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Synthesis and Characterization of Planar Five-Ring-Fused Dithiophene-dione

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A series of new organic semiconductors based on s-indaceno[1,2-*b*:5,6-*b*']dithiophene-4,9-dione was successfully synthesized and characterized. The electron withdrawing carbonyl group lowers the LUMO energy levels, leading to increased electronegativities, which is beneficial for high photo-stability in air. The *n*-alkyl substituted compounds, **1c** and **1d**, crystallize with the rigid coplanar systems packed into slipped face-to-face π-stacks. Interestingly, **1c** and **1d** also show liquid crystalline behaviors, which give highly ordered molecular packing over large area.

Keywords semiconductors, fused-ring systems, liquid-crystals

Introduction

Significant progress has been made in organic field-effect transistors (OFETs) in the past few years.[1-4] A large number of organic semiconductors have been prepared, and some materials, like pentacene, even exhibited OFET performance comparable to amorphous silicon.[5-7] However, pentacene and its derivatives often suffer from rapid degradation in ambient conditions, due to photoinduced decomposition and formation of dimeric Diels-Alder adducts on the electron-rich central ring.[8] Great efforts have been devoted to design new materials with high charge-carrier mobilities and high stability.[9-11] It is understood that the enhancement of stability is possible by regulating the HOMO-LUMO energy levels by incorporating heteroatoms (*e.g.*, N, S, O, *etc.*).[9,12] For instance, the incorporation of fused thiophene units into heteroacenes widens the HOMO-LUMO gap and stabilizes the HOMO level.[2] Meanwhile, design and synthesis of new conjugated systems for electronically complementary n-type organic semiconductors is another urgent aspect for the development of OFETs.[4,13] A common strategy to achieve n-type organic semiconductors is incorporation of electron withdrawing groups[4] into the π-conjugated cores, which could reduce the LUMO energy and facilitate electron injection.

The good device properties and desirable longevity of the indenofluorene-6,12-dione family[14-16] has stimulated the interest toward dithiophene-dione heteroacenes. The five-ring-fused heteroacence framework possesses linear π-conjugated structure similar to pentacene and indenofluorene-6,12-dione. Having the thiophene units as the terminal rings and carbonyl groups on the second ring ensures the conjugated framework to exist as a rigid coplanar configuration, which is crucial for high mobility.[17] Ng's group reported the first synthesis of dithiophene-dione framework and the applications of thienyl-substituted derivatives in polymer photovoltaic devices.[18,19]

In this work, we synthesized four new compounds based on the dithiophene-dione framework. The synthetic route was slightly modified from that developed by Ng. Moreover, by using different *n*-alkyl substitutions, we were able to investigate the effects of systematic substitution variation on their spectroscopic, electrochemical, thermal properties and molecular packing in solid states. Liquid crystalline phase and single crystal structures of two new compounds were obtained. During the preparation of this manuscript, the FET devices of compound **1c** were reported by Geng *et al.*[20]

Experimental

Reagents and methods

All chemicals and solvents were obtained from commercial suppliers and used without further purification unless otherwise noted. The THF was dried by distillation over sodium wires/benzophenone. ^{1}H NMR spectra were recorded on either a 300 or 400 spectrometer and calibrated to the residual protonated sol-

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vent at δ 0.00 for deuterated chloroform ($CDCl_3$), 4.79 for water (D_2O) and 2.50 for deuterated dimethyl sulfoxide (DMSO-d_6). ^{13}C NMR experiments were carried out in $CDCl_3$ or DMSO-d_6 and calibrated at δ 77.00 or 39.52. UV-Vis absorption spectra were recorded using a T6 UV-Vis spectrometer. IR spectra were obtained as KBr discs on a Bruker V70 FT-IR spectrometer. Elemental analyses were obtained at the UBC Microanalytical facility. Single crystal X-ray diffraction measurements were made on a Bruker X8 APEX diffractometer with graphite monochromated Mo-Kα radiation ($\lambda=0.71073$ Å) at 296(2) K.

The electrochemical measurement was conducted using a CHI660B electrochemistry work station. All measurements were carried out at room temperature with a conventional three-electrode configuration consisting of a platinum disk working electrode, an auxiliary platinum wire electrode, and a nonaqueous $Ag/AgNO_3$ reference electrode. The supporting electrolyte was 0.1 mol•L^{-1} tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in THF and the scan rate was set to 100 mV•s^{-1}. The ferrocene/ferrocenium couple was used as an internal standard, and all potentials are reported vs. SCE.

Thermogravimetric analysis (TGA) was carried out on a PE TGA7. A heating rate of 10 ℃•min^{-1} under flowing N_2 was used with runs being conducted from room temperature to high temperature. Differential scanning calorimetry (DSC) was carried out on a NETZSCH STA 449 C. DSC scans under nitrogen at a scan rate of 10 ℃•min^{-1}. Liquid-crystal micrographs were taken on an XPR-300C polarized optical microscope.

Synthesis of sodium 2-thienyl boronate (4a)

Thiophene (1.05 g, 12.50 mmol) was dissolved in dry THF (20 mL) and the solution was stirred at −78 ℃ under argon. *n*-BuLi (6 mL, 15.00 mmol, 2.5 mol•L^{-1} solution in hexane) was then added dropwise to the solution over a period of 30 min. The reaction mixture was allowed to warm to room temperature and stirred for a further 1.5 h. The mixture was then slowly added over a period of 1 h to a solution of trimethylborate (2.60 g, 25.00 mmol) in dry THF (15 mL) which had been pre-cooled to −78 ℃. The resulting mixture was allowed to slowly warm to room temperature and left stirring overnight. Dilute hydrochloric acid (5 mL, 2 mol•L^{-1}) was added and the mixture extracted with diethyl ether (10 mL×3). The combined organic layers were dried, filtered, and the solvent removed under vacuum to get compound **3a**. The crude product **3a** was dissolved in a minimum amount of warm toluene under stirring and the solution allowed cooling to room temperature. Saturated NaOH solution was added dropwise until no further precipitate formed. The mixture was allowed to stir for 30 min. The precipitate obtained was filtered off, washed with toluene and petroleum ether and dried under vacuum to give the compound as a white amorphous solid, which was used for next step without further purification (1.37 g, 65% yield). m.p.>300 ℃; ^1H NMR (D_2O, 400 MHz) δ: 7.32 (dd, J=4.8, 1.2 Hz, 1H), 7.04 (dd, J=3.6, 1.2 Hz, 1H), 7.01 (dd, J=4.8, 3.6 Hz, 1H); IR (KBr) ν: 3217, 1454, 1194, 810, 726, 645, 546 cm^{-1}.

Compound **4b** was prepared from compound **2b** (1.40 g, 12.50 mmol) according to the procedure for compound **4a** to yield a white amorphous solid, which was used for next step without further purification (1.47 g, 60% yield). m.p.>300 ℃; ^1H NMR (D_2O, 400 MHz) δ: 6.78 (d, J=3.6 Hz, 1H), 6.65 (d, J=3.6 Hz, 1H), 2.75 (q, J=7.6 Hz, 2H), 1.32 (t, J=7.6 Hz, 3H); IR (KBr) ν: 3414, 2958, 1443, 1229, 936, 530 cm^{-1}.

Compound **4c** was synthesized by the literature method.[21]

Compound **4d** was prepared from compound **2d** (3.15 g, 12.50 mmol) according to the procedure for compound **4a** to yield a white amorphous solid, which was used for next step without further purification (2.94 g, 70% yield). m.p.>300 ℃; ^1H NMR (D_2O, 400 MHz) δ: 6.76 (d, J=3.6 Hz, 1H), 6.64 (d, J=3.6 Hz, 1H), 2.70 (t, J=7.6 Hz, 2H), 1.56—1.63 (m, 2H), 1.20—1.32 (m, 18H), 0.84 (t, J=6.8 Hz, 3H); IR (KBr) ν: 3371, 2920, 1465, 1441, 1237, 931, 524 cm^{-1}.

Synthesis of dimethyl 2,5-di(2-thienyl)terephthalate (6a)

The aryl trihydroxyboronate salt **4a** (1.68 g, 10.00 mmol), aryl halide **5** (880 mg, 2.50 mmol), $Pd(PPh_3)_4$ (115 mg, 0.10 mmol) and a saturated aqueous solution of $NaHCO_3$ (840 mg, 10.00 mmol) were placed in a flame flask under argon. Freshly distilled and de-gassed THF (10 mL) was added and the mixture heated and stirred at reflux for 24 h. After cooling to room temperature the mixture was poured into a saturated solution of ammonium chloride, and extracted with ethyl acetate (10 mL×3). The combined organic layers were washed with saturated brine and dried over Na_2SO_4. The solution was then filtered, the solvent removed and the residue purified by column chromatography, using a mixture of hexane and dichloromethane (1∶1, volume ratio) as the eluent to yield a kelly solid (358 mg, 40% yield). m.p. 170—172 ℃; ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.82 (s, 2H), 7.39 (dd, J=4.8, 1.2 Hz, 2H), 7.11 (dd, J=3.6, 1.2 Hz, 2H), 7.08 (dd, J=4.8, 3.6 Hz, 2H), 3.78 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.1, 140.3, 133.6, 133.4, 131.9, 127.5, 127.0, 126.7, 52.6; IR (KBr) ν: 3444, 2952, 1729, 1428, 1288, 1247, 1209, 1109, 848, 718 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{14}O_4S_2$ 358.0406, found 359.0411 $[M+H]^+$.

Compound **6b** was prepared by coupling of compound **4b** (1.96 g, 10.00 mmol) with **5** (880 mg, 2.50 mmol) according to the procedure for compound **6a** and purified by column chromatography, using a mixture of hexane and dichloromethane (4∶1, volume ratio) as the eluent to yield a kelly solid (673 mg, 65% yield). m.p. 86—90 ℃; ^1H NMR ($CDCl_3$, 400 MHz) δ: 7.75 (s, 2H), 6.91 (d, $J=3.6$ Hz, 2H), 6.75 (d, $J=3.6$ Hz, 2H), 3.80 (s, 6H), 2.87 (q, $J=7.6$ Hz, 4H), 1.34 (t, $J=7.6$ Hz, 6H), ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.4, 149.1, 137.5, 133.2, 133.1, 131.5, 126.6, 123.9, 52.5, 23.5, 15.8; IR (KBr) v: 3440, 2969, 2848, 1727, 1433, 1289, 1238, 1189, 1108, 815 cm^{-1}. HRMS (ESI) calcd for $C_{22}H_{22}O_4S_2$ 414.0852, found 437.0846 $[M+Na]^+$.

Compound **6c** was prepared by coupling of compound **4c** (2.52 g, 10.00 mmol) with **5** (880 mg, 2.50 mmol) according to the procedure for compound **6a** and purified by column chromatography, using a mixture of hexane and dichloromethane (5∶1, volume ratio) as the eluent to yield a kelly solid (1.10 g, 84% yield). m.p. 88—90 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.74 (s, 2H), 6.90 (d, $J=3.6$ Hz, 2H), 6.73 (d, $J=3.6$ Hz, 2H), 3.79 (s, 6H), 2.82 (t, $J=7.6$ Hz, 4H), 1.66—1.73 (m, 4H), 1.30—1.40 (m, 12H), 0.90 (t, $J=6.8$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.5, 147.7, 137.6, 133.2, 133.1, 131.4, 126.4, 124.5, 52.6, 31.6 (overlapping signal), 30.2, 28.8, 22.6, 14.0; IR (KBr) v: 3440, 2924, 2852, 1725, 1433, 1290, 1235, 1188, 1110, 805 cm^{-1}. HRMS (ESI) calcd for $C_{30}H_{38}O_4S_2$ 526.2284, found 527.2272 $[M+H]^+$.

Compound **6d** was prepared by coupling of compound **4d** (3.36 g, 10.00 mmol) with **5** (880 mg, 2.50 mmol) according to the procedure for compound **6a** and purified by column chromatography, using a mixture of hexane and dichloromethane (7∶1, volume ratio) as the eluent to yield a kelly solid (1.53 g, 88% yield). m.p. 74—76 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.74 (s, 2H), 6.90 (d, $J=3.6$ Hz, 2H), 6.73 (d, $J=3.6$ Hz, 2H), 3.79 (s, 6H), 2.82 (t, $J=7.6$ Hz, 4H), 1.66—1.73 (m, 4H), 1.26—1.38 (m, 36H), 0.88 (t, $J=6.8$ Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 168.5, 147.7, 137.6, 133.2, 133.1, 131.4, 126.5, 124.6, 52.5, 31.9, 31.6, 30.2, 29.7, 29.6, 29.5, 29.4, 29.3, 29.1 (overlapping signal), 22.7, 14.1; IR (KBr) v: 3440, 2918, 2850, 1726, 1434, 1291, 1236, 1190, 1111, 803 cm^{-1}. HRMS (ESI) calcd for $C_{42}H_{62}O_4S_2$ 694.4162, found 695.4156 $[M+H]^+$.

Synthesis of 2,5-di(2-thienyl)terephthalic acid (7a)

A mixture of compound **6a** (483 mg, 1.35 mmol) and sodium hydroxide (216 mg, 5.40 mmol) in ethanol (27 mL) and water (3 mL) were refluxed overnight. The solvent was evaporated under vacuum to about half of its original volume. Water was added, and the resulting aqueous layer was treated with HCl to obtain a solid, which was filtered and dried to afford yellow solid (290 mg, 65% yield). m.p. 308—310 ℃; ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 13.44 (brs, 2H), 7.70 (s, 2H), 7.67 (d, $J=4.8$ Hz, 2H), 7.25 (d, $J=3.6$ Hz, 2H), 7.15 (dd, $J=4.8$, 3.6 Hz, 2H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 169.7, 139.7, 134.5, 131.5, 130.2, 127.9, 127.5, 127.2; IR (KBr) v: 2880, 2641, 2530, 1685, 1438, 1405, 1285, 1255, 1211, 1127, 837, 708 cm^{-1}. HRMS (ESI) calcd for $C_{16}H_{10}O_4S_2$ 329.9948, found 328.9952 $[M-H]^-$.

Compound **7b** was prepared from compound **6b** (559 mg, 1.35 mmol) according to the procedure for compound **7a**, which was filtered and dried to afford yellow solid (443 mg, 85% yield). m.p. 210—214 ℃; ^{1}H NMR (DMSO-d_6, 400 MHz) δ: 13.38 (brs, 2H), 7.61 (s, 2H), 7.06 (d, $J=3.6$ Hz, 2H), 6.87 (d, $J=3.6$ Hz, 2H), 2.85 (q, $J=7.6$ Hz, 4H), 1.27 (t, $J=7.6$ Hz, 6H); ^{13}C NMR (DMSO-d_6, 100 MHz) δ: 168.9, 148.3, 136.9, 134.2, 131.1, 129.7, 126.8, 124.6, 22.8, 15.7; IR (KBr) v: 2978, 2848, 2655, 2564, 1683, 1423, 1288, 1244, 1209, 1140, 814 cm^{-1}. HRMS (ESI) calcd for $C_{20}H_{18}O_4S_2$ 386.0574, found 385.0571 $[M-H]^-$.

Compound **7c** was prepared from compound **6c** (710 mg, 1.35 mmol) according to the procedure for compound **7a**, which was filtered and dried to afford yellow solid (645 mg, 96% yield). m.p. 130—132 ℃; ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 13.44 (b, 2H), 7.61 (s, 2H), 7.05 (d, $J=3.3$ Hz, 2H), 6.85 (d, $J=3.3$ Hz, 2H), 2.80 (t, $J=7.5$ Hz, 4H), 1.58—1.65 (m, 4H), 1.20—130 (m, 12H), 0.86 (t, $J=6.6$ Hz, 6H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 169.1, 146.9, 137.1, 134.2, 131.2, 129.7, 126.8, 125.4, 31.2, 31.0, 29.4, 28.3, 22.1, 14.0; IR (KBr) v: 2923, 2854, 2634, 2558, 1699, 1425, 1289, 1242, 1211, 1125, 803 cm^{-1}; HRMS (ESI) calcd for $C_{28}H_{34}O_4S_2$ 498.1826, found 497.1816 $[M-H]^-$.

Compound **7d** was prepared from compound **6d** (937 mg, 1.35 mmol) according to the procedure for compound **7a**, which was filtered and dried to afford yellow solid (818 mg, 91% yield). m.p. 318—320 ℃; ^{1}H NMR (DMSO-d_6, 300 MHz) δ: 13.44 (brs, 2H), 7.56 (s, 2H), 7.04 (d, $J=3.6$ Hz, 2H), 6.81 (d, $J=3.6$ Hz, 2H), 2.78 (t, $J=7.5$ Hz, 4H), 1.60—1.64 (m, 4H), 1.15—1.41 (m, 36H), 0.84 (t, $J=6.6$ Hz, 6H); ^{13}C NMR (DMSO-d_6, 75 MHz) δ: 169.2, 146.5, 137.3, 134.5, 130.9, 129.5, 126.6, 125.2, 31.4, 31.2, 29.4 (overlapping signals), 29.1, 29.0 (overlapping signal), 28.8, 28.6, 22.2, 14.0; IR (KBr) v: 2919, 2850, 2639, 2559, 1702, 1405, 1288, 1240, 1209, 1126, 802 cm^{-1}. HRMS (ESI) calcd for $C_{40}H_{58}O_4S_2$ 666.3704, found 665.3715 $[M-H]^-$.

Synthesis of 2,5-bis(2-thienyl)terephthaloyl chloride (8a)

A solution of compound **7a** (178 mg, 0.54 mmol) and oxalyl chloride (0.5 mL, 5.70 mmol) in dry CH_2Cl_2 (30 mL) and several drops DMF was stirred for 12 h at room temperature. The solvent was removed under vacuum to obtain the corresponding crude terephthaloyl chloride, which was used for next step without further purification.

Compound **8b** was prepared from compound **7b** (208 mg, 0.54 mmol) and oxalyl chloride (0.5 mL, 5.70 mmol) according to the procedure for compound **8a**, which was used for next step without further purification.

Compound **8c** was prepared from compound **7c** (269 mg, 0.54 mmol) and oxalyl chloride (0.5 mL, 5.70 mmol) according to the procedure for compound **8a**, which was used for next step without further purification.

Compound **8d** was prepared from compound **7d** (360 mg, 0.54 mmol) and oxalyl chloride (0.5 mL, 5.70 mmol) according to the procedure for compound **8a**, which was used for next step without further purification.

Synthesis of 4,9-dihydro-s-indaceno[1,2-*b*:5,6-*b*']dithiophene-4,9-dione (1a)

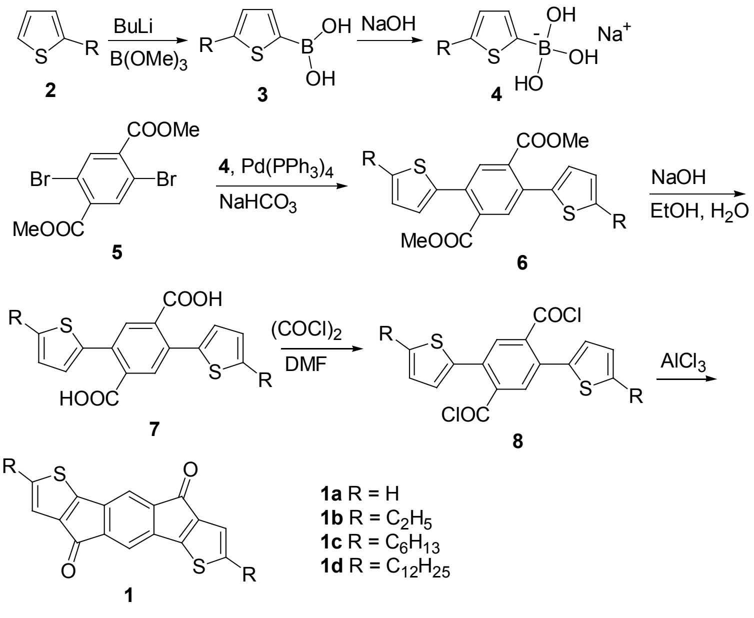
A solution of compound **8a** (198 mg, 0.54 mmol) in dry CH_2Cl_2 (30 mL) was added to a suspension of anhydrous $AlCl_3$ (216 mg, 1.62 mmol) in dry CH_2Cl_2 (10 mL) at 0 ℃. The resulting mixture was further stirred for 20 min, then at room temperature for 3 h. The reaction mixture was poured into ice water then filtered and washed by hexane, ethanol to yield a blue solid (103 mg, 65% yield). m.p. 350—352 ℃; we can not get its NMR spectra because of its poor solubility. IR (KBr) v: 3387, 3107, 3072, 1711, 1435, 1320, 778, 463 cm^{-1}; LRMS (APCI) *m*/*z*: 294, found 295 $[M+H]^+$. Anal. calcd for $C_{16}H_6O_2S_2$: C 65.29, H 2.05, S 21.79; found C 65.35, H 2.08, S 21.77.

Compound **1b** was prepared from compound **8b** (228 mg, 0.54 mmol) according to the procedure for compound **1a**. The crude product was purified by flash chromatography, using a mixture of hexane and dichloromethane (3 : 1, volume ratio) as the eluent to yield a green solid (132 mg, 70% yield). m.p. 256—258 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.11 (s, 2H), 6.81 (s, 2H), 2.83 (q, J=7.6 Hz, 4H), 1.33 (t, J=7.6 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 186.5, 156.0, 153.1, 140.8, 140.0, 139.9, 117.5, 114.0, 24.0, 15.6; IR (KBr) v: 3396, 2924, 2854, 1708, 1434, 1315, 776, 474 cm^{-1}; LRMS (APCI) *m*/*z*: 350, found 351 $[M+H]^+$. Anal. calcd for $C_{20}H_{14}O_2S_2$: C 68.54, H 4.03, S 18.30; found C 68.53, H 4.06, S 18.31.

Compound **1c** was prepared from compound **8c** (289 mg, 0.54 mmol) according to the procedure for compound **1a**. The crude product was purified by flash chromatography, using a mixture of hexane and dichloromethane (5 : 1, volume ratio) as the eluent to yield a green solid (174 mg, 70% yield). m.p. 168—170 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.12 (s, 2H), 6.80 (s, 2H), 2.78 (t, J=7.6 Hz, 4H), 1.64—1.70 (m, 4H), 1.29—1.40 (m, 12H), 0.90 (t, J=6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ : 186.5, 156.1, 151.5, 140.8, 139.9, 139.8, 118.2, 114.0, 31.5, 31.3, 30.6, 28.6, 22.5, 14.0; IR (KBr) v: 3392, 2918, 2848, 1729, 1468, 1321, 773, 480 cm^{-1}; LRMS (APCI) *m*/*z*: 462, found 463 $[M+H]^+$. Anal. calcd for $C_{28}H_{30}O_2S_2$: C 72.69, H 6.54, S 13.85; found C 72.75, H 6.57, S 13.77.

Compound **1d** was prepared from compound **8d** (380 mg, 0.54 mmol) according to the procedure for compound **1a**. The crude product was purified by flash chromatography, using a mixture of hexane and dichloromethane (5 : 1, volume ratio) as the eluent to yield a green solid (221 mg, 65% yield). m.p. 146—148 ℃; ^{1}H NMR ($CDCl_3$, 400 MHz) δ: 7.11 (s, 2H), 6.79 (s, 2H), 2.78 (t, J=7.6 Hz, 4H), 1.66—1.69 (m, 4H), 1.19—1.41 (m, 36H), 0.88 (t, J=6.8 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ: 186.5, 156.1, 151.6, 140.8, 140.0, 139.9, 118.2, 114.0, 31.9, 31.3, 30.6, 29.6 (overlapping signal), 29.5, 29.4, 29.3, 28.9 (overlapping signal), 22.7, 14.1; IR (KBr) v: 3388, 2951, 2850, 1697, 1466, 1317, 774, 483 cm^{-1}; LRMS (APCI) *m*/*z*: 630, found 631 $[M+H]^+$. Anal. calcd for $C_{40}H_{54}O_2S_2$: C 76.14, H 8.63, S 10.16; found C 76.23, H 8.55, S 10.10.

Scheme 1 Synthesis of compounds **1a**—**1d**



Results and discussion

Materials synthesis

The synthesis of compounds **1a**—**1d** is depicted in Scheme 1. The starting compounds, 2-dodecylthiophene (**2d**) and dimethyl 2,5-dibromoterephthalate (**5**) were prepared according to the literature methods.[22,23] Compounds **4a**—**4d** were synthesized by a similar process as reported before.[21] Instead of Still-coupling reaction used in previous synthesis,[18] Suzuki coupling was used in our work to avoid using toxic tin compounds. A two-folded palladium-catalyzed Suzuki cross-coupling reaction between compounds **4** and **5** furnished dithienyl-substituted terephthalate diesters **6**. Saponification of the diesters **6** smoothly provided 2,5-bis(5-alkylthiophen-2-yl)terephthalic acids (**7**), which were readily transformed into the corresponding terephthaloyl chlorides **8**. Upon removal of the volatile materials *in vacuo*, a Lewis acid-promoted intramolecular Friedel-Crafts cyclization of compound **8** took place to give the conjugated diketones **1**. Compound **1a** gave blue crystal, which was only slightly soluble in high polar solvents. Compounds **1b**, **1c** were obtained as shining turquoise crystals and **1d** was aquamarine crystal. They were readily dissolved by most common organic solvents.

Optical properties

The UV-vis absorption spectra of the new materials in dichloromethane (DCM) are shown in Figure 1a. Compounds **1a**—**1d** exhibit intense absorption bands at about 295 nm, which are attributable to the π-π* transition of the conjugated backbone. The weak lowest-energy absorptions at 560—605 nm can be also assigned to a π-π* transition.[18,24-26] The UV-vis absorption profiles for compounds **1a**—**1d** are very similar, suggesting the length of *n*-alkyl groups have little effect on the molecular π-system.[27] When the new materials are deposited as thin films, their high-energy absorption maxima are observed at around 310—330 nm, red-shifted by *ca.* 13—33 nm versus the corresponding solution absorption maxima. Meanwhile, the lowest-energy absorption edges at longer wavelengths appear at 605—670 nm, showing significant red-shifts of *ca.* 45—67 nm. Interestingly, the red-shifts of the lowest-energy absorption edges increase with the lengthening of the *n*-alkyl chains (Table 1, Figure 1b), revealing strongly enhanced molecular interaction in the solid phase with the increasing of the side-chain length. Solution and solid state optical band gaps are estimated from the lowest-energy absorption edges of their optical spectra,[28] and the results are listed in Table 1. The optical band gaps of compounds **1a**—**1d** are smaller than that of pentacene. In solution, the *n*-alkyl substituted compounds **1b**—**1d** give very similar optical band gap. However, the thin film band gaps of **1a**—**1d** gradually decrease with the lengthening of *n*-alkyl chains.

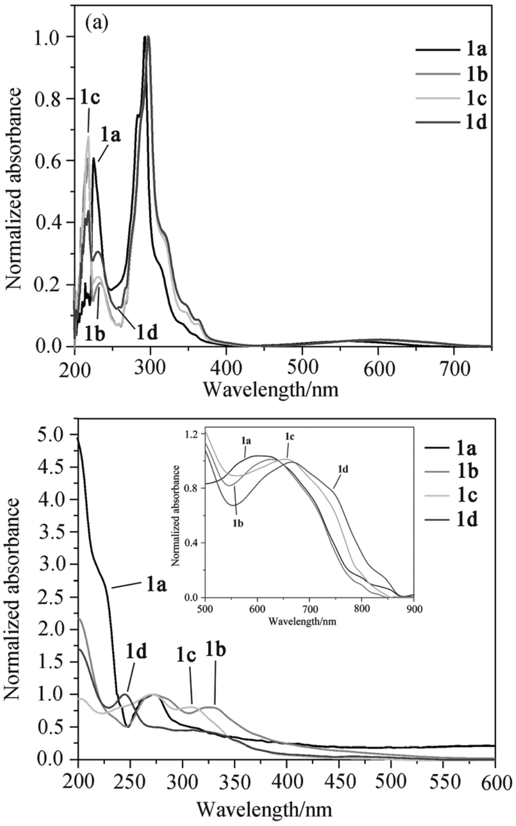


Figure 1 (a) Normalized UV-vis absorption recorded in DCM. (b) Thin-film UV-vis absorption spectra of **1a**—**1d**.

In contrast to the solution of pentacene, which deteriorated in a few minutes,[8,29] the solutions and solids of the new materials show much higher stability in air. The photo-stability of compounds **1a**—**1d** were investigated by monitoring the reduction in the absorbances at $\lambda_{\max}$ in an air-saturated 1.0×10^{-4} mol•L^{-1} toluene solution under ambient light at 25 ℃ (Figure 2). Compound **1c**, whose long wavelength absorption diminished only 20% in a one week period ($t_{1/2} \approx 19.4$ d), possessed the highest stability. Compound **1b**, whose absorption diminished 80% in 7 d, showed the lowest stability.

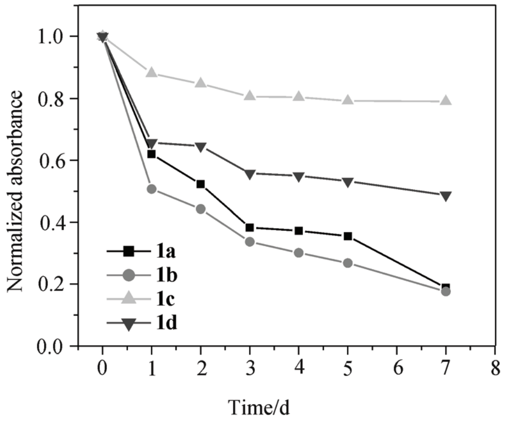


Figure 2 Photo-stability of **1a**—**1d** monitored by recording their absorption decrease at $\lambda_{\max}$ upon exposure to ambient light and air at 25 ℃.

The observed stability order is: **1c**>**1d**>**1a**≈**1b**. The significantly improved stabilities of the new compounds compared to pentacene could be attributed to their much lower HOMO levels.[27]

Electrochemical properties

Cyclic voltammograms (CV) were recorded in THF to investigate the electrochemical properties. The CV of compound **1a** could not be recorded because of insufficient solubility. In THF, compounds **1b**—**1d** exhibit two reduction peaks but no clear oxidation peak in the electrochemical window (Figure 3). The high reversibility of the two redox pairs in the potential range of −0.8 to −1.6 V demonstrates the high stability of the diketone structure upon electron injection. From the first half-wave reduction potentials, the LUMO energies can be estimated by taking the SCE energy level to be −4.44 eV below the vacuum level,[16] and the results are listed in Table 1. The low LUMO energies (⩽−3.4 eV) for compounds **1b**—**1d** suggest that they have high electron affinities. The HOMO levels were estimated from the LUMO levels and the optical band gaps of the solutions (Table 1). The experimental HOMO, LUMO energies indicate that the lengthening of *n*-alkyl chains results in a gradual increase of the HOMO, LUMO energies and reduction of the HOMO-LUMO energy gaps, consistent with a more effective conjugation between the heteroacene cores.[30] The LUMO levels of the new compounds are approximately 0.5 eV lower than that of pentacene.

Thermal properties

The thermal properties of compounds **1a**—**1d** were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Table 1). Compounds **1a**—**1d** showed high thermal decomposition temperatures at about 340, 295, 360 and 375 ℃, respectively; comparable to pentacene, which decomposes at 330 ℃. Comparing the *n*-alkyl substituted compounds **1b**—**1d**, the longer *n*-alkyl chain results in a higher decomposition temperature.

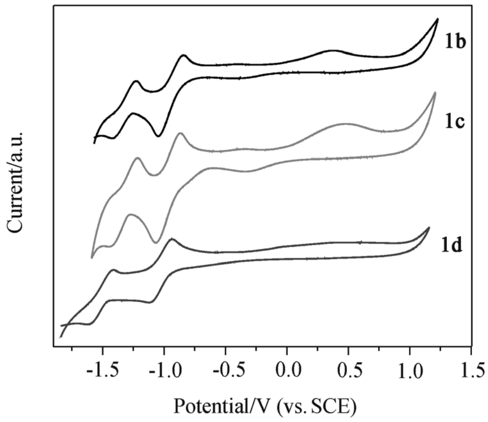


Figure 3 Cyclic Voltammograms of **1b**—**1d**.

All of the present compounds exhibit reversible thermal features in DSC scans, in accordance with the aforementioned good thermal stabilities (Figure 4). It was found that the *n*-alkyl chains and the core structures had a significant effect on the phase transition. Compound **1a** shows no phase transition or melting at temperatures lower than the decomposition point. All the *n*-alkyl substituted compounds, **1b**—**1d** exhibit one endothermic peak at the second heating cycle and one exothermic peak at the first cooling cycle, corresponding to phase change temperatures. With the lengthening of *n*-alkyl chain, the transition temperatures decrease significantly. The molecular organizations of all the four compounds were further examined by polarized optical microscope (POM). No texture was observed on

Table 1 Optical absorption wavelength (λ), caculated energy gap (E_g), electrochemical properties, decomposition temperatures and DSC measurements for compounds **1a**—**1d**

Compound	λ/nm		Energy gap		$E_{1/2}^{\mathrm{red}\,b}$/V	E_{HOMO}/ $E_{\mathrm{LUMO}}{}^{b}$/eV	T_{DSC}/℃		T_{TGA}/℃	Half-life time^{c}/d
	Film	Soln	E_g/eV (Film)^a	E_g/eV (Soln)^a			Second heating	First cooling		
	310	292								
1a	605	560	1.58	1.86	—	—	—	—	340	2.5
	327	297				−5.18/				
1b	626	596	1.57	1.70	−0.96	−3.48	251	220	295	1.9
	310	297				−5.17/				
1c	655	598	1.53	1.72	—	−3.45	170	151	360	19.4
	330	297				−5.12/				
1d	670	603	1.48	1.71	−1.03	−3.41	147	129	375	5.1
pentacene	670	577	1.85	2.15[31]	—	—	—	—	330	5

^{a} Optical HOMO−LUMO gaps determined from the onset of lowest-energy visible absorption band. ^{b} Recorded $E_{1/2}$ values vs SCE in THF with TBAPF$_6$ as supporting electrolyte. LUMO energies determined from the equation: $E_{\mathrm{LUMO}} = -E_{1/2}^{\mathrm{red}} - 4.44$. ^{c} Half-life time was obtained by fitting the data in Figure 2 according to unimolecular first-order kinetics mechanism.

compounds **1a** and **1b**. However, both **1c** and **1d** experienced obvious texture changes at temperatures where the phase changes occurred in the DSC diagrams. Figure 4b and 4c show the POM images of compounds **1c** and **1d** in their mesophases. Both compounds showed a clear dendritic texture during cooling from the isotropic melt. Our results reveal that flexible *n*-alkyl chains with suitable length are needed to obtain liquid crystalline phase. For device applications, it is of importance that the organic semiconductor molecules can self-assemble into long-range ordered structures, and the alignment of conjugated liquid crystals at the interface with the dielectric layer is critical to the OFET performance.[32] The liquid crystal behaviours of compounds **1c** and **1d** are advantageous for future device applications.

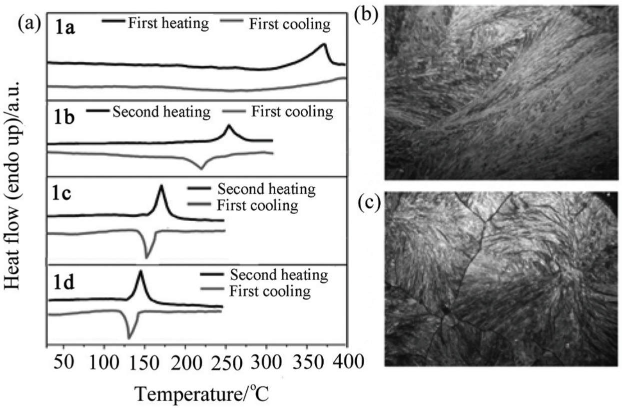


Figure 4 (a) Differential scanning calorimetry (DSC) of the compounds **1a**—**1d** at a temperature ramp of 10 ℃•min^{-1} under N_2. (b) Optical textures, as taken by polarized optimal microscopy of **1c** (at 156 ℃). (c) Optical textures, as taken by polarized optimal microscopy of **1d** (at 145 ℃).

X-ray single-crystal analysis

Single crystals of compounds **1c** and **1d**, which were successfully obtained by slow evaporation of solution in a chloroform/ethanol mixture, have been analyzed by X-ray diffraction. **1c** forms a triclinic unit cell and belongs to a *P*-1 space group with the crystallographic data a=5.1056(4) Å, b=7.8568(6) Å, c=15.7812(12) Å, α=85.276(4)°, β=87.953(4)°, γ=76.426(4)°, V=613.18(8) Å^3, Z=2, D_x=1.253 Mg/m^3, and CCDC reference number 751385. **1d** forms a triclinic unit cell and belongs to a *P*-1 space group with the crystallographic data a=5.4953(16) Å, b=7.0700(19) Å, c=24.359(8) Å, α=94.948(16)°, β=92.776(17)°, γ=106.352(14)°, V=902.1(5) Å^3, Z=2, D_x=1.161 Mg/m^3, and CCDC reference number 751386. The main five-ring-fused backbone shows planar structure in both crystals, while the *n*-alkyl chains on the α-position of thienyl groups lie outside of the skeleton plane (Figure 5). Both **1c** and **1d** form slipped face-to-face π-stacking motifs in the crystals. This type of molecular arrangement is expected to give stronger electronic coupling between molecules than the herringbone arrangement.[33,34] The interplanar distances for **1c** and **1d** are 3.255 and 3.427 Å, respectively; lower than the sum of van der Waals radii,[35] indicating strong π-π interactions between the stacks. Remarkably, marked S···O short contacts (3.118 Å) were found between the neighboring columns of **1d**. The strong intraplanar S···O interactions link the columns into layered structures. Bao[36] and Zhu[37,38] have demonstrated that such double-channel fashion of molecular packing could facilitate carrier transport and result in high device performance.

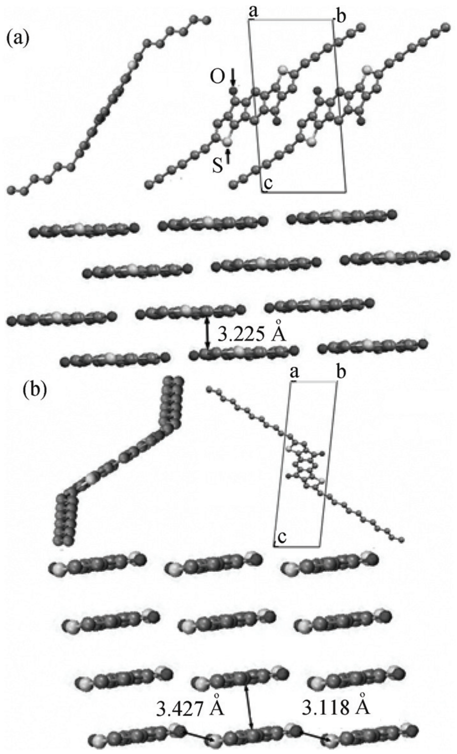


Figure 5 (a) X-ray crystal structure of compound **1c**. (b) X-ray crystal structure of compound **1d**. *n*-Alkyl group and hydrogen atoms have been omitted for clarity in packing.

Conclusions

In conclusion, we have designed and synthesized a new family of dithiophene-dione heteroacenes materials. These materials exhibit much higher solubility, along with higher thermal and photo-stability compared to pentacene. The low LUMO energies and high reversibility for electron injection revealed that they have high electron affinities and are potentially candidates for *n*-channel liquid-crystal semiconductors. Further works including device fabrication are underway in our group.

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