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Supplementary Information

Supramolecular Formation of Fibrous Nanostructure in Donor-Acceptor Dyad Film

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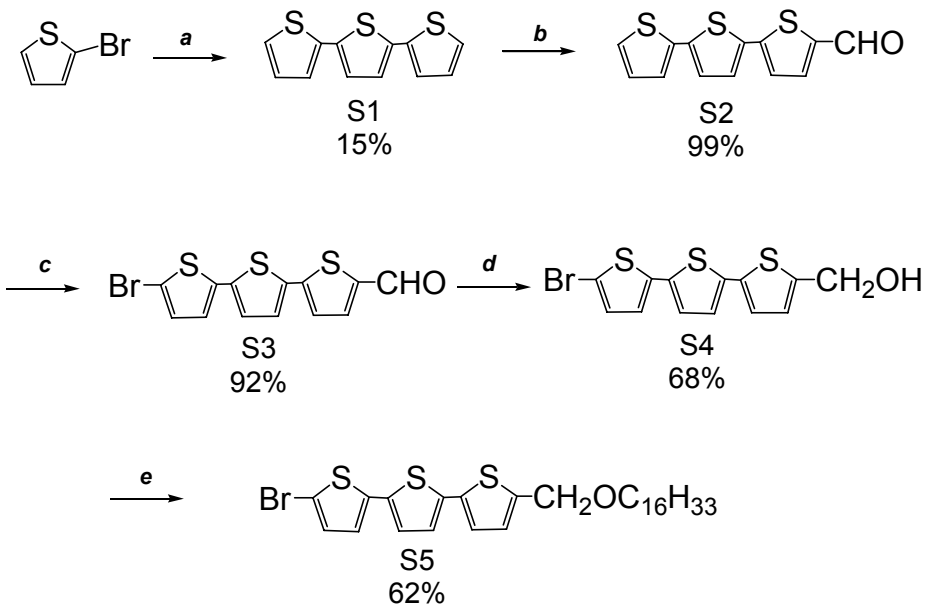
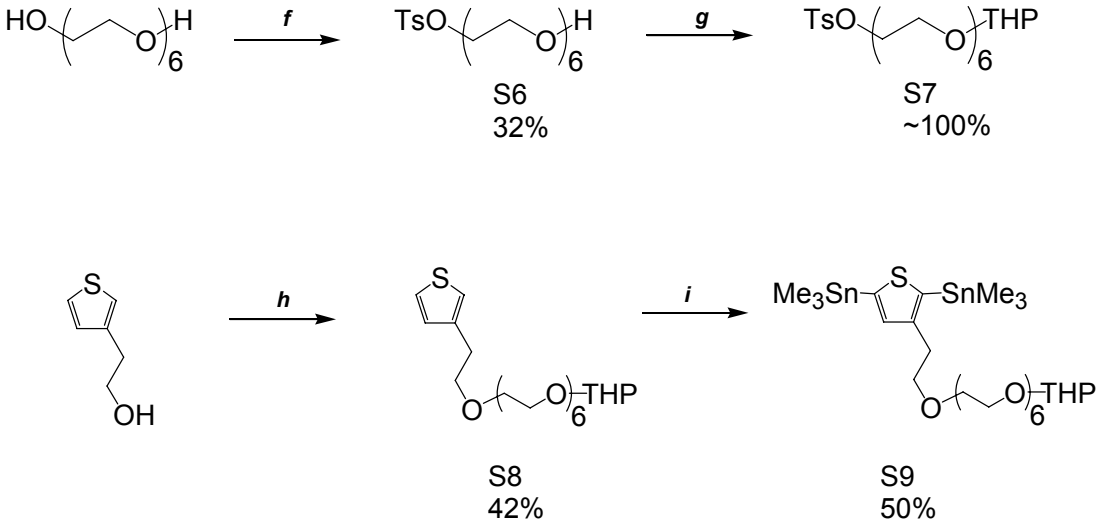
Synthetic Schemes

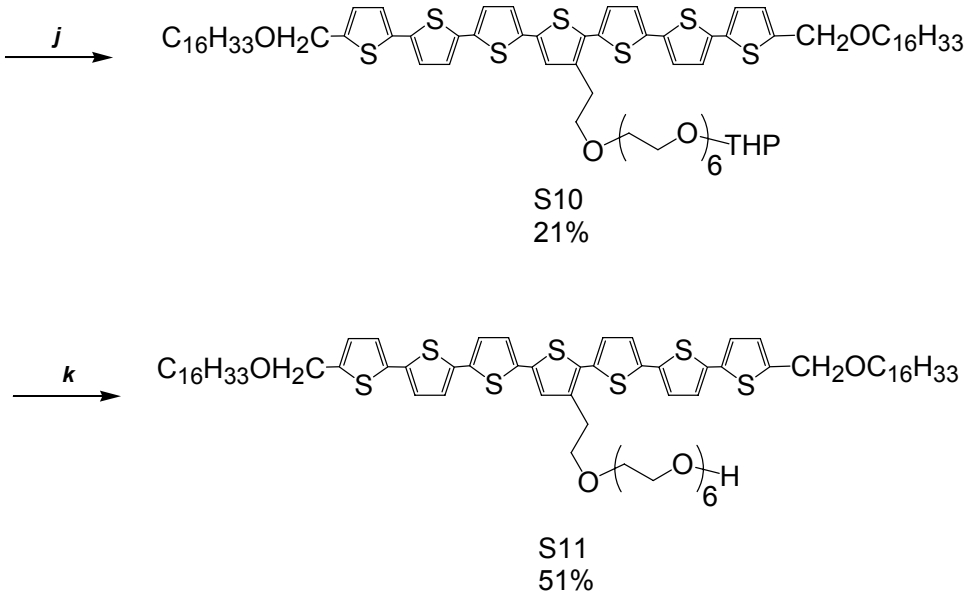
Oligothiophene **1** (S11) was synthesized via Stille cross coupling reaction of a terthiophene derivative (S5) and a 2, 5-bis (trimethylstannyl) thiophene derivative (S9). Subsequently, esterification reaction with a fullerene derivative with a carboxylic chloride group (S14) yielded oligothiophene-fullerene dyad **2** (S15). The synthetic schemes and the detail of the synthetic procedures are described below.



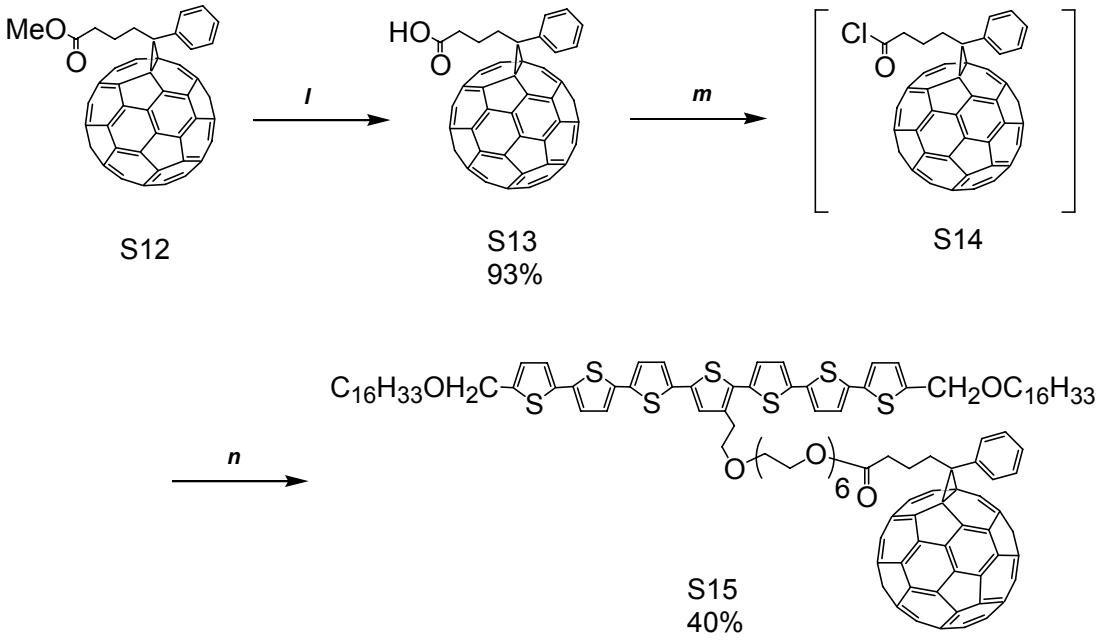
Scheme 1 Synthesis of the side unit of oligothiophene ***(a)*** 1. Mg, THF; 2. 2, 5-Dibromothiophene, $Ni(dppp)Cl_2$, THF ***(b)*** DMF, CH_2Cl_2, $POCl_3$ ***(c)*** CH_2Cl_2/AcOH, NBS ***(d)*** MeOH/THF, $NaBH_4$ ***(e)*** NaH, DMF, 1-Bromohexadecane



Scheme 2 Synthesis of the central unit of oligothiophene ***(f)*** NaOH, THF/H_2O, TsCl ***(g)*** CH_2Cl_2, PPTS, DHP ***(h)*** NaH, THF, S7 ***(i)*** LDA, Me_3SnCl



Scheme 3 Synthesis of oligothiophene ***(j)*** S5, S9, $Pd^0(PPh_3)_4$, toluene ***(k)*** PPTS, EtOH/$CHCl_3$



Scheme 4 Synthesis of oligothiophene-fullerene dyad ***(l)*** toluene, AcOH, HCl, reflux ***(m)*** CS_2, $SOCl_2$, reflux ***(n)*** S11, NaH, toluene

2,2':5',2''-Terthiophene (S1)[1]

To a solution of 2-Bromothiophene (67 g, 0.41 mol) and Mg (powder, 12 g, 0.49 mol) in 100 ml of dry THF was added a little amount of I_2 at 0 ºC, then the solution was stirred intermittently. The solution was stirred at rt for an additional 1 h after it turned dark color. The synthesized Grignard reagent was added dropwise to a stirred solution of 2, 5-Dibromothiophene (31g, 0.13 mol) and 1, 3-bis(diphenylphosphino)propane nickel (II) chloride (1.1 g, 0.64 mmol) in 300 ml of dry THF at -30 ºC. After stirring 23 h, the reaction was quenched by adding H_2O at 0 ºC and the product was extracted with CH_2Cl_2. The organic layer was washed with H_2O, dried over $MgSO_4$, and evaporated. The crude product was then recrystallized from hexanes, yielding 15.4 g (15 %) of S1. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.22 (d, J = 2.8 Hz, 2H), 7.17 (d, J = 2.8 Hz, 2H), 7.08 (s, 2H), 7.03 (d, J = 4.8 Hz, 1H), 7.02 (d, J = 5.2 Hz, 1H).

5-Formyl-2,2':5',2''-terthiophene (S2)[2]

To a stirred solution of DMF (6.8 g, 93 mmol) in 35 ml of CH_2Cl_2 was added $POCl_3$ at 0 ºC and the solution was stirred for 30 min at 40 ºC. The synthesized Vilsmeier reagent was added dropwise to a solution of S1 (15.4 g, 62 mmol) in 70 ml of CH_2Cl_2 at 0 ºC. After stirring 28 h at rt, the solvent

was evaporated, 200 ml of cold 1M NaOH aq was added, and the solution was stirred overnight. The orange precipitate was washed with H_2O and filtrated. The filtrate was recrystallized from CH_2Cl_2/hexanes, yielding 17 g (~100%) of S2. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.88 (s, 1H), 7.67 (d, J = 4.0 Hz, 1H), 7.29-7.26 (m, 2H), 7.24-7.22 (m, 2H), 7.13 (d, J = 4.0 Hz, 2H), 7.05 (d, J = 4.0 Hz, 1H), 7.03 (d, J = 3.2 Hz, 1H).

5-Bromo-5"-formyl-2,2':5',2"-terthiophene (S3)[2]

N-Bromosuccinimide (11 g, 62 mmol) was added portionwise to a stirred solution of S2 (17 g, 62 mmol) in 600 ml of CH_2Cl_2/acetic acid (1:1), and the solution was stirred at rt for 25 h. Then the precipitate was filtrated, washed with H_2O and extracted with $CHCl_3$. The organic layer was washed with H_2O, dried over $MgSO_4$, and evaporated. The crude product was recrystallized from CH_2Cl_2/hexanes, yielding 20 g (92%) of S3. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 9.86 (s, 1H), 7.67 (d, J = 4.0 Hz, 1H), 7.25 (d, J = 4.0 Hz, 1H), 7.24 (d, J = 4.0 Hz, 1H), 7.06 (d, J = 3.6 Hz, 1H), 7.00 (d, J = 4.0 Hz, 1H), 6.96 (d, J = 3.6 Hz, 1H).

5-Bromo-5"-hydroxymethyl-2,2':5',2"-terthiophene (S4)[2]

$NaBH_4$ (25 g, 661 mmol) was added to a solution of S3 (20 g, 55 mmol) in 800 ml of dry methanol/THF (1:1) at 0 ºC. After stirring 10 h, the solution was neutralized with diluted HCl aq and the product was extracted with $CHCl_3$. The organic layer was washed with H_2O and evaporated. The crude product was recrystallized from $CHCl_3$, yielding 13.3 g (68%) of S4. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.03 (d, J = 3.5 Hz, 1H), 7.02 (d, J = 4.0 Hz, 1H), 7.00 (d, J = 4.5 Hz, 1H), 6.96 (d, J = 4.5 Hz, 1H), 6.91 (d, J = 4.5 Hz, 1H), 6.90 (d, J = 3.5 Hz, 1H), 4.80 (d, J = 6.0 Hz, 2H), 1.72 (t, J = 6.0 Hz, 1H).

5-Bromo-5"-hexadecyloxymethyl-2,2':5',2"-terthiophene (S5) [2]

NaH (1.2 g, 50 mmol) was added to a solution of S4 (4.5 g, 13 mmol) in 300 ml of dry DMF at 0 ºC. After stirring 3 h at 0 ºC, 1-Bromohexadecane (4.2 g, 14 mmol) was added dropwise to the solution at rt. After stirring for 16 h, the reaction was quenched by adding H_2O, and the product was extracted with $CHCl_3$. The organic layer was washed with H_2O, dried over $MgSO_4$, and evaporated. The crude product was purified by silica column chromatography eluting with $CHCl_3$. Further purification was done by recrystallization from $CHCl_3$/hexanes, yielding 4.5 g (62%) of S5. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.03 (d, J = 4.4 Hz, 1H), 7.02 (d, J = 3.2 Hz, 1H), 7.00 (d, J = 3.2 Hz, 1H), 6.97 (d, J = 4.0 Hz, 1H), 6.90 (d, J = 4.0 Hz, 1H), 6.88 (d, J = 3.6 Hz, 1H), 4.62 (s, 2H), 3.49 (t, J = 6.8 Hz, 2H), 1.61 (p, J = 7.0 Hz, 2H), 1.45-1.20 (m, 26H), 0.88 (t, J = 6.6, 3H).

17-Tosyloxy-3,6,9,12,15-pentaoxaheptadecane-1-ol (S6)[3]

A solution of hexa(ethyleneglycol) (15 g, 53 mmol) in 50 ml of THF and a solution of NaOH (5 g, 125 mmol) in 50 ml of H_2O were mixed and stirred at 0 ºC for 30 min. *p*-Toluenesulfoyl chloride (11g, 58 mmol) dissolved in 200 ml of THF was added dropwise to the mixed solution at 0 ºC. After stirring 4 h, cold water was added and the product was extracted with CH_2Cl_2. The organic layer was washed with H_2O, dried over $MgSO_4$, and evaporated. The product was purified by silica column chromatography eluting with ethyl acetate, yielding 7.4 g (32%) of S6. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.77 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 8.4 Hz), 4.13 (t, J = 4.8 Hz, 1H), 3.72-3.54 (m, 22H), 2.76 (br, 1H), 2.43 (s, 3H).

1-(2H-Tetrahydropyran-2-yloxy)-17-tosyloxy-3,6,9,12,15-pentaoxaheptadecane (S7)[4]

Pyridinium *p*-toluenesulfonate (0.85 g, 3.4 mmol) and 3,4-dihydro-2H-pyran (2.1 g, 25 mmol) were added to a solution of S6 (7.4 g, 17 mmol) in 40 ml of CH_2Cl_2, and the solution was stirred 5 h at rt. The solution of the product was then washed with H_2O, dried over $MgSO_4$, and evaporated, yielding 9.0 g (~100%) of S7. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 7.78 (d, J = 8.4 Hz, 2H), 7.32 (d, J = 7.6 Hz, 2H), 4.61 (t, J = 3.6 Hz, 1H), 4.14 (t, 4.8 Hz, 2H), 3.89-3.80 (m, 2H), 3.69-3.44 (m, 22H), 2.43 (s, 3H), 1.88-1.44 (m, 6H).

1-(2H-Tetrahydropyran-2-yloxy)-17-(thiophene-3-ethoxy)-3,6,9,12,15-pentaoxaheptadecane (S8)

3-Thiopheneethanol (2.4 g, 19 mmol) was added to a solution of NaH (1.6 g, 67 mmol) in 300 ml of dry THF, and the solution was stirred for 15 h at rt. S7 (8.8 g, 17 mmol) was added dropwise to the stirred solution. After 7 h, the reaction was quenched by adding H_2O and the product was extracted with $CHCl_3$. The organic layer was washed with H_2O, dried over $MgSO_4$, and evaporated. The product was purified by silica column chromatography eluting with ethyl acetate, yielding 3.4 g (42%) of S8. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.26-7.23 (m, 1H), 7.02 (d, J = 2.4 Hz, 1H), 6.98 (d, J = 4.8 Hz, 1H), 4.63 (t, J = 3.6 Hz, 1H), 3.91-3.83 (m, 2H), 3.72-3.47 (m, 26H), 2.93 (t, J = 7.2 Hz, 2H), 1.90-1.46 (m, 6H).

1-(2H-Tetrahydropyran-2-yloxy)-17-{2,5-bis(trimethylstannyl)thiophene-3-ethoxy}-3,6,9,12,15-pentaoxaheptadecane (S9)

Butyl lithium (1.6 M hexanes solution, 44 ml, 70 mmol) was added dropwise to a solution of diisopropylamine (7.16 g, 71 mmol) in 60 ml of dry THF at -84 ºC, and the solution was stirred for 30 min at rt. The solution containing LDA was cooled -84 ºC and added dropwise to a stirred solution of S8 (3.4 g, 7.1 mmol) in 30 ml of dry THF. After stirring 1 h, trimethyltin chloride (1 M THF solution, 72 ml, 72 mmol) was added dropwise, and the solution was stirred for additional 7 h. Saturated aq NH_4Cl was added to the solution, and the product was extracted with $CHCl_3$. The

organic layer was washed with H_2O, dried over $MgSO_4$, and evaporated. The product was purified by silica column chromatography eluting with ethyl acetate, yielding 2.9 g (50%) of S9. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.20 (s, 1H), 4.63 (t, J = 3.4 Hz, 1H), 3.91-3.81 (m, 2H), 3.70-3.47 (m, 26H), 2.99 (t, J = 7.8 Hz, 2H), 1.87-1.46 (m, 6H), 0.38 (s, 9H), 0.34 (s, 9H).

Compound S10

S5 (4.0 g, 6.9 mmol), S9 (2.8 g, 3.5 mmol), and tetrakis(triphenylphosphine) palladium(0) (1 g, 0.87 mmol) were dissolved in 100 ml of dry toluene. The solution was treated with N_2 bubbling for 5 min, and then heated to reflux for 22 h. The solution was filtrated to remove Pd catalysts and evaporated. The crude product was purified by silica column chromatography eluting with ethyl acetate/hexanes (4:1), yielding 1.1 g (21%) of S10. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.12-7.03 (m, 11H), 6.85 (d, J = 3.6 Hz, 2H), 4.63 (s, 5H), 3.88-3.83 (m, 2H), 3.78-3.47 (m, 26H), 3.50 (t, J = 6.8Hz, 4H), 3.08 (t, J = 6.8Hz, 2H), 1.90-1.50 (m, 6H), 1.63-1.55 (m, 4H),1.45-1.10 (m, 56H), 0.88 (t, J = 6.8, 6H). MALDI TOF-MS m / z: 1478.28 (calc.), 1476.77 (found, M^+).

Oligothiophene 1 (S11)

S10 (1.1 g, 0.73 mmol) and pyridinium *p*-toluenesulfonate (0.24 g, 0.96 mmol) were dissolved in 70 ml of $CHCl_3$/EtOH (1:1), and the solution was heated at 60 ºC for 19 h. The solution was evaporated, and the crude product was purified by silica column chromatography eluting with $CHCl_3$/ethyl acetate/methanol (50:30:1), yielding 0.52 g (51%) of S11. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.13-7.02 (m, 11H), 6.89 (d, J = 3.0 Hz, 2H), 4.63 (s, 4H), 3.78-3.58 (m, 26H), 3.50 (t, J = 6.4 Hz, 4H), 3.08 (t, J = 7.0 Hz, 2H), 1.61 (p, J = 7.0 Hz, 4H), 1.39-1.21 (m, 52H), 0.88 (t, 7.0 Hz, 6H). MALDI TOF-MS m / z: 1392.64 (calc.), 1392.1 (found).

Phenyl-C_{61}-butyricacid methyl ester (**PCBM**, **S12**) was synthesized according to the report of Hummelen et al.[5]

^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.93 (d, J = 7.6 Hz, 2H), 7.60-7.52 (m, 2H), 7.51-7.42 (m, 1H), 3.68 (s, 3H), 2.94-2.87 (m, 2H), 2.53 (t, J = 7.4, 2H), 2.24-2.14 (m, 2H). MALDI TOF-MS m / z: 911.11 (calc.), 910.10 (found, M^+).

Phenyl-C_{61}-buryric acid (S13)[5]

Acetic acid (250 ml) and HCl (100 ml) were added to a solution of S12 (1.1 g, 1.2 mmol) in 250 ml of toluene, and the mixed solution was heated to reflux for 18 h. After the solution was evaporated, the crude product was treated with methanol, centrifuged to collect the suspension. This procedure was repeated with diethyl ether, toluene, and twice with diethyl ether, yielding 1.0 g (93%) of S13. ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.66 (d, J = 7.2 Hz, 2H), 7.31-7.22 (m, 2H),

7.22-7.16 (m, 1H), 2.72-2.62 (m, 2H), 2.67 (t, J = 7.2 Hz, 2H), 2.00-1.89 (m, 2H). MALDI TOF-MS m / z: 897.09 (calc.), 896.50 (found).

Dyad 2 (S15)

Thienyl chloride (0.98 g, 8.2 mmol) was added to a solution of S13 (80 mg, 0.089 mmol) in 20 ml of freshly distilled CS_2, and the solution was heated to reflux for 21 h. After all the volatile components were removed in vacuo, sodium hydride (5 mg, 0.22 mmol), toluene (10 ml), and S11 (62 mg, 0.045 mmol) dissolved in 10 ml of toluene were added to the residue (S14). The mixed solution was stirred for 3 days, and then the solution was evaporated. The product was purified by silica column chromatography eluting with ethyl acetate/hexanes (4:1), yielding 41 mg (40%) of S15. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 7.90 (d, J = 7.5 Hz, 2H), 7.53 (t, J = 7.5 Hz, 2H), 7.49-7.42 (m, 1H), 7.13-7.02 (m, 11H), 6.89 (d, J = 3.0 Hz, 2H), 4.63 (s, 4H), 4.22 (t, J = 4.7 Hz, 2H), 3.77-3.60 (m, 24H), 3.50 (t, J = 6.6 Hz, 4H), 3.07 (t, J = 6.8 Hz, 2H), 2.91-2.86 (m, 2H), 2.53 (t, J = 7.5 Hz, 2H), 2.20-2.14 (m, 2H), 1.61 (p, J = 6.9 Hz, 4H), 1,38-1.23 (m, 52H), 0.88 (t, J = 6.6 Hz, 6H). MALDI TOF-MS m / z: 2270.71 (calc.), 2270.4 (found).

NMR and MALDI-TOF-MS Spectra of the Oligothiophene 1 (S11) and the Dyad 2 (S15)

^{1}H-NMR spectra were measured in $CDCl_3$ containing 0.03% v/v TMS by OXFORD Superconducting magnet system (500 MHz). MALDI-TOF-MS spectra were measured with a dithranol as a matrix by Applied Biosystems BioSpectrometry Workstaion model Voyager-DE STR spectrometer.

The NMR spectrum of the Oligothiophene 1

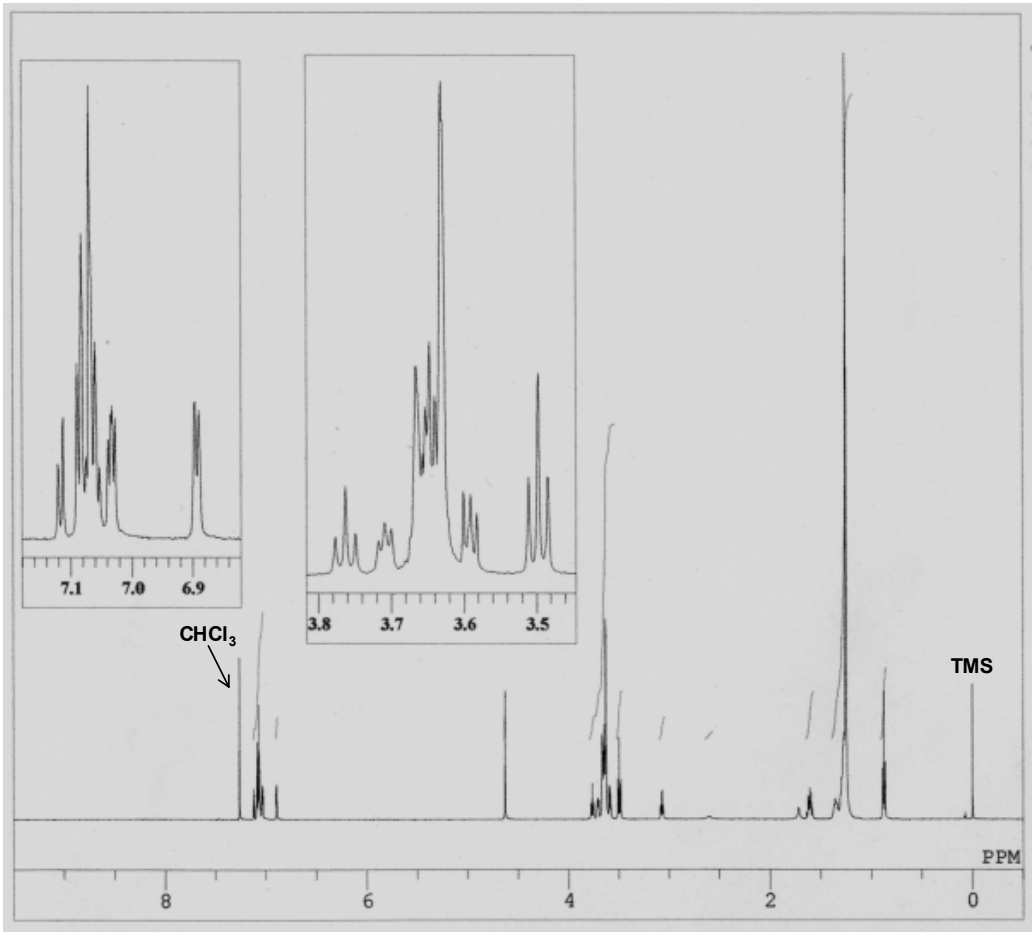


Fig. S1 The NMR spectrum of the oligothiophene **1**

The MALDI-TOF-MS Spectrum of the Oligothiophene 1

m/z: 1392.64 (calculated), 1392.1 (measured). #(M-$OCH_2C_{16}H_{33}$ fraction): 1151.38 (calculated), 1151.17 (measured). **&**($M+Na^+$): 1415.62 (calculated), 1416.24 (measured).

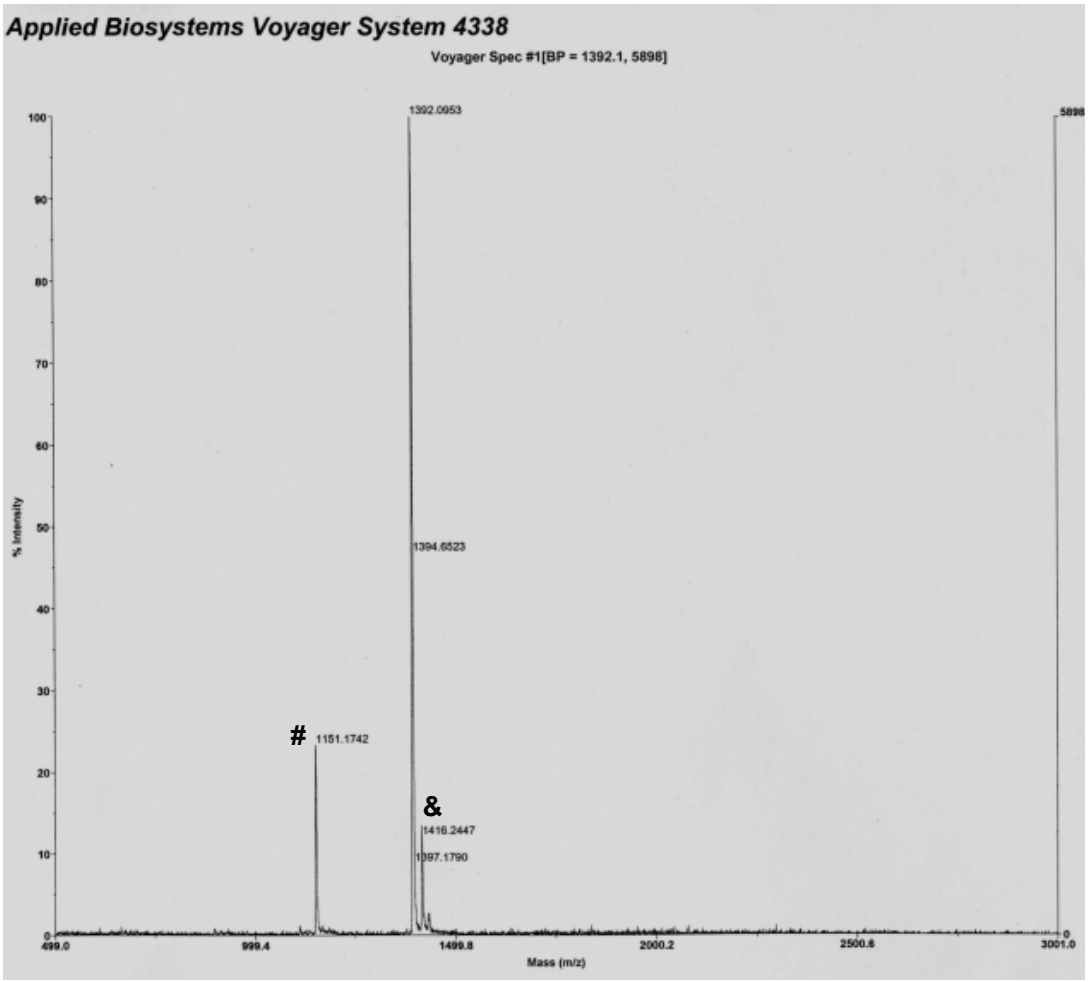


Fig. S2 The MALDI-TOF-MS spectrum of the oligothiophene **1**

The NMR Spectrum of the Dyad 2

#: Ethyl acetate (The peak at around 1.3 ppm is superposed on the peak of dyad **2**.)

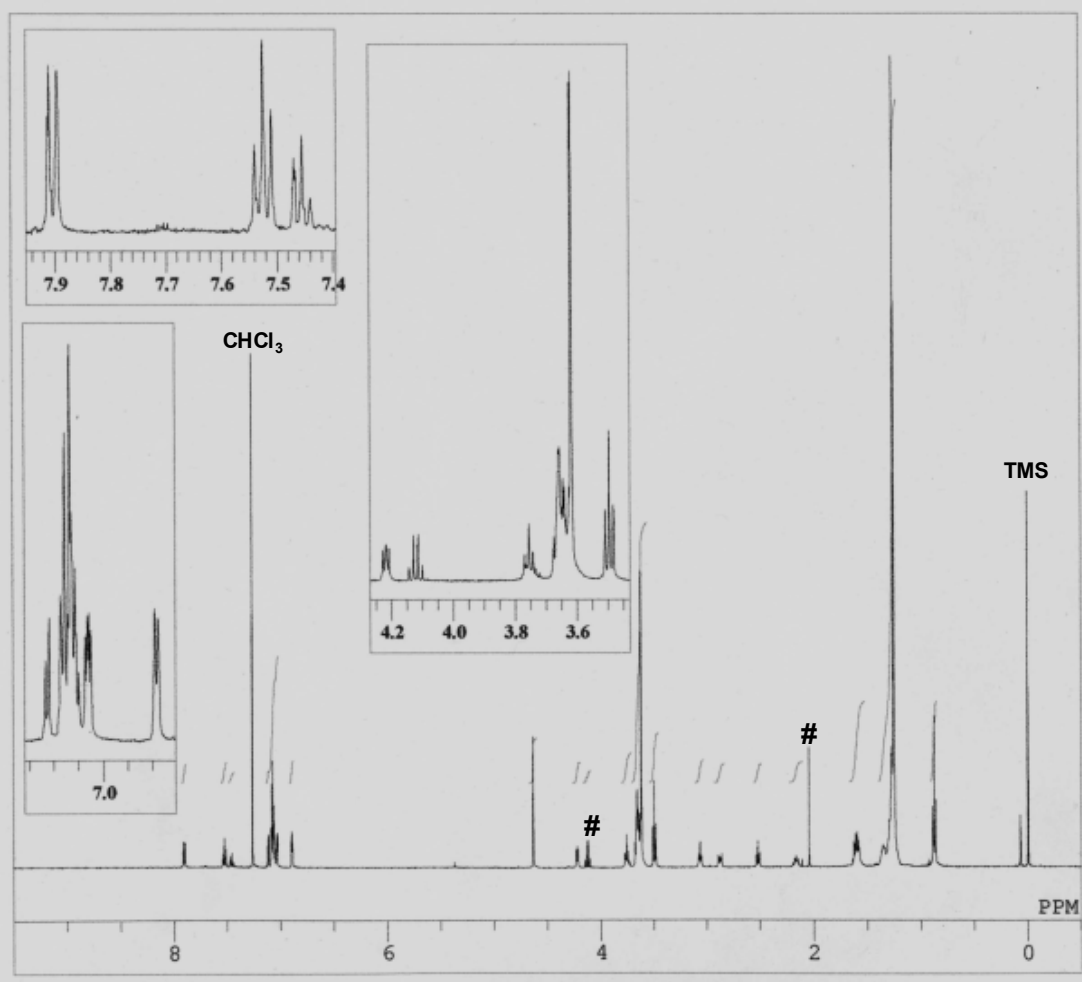


Fig. S3 The NMR spectrum of the dyad **2**

The MALDI-TOF-MS Spectrum of the Dyad 2

m/z: 2270.71 (calculated), 2270.4 (measured). #(M-$OCH_2C_{16}H_{33}$ fraction): 2029.46 (calculated), 2029.89 (measured).

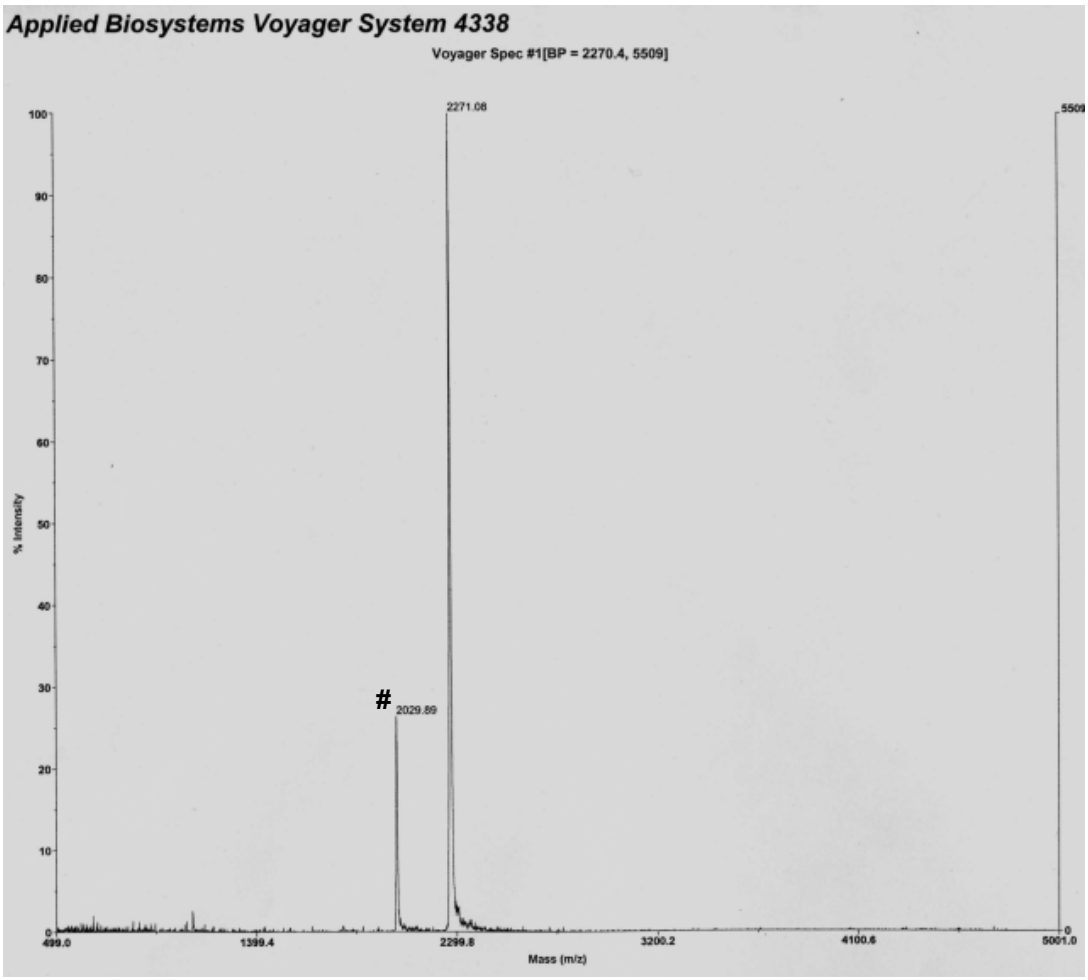


Fig. S4 The MALDI-TOF-MS spectrum of the dyad **2**

The DSC Chart of the Dyad 2

The DSC chart (Fig. S3) showed a broad endothermic peak at 52 ºC on heating, at which crystalline phase turned to isotropic phase, observed by a polarized optical microscope.

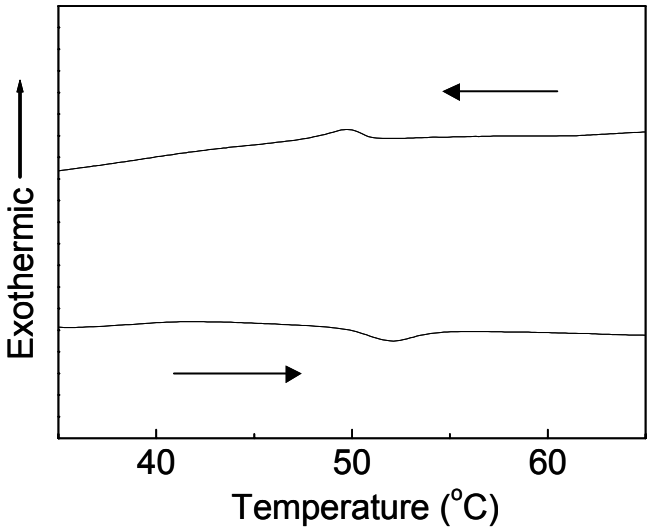


Fig. S3 The DSC chart of the dyad **2**, measured at a heating/cooling rate of 10 ºC/min

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