions:

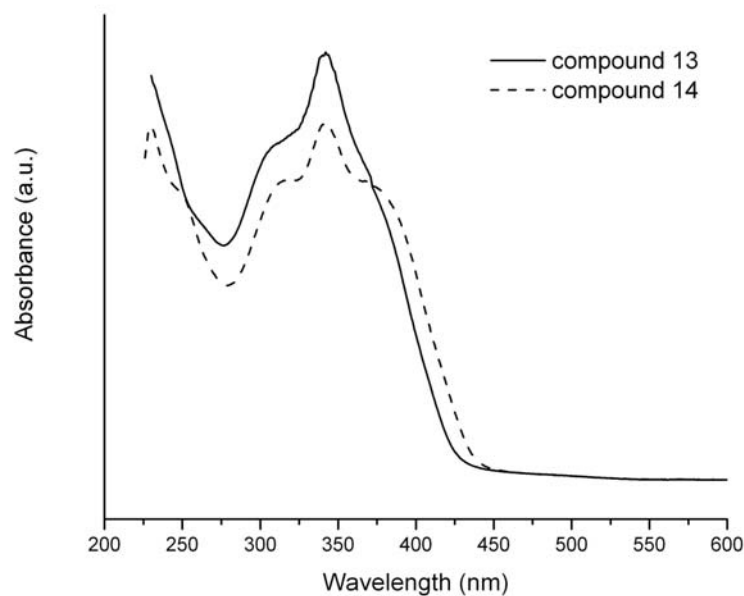


**Figure S1** Deposition on glassy carbon disk working electrode, Pt wire counter electrode, Ag wire pseudo reference electrode, *vs* Fc/Fc<sup>+</sup>. The solvent was 2:1 CH<sub>2</sub>Cl<sub>2</sub>:hexane, substrate concentration *ca.* 10<sup>-3</sup>M, TBAPF<sub>6</sub> as supporting electrolyte (0.1 M). Scan rate 0.1 V/s.

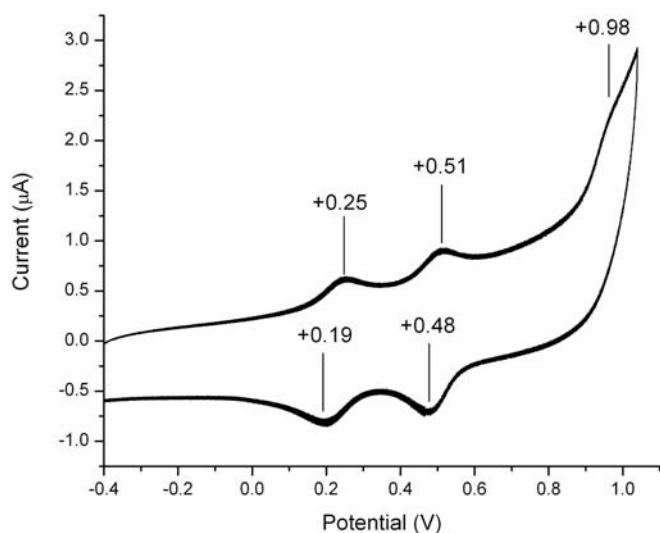


**Figure S2** Scan rate *vs* peak current (taken from the first oxidation wave) for compound **1**. The straight line shows that the current is not limited by the diffusion of the counter-anions.

### [3] Absorption spectra of compounds **13** and **14**



**Figure S3** Absorption spectra of terthiophenes **13** and **14** in dichloromethane solution.



**Figure S4** Cyclic voltammogram of compound **13** on Pt disk working electrode, Pt wire counter electrode, Ag wire pseudo reference electrode, vs  $\text{Fc}/\text{Fc}^+$ . The solvent was 1:1  $\text{CH}_2\text{Cl}_2$ :hexane, substrate concentration *ca.*  $10^{-3}\text{M}$ , TBAPF<sub>6</sub> as supporting electrolyte (0.1 M).  $E_{1/2}^{1\text{ox}} = +0.22$  V,  $E_{1/2}^{2\text{ox}} = +0.495$  V,  $E^{3\text{ox}} = +0.98$  V. The redox potentials are higher than those obtained in 100% dichloromethane solution (see page 2 of the manuscript). This discrepancy is due to increased solvent polarity in the case

of 100% dichloromethane (compared to a 1:1 CH<sub>2</sub>Cl<sub>2</sub>:hexane medium), which leads to the stabilisation of charged intermediates and a lowering of redox potentials.