Supporting Information

Partially Ladder-Type Molecule-Based Donor-Acceptor Conjugated Oligomer: Synthesis and Properties

Mithrabinda K. K. Poduval, So-Jung Hahn, and Tae-Hyun Kim*

Organic Material Synthesis Laboratory, Department of Chemistry, University of Incheon, Incheon 406-840, Korea
**E-mail: tkim@incheon.ac.kr*
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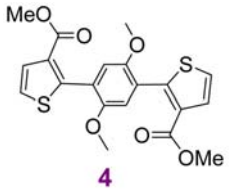
Experimental

Melting points were determined using Büchi 510 melting point apparatus and uncorrected. IR spectra were recorded on a Nicolet MAGNA 560-FTIR spectrometer. ^{1}H NMR spectra were recorded on a Bruker Advance DPX-300, Bruker Advance DPX-500 instruments and Varian UNITYINOVA 400 instruments using deuterochloroform as reference or internal deuterium lock. The chemical shift data for each signal are given in units of δ (ppm) relative to tetramethylsilane (TMS) where δ(TMS) = 0, and referenced to the solvent residual. ^{13}C NMR spectra were recorded on a Bruker Advance-300 (75.4 MHz) instrument and Agilent DD2 NMR 400 (100 MHz) instrument using internal deuterium lock and proton decoupling. Mass spectra were obtained on a JEOL JMS-AX505WA instrument. UV-visible absorption spectra were measured with Hewlett Packard 8452A diode array spectrometer using spectral grade chloroform as a solvent. The measurements were carried out at 25 °C using a quartz cell with a path length of 1 cm. All electrochemical measurements were made with a COMPACTSTAT potentiostat (IVIUM Technologies) using an Pt wire reference electrode in 0.1 M tetrabutylammonium hexafluorophosphate (n-Bu_4NPF_6) in anhydrous CH_3CN. Typical cyclic voltammograms were recorded using ITO electrodes as the working electrode and a platinum coil counter electrode. The ferrocene/ferrocenium (Fc/Fc^+) redox couple was used as an external reference. The potential values were converted to versus Ag/AgCl. Molar masses were determined by Gel Permeation Chromatography (GPC) using two PL Gel 30 cm 5 μm mixed C columns at 30 °C running in $CHCl_3$ and calibrated against polystyrene (M_n = 600-10^6 g/mol) standards using a Knauer refractive index detector. The X-ray diffraction patterns of the oligomer thin film were recorded using a Philips XPERT-PRO MRD diffractometer by employing a scanning range (2θ) from 1° to 30° with a Cu Kα1 X-ray (λ =1.540598 Å).

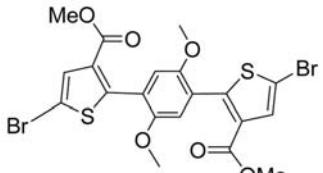
Reagents were purified and dried by standard technique. All air and water-sensitive synthetic manipulations were performed under a nitrogen atmosphere using standard Schlenk techniques.



4

Synthesis of the dimethoxy diester 4.

The diboronic acid **3** (1.00 g, 4.40 mmol) and 2-bromo-3-thiophene carboxylic acid methyl ester **2** (1.97 g, 8.88 mmol) was added in a shlenk flask which was purged with nitrogen. To this flask tetrakis(triphenyl phosphine) palladium (0.34 g, 0.22 mmol) was added, followed by the addition of dimethyl formamide (10 mL) and aqueous 2 M potassium phosphate solution (17.6 mmol, 7 mL). The reaction mixture was heated up to 110 °C for 12 h. To the resulting black solution water was added at r.t. and the organic layer was separated with dichloromethane, dried over $MgSO_4$, filtered and concentrated by vacuum. The crude product was purified by recrystallization from ethyl acetate-chloroform mixture to give the compound **4**. (1.02 g, 55%); mp 226-227 °C; R_f 0.30 (5:1, Hex: EtOAc); ν_{max} (KBr)/cm^{-1} 2913, 2848,1718, 1530, 1498, 1394, 1184, 1045 and 761; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 7.5 (2H, d, J = 7.5 2xAr*H*), 7.31 (2H, d, J = 7.5, 2xAr*H*), 6.93 (2H, s, 2xAr*H*), 3.70 (12H, s, 2xCOOC*H*$_3$ and 2xOC*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 163.1, 150.1, 143.9, 131.0, 129.7, 124.5, 123.0, 112.9, 56.1 and 51.5.

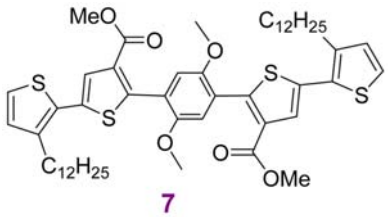


5

Bromination of 4 to give compound 5.

To the compound **4** (1.00 g, 2.38 mmol) dissolved in chloroform (40 mL) N-bromo succinimide (0.93 g, 5.25 mmol) was added by portion at r.t. The reaction mixture was stirred for 6 h at r.t., after this time a yellow precipitate was formed, and this was washed with water several times.

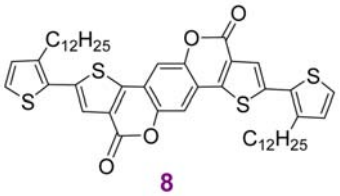
Removal of the solvent gave the pure compound **5** (1.30 g, 95%); mp 175-176 °C; R_f 0.33 (5:1, Hex:EtOAc); ν_{max} (KBr)/cm^{-1} 2918, 2850, 1718, 1550, 1480, 1396, 1180, 1035, 800 and 760; ^{1}H NMR (300 MHz, $CDCl_3$ δ) 7.45 (2H, s, 2xAr*H*), 6.87 (2H, s, 2xAr*H*), 3.72 (12H, s, 2xCOOC*H*$_3$ and 2xOC*H*$_3$); ^{13}C NMR (75 MHz, $CDCl_3$, δ) 163.1, 150.1, 147.1, 132.2, 131.3, 123.1, 112.8, 112.6, 56.1 and 51.4; *m/z* (FAB) 559 (5%), 543 (6%), 81 (100%).



7

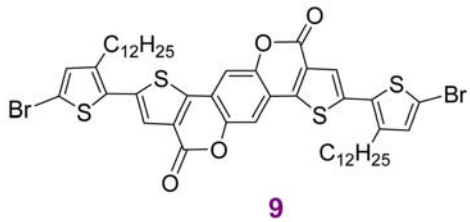
Synthesis of compound 7.

The dibrominated compound **5** (0.40 g, 0.69 mmol) and the corresponding thiophene boronic ester (0.95 g, 1.38 mmol) and aqueous potassium phosphate solution (2.4 mmol, 1 mL) were taken in a shlenk flask and purged with nitrogen. To this tetrakis (triphenyl phosphine) palladium (0.055 g, 0.05 mmol) was added, followed by the addition of nitrogen-purged toluene (5 mL). The whole reaction mixture was heated at 110 °C under nitrogen for 24 h to produce brown suspension. The mixture was extracted with dichloromethane (3 times) and the combined organic layers were washed with HCl (1 M; 20 mL), water and brine. The organic layer was dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was purified by column chromatography to give pure product **7** (0.30 g, 47%); mp 88-89 °C; R_f 0.25 (10:1, Hex: EtOAc); ν_{max} (KBr)/cm^{-1} 2913, 2846, 1718, 1553, 1427, 1396, 1245, 1051, 1045, 881 and 761; ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.48 (2H, s, 2xAr*H*), 7.20 (2H, d, J = 7.5 2xAr*H*), 6.98 (2H, s, 2xAr*H*), 6.95 (2H, d, J = 7.5, 2xAr*H*), 3.78 (6H, s, 2x(-OC*H*$_3$)) 3.76 (6H, s, 2x(COOC*H*$_3$)), 2.79 (4H, t, J = 7.7), 1.63 (4H, quintet, J = 7), 1.25 (36H, multiplet containing quintet, J = 7, (-CH_2)$_9$), 0.86 (3H, t, J = 6.7, (*CH*$_3$)); ^{13}C NMR (100 MHz, $CDCl_3$, δ) 163.9, 150.3, 140.2, 135.4, 130.3, 130.0, 129.4, 127.3, 124.2, 123.2, 114.6, 56.2, 51.6, 31.9, 30.7, 30.4, 30.3, 29.6, 29.5, 29. 3, 29.2, 22.7 and 14.1; *m/z* (FAB) 918 (M^+, 54%), 919 (44%) and 43 (100%); [Found M^+ 918.4055. $C_{52}H_{70}O_6S_4$ requires *M*, 918.4055].



8

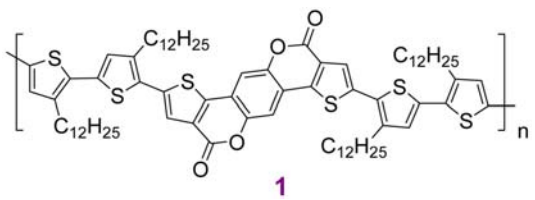
Cyclization of the compound 7 to give 8: To a solution of the non-cyclized precursor **7** (0.11 g, 0.11 mmol) in 2 mL of dichloromethane, BBr_3 (1.50 mL, 1.14 mmol) was added at r.t. under nitrogen. TLC analysis of the reaction mixture revealed complete conversion to cyclization. The reaction mixture was further left to stir for 30 min, followed by the addition of water. The solution was extracted with dichloromethane and dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was recrystallized from ethyl acetate to give the cyclized product **8 as** a bright yellow crystal. (0.095 g, 100%); mp 194-195 °C; R_f 0.43 (10:1, Hex: EtOAc); ν_{max} (KBr)/cm^{-1} 2917, 2846, 1733, 1542, 1461, 1457, 118, 1076 and 750; ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.67 (2H, s, 2x*ArH*), 7.65 (2H, s, 2x*ArH*), 7.34 (2H, d, J = 7.5, 2x*ArH*,), 7.01 (2H, d, J = 7.5, 2x*ArH*), 2.84 (4H, t, J = 7.7, *(-CH*$_2$*)*), 1.66 (4H, quintet, J = 7, *(-CH*$_2$*)*), 1.25 (36H, multiplet containing quintet, J = 7, *(-CH*$_2$*)*$_9$), 0.87 (3H, t, J = 6.7, *(CH*$_3$*)*); C^{13} (100 MHz, $CDCl_3$, δ) 152.5, 149.2, 145.3, 138.3, 137.3, 131.0, 127.7, 126.0, 124.9, 119.5, 31.9, 29.7, 29.3, 22.6 and 14.1; *m/z* (FAB) 827 (M^+, 9%), 826 (6%) and 154 (100%); [Found M^+ 827.3290. $C_{48}H_{58}O_4S_4$ requires *M*, 827.3296].



9

Bromination of 8 to give the compound 9.

To the solution of compound **8** (0.09 g, 0.11 mmol) in (2 mL) chloroform, N-bromo succinimide (0.06 g, 0.32 mmol) was added by portionwise at r.t. The reaction mixture was stirred for 3 h at r.t.. After this time, the resulting mixture was poured into water and the organic layer was washed with water and dried over magnesium sulfate, and the solvent was evaporated under reduced pressure. The crude product was purified by column chromatography to give the monomer **9**. (0.095 g, 86%); mp 210-211 °C; R_f 0.46 (10:1, Hex: EtOAc); ν_{max} (KBr)/cm^{-1} 2915, 2847, 1735,1542, 1461, 1457, 118, 1076 and 751; ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.61 (2H, s, 2x*ArH*), 7.60 (2H, s, 2x*ArH*), 6.96 (2H, s, 2x*ArH*), 2.47 (4H, t, J = 7.7, *(-CH*$_2$*)*), 1.49 (4H, quintet, J = 7, *(-CH2)*), 1.18 (36H, multiplet containing quintet, J = 7, *(-CH2)*$_9$), 0.79 (3H, t, J = 6.7, *(CH*$_3$*)*); C^{13} (100 MHz, $CDCl_3$, δ) 152.3, 148.2, 145.3, 140.5, 138.3, 133.9, 131.0, 129.8, 124.9, 118.0, 112.1, 31.9, 29.7, 29.3, 22.6 and 14.1.



1

Polymerization to give the D-A cooligomer 1.

The monomer **9** (0.09 g, 0.09 mmol) and bis(dodecyl thiophene boronic ester) **10** (0.07 g, 0.09 mmol) were taken in a shlenk flask filled with nitrogen. To this flask $Pd(PPh_3)_4$ (0.015 mg, 0.01 mmol), aqueous K_3PO_4 (0.2 mL, 0.36 mmol) and nitrogen purged toluene (3 mL) were added. The

reaction mixture was heated at 110 °C under nitrogen for 24 h to produce brown suspension. The organic layer was washed with HCl (1 M; 20 mL), water and brine. The aqueous layers were extracted with chloroform (3 times), dried over $MgSO_4$ and evaporated under reduced pressure. The resulting crude black powder was redissolved in $CHCl_3$ and precipitated into methanol. The black powder was further purified by Soxhlet extraction using methanol, acetone and hexane to give the desired cooligomer 1 as a black powder (ν_{max} (KBr)/cm^{-1} 2919, 2848, 1735, 1542, 1461, 1457, 1259, 1079 and 798; ^{1}H NMR (400 MHz, $CDCl_3$, δ) 7.58 (2H, br s, 2xArH), 7.57 (2H, br s, *2xArH*, s), 6.92 (2H, br s, *2xArH*), 2.69 (4H, t, J = 7.7, *(-CH_2)*), 2.48 (4H, t, J = 7.7, *(-CH_2)*), 1.56 (4H, quintet, J = 7, *(-CH_2)*), 1.18 (36H, multiplet containing quintet, J = 7, *(-CH_2)$_9$*), 0.81 and (3H, t, J = 6.7, *(CH_3)*); GPC($CHCl_3$, RI)Da M_n 4.9 × 10^3 and M_w 6.6 × 10^3; TGA (%/°C) 95/293, 90/373.