JOC The Journal of Organic Chemistry

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Pentacenobis(thiadiazole)dione, an n-Type Semiconductor for Field-Effect Transistors

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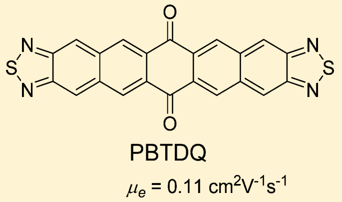
Supporting Information

ABSTRACT: A new heteroacenequinone, pentaceno[2,3-*c*:9,10-*c*′]bis([1,2,5]thiadiazole)-6,13-dione (PBTDQ), with two peripheral thiadiazole rings was synthesized, and its solid-state properties were characterized. The fused planar structure with a low-lying LUMO and low reorganization energy facilitates electron transport, affording μ_e values of up to 0.11 cm^2 V^{-1} s^{-1} in field-effect transistor devices.

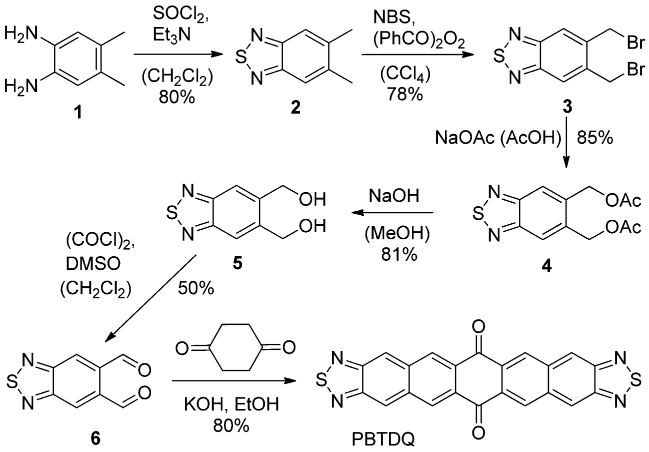


Organic semiconductors based on linear acenes[1] and heteroacenes[2] are important materials for organic field-effect transistors (OFETs), often possessing high charge mobilities as a result of their fused planar structures. Anthracene,[3] tetracene,[4] pentacene,[5] and hexacene[6] have been successfully incorporated into OFET devices, showing a general improvement in charge mobility as the number of fused rings is increased. The increased biradical character and concomitant instability[7] of longer acenes has limited studies on heptacene[8] through nonacene[9] to derivatives with bulky substituents, which prevent cofacial approach and therefore do not maintain the attractive semiconductor properties (i.e., $\pi-\pi$ interactions and high charge mobility).

Acenequinones, the products of oxidative degradation of acenes, are significantly more stable as a result of disruption of π delocalization across the quinoidal ring. At the same time, planarity is maintained over the entire backbone, and therefore, acenequinones still have a tendency to exhibit strong $\pi-\pi$ interactions in the solid state. While many acenequinones have been utilized as precursors to substituted acenes,[10] only a few studies have investigated the semiconducting properties of these materials. Pentacene-6,13-dione was found to be an insulator and was successfully used as dielectric layer for pentacene OFET devices.[11] On the other hand, its tetraaza and octafluoro derivatives are semiconductors with electron mobilities (μ_e) on the order of 0.1 cm^2 V^{-1} s^{-1}.[12] n-Channel OFETs with μ_e on the order of 0.1 cm^2 V^{-1} s^{-1} were also reported for anthraquinone and benzodithiophenequinone derivatives substituted with electron-deficient aromatic moieties.[13]

In this note, we report the synthesis, characterization, and field-effect transistor properties of pentaceno[2,3-*c*:9,10-*c*′]bis([1,2,5]thiadiazole)-6,13-dione (PBTDQ), a new heteroacenequinone with seven linearly fused rings. Peripheral thiadiazole rings were introduced in order to reduce the energy of the lowest unoccupied molecular orbital (LUMO) and facilitate electron injection (i.e., from common electrode materials such as Au). Our synthetic pathway relied on condensation between *o*-aryldialdehydes and 1,4-cyclohexanedione[14] (Scheme 1).

Scheme 1. Synthetic Route to Pentacenobis(thiadiazole)dione (PBTDQ)



Commercially available 4,5-dimethyl-1,2-phenylenediamine enabled the preparation of dialdehyde precursor **6** through an efficient route beginning with thiadiazole cyclization using thionyl chloride followed by radical bromination of the methyl groups using NBS. Subsequent acetoxylation and hydrolysis steps afforded **5** in good yield, and this diol was converted to the previously undescribed dialdehyde **6** via Swern oxidation. The final condensation reaction led to precipitation of PBTDQ

Received: April 2, 2014
Published: May 28, 2014

dx.doi.org/10.1021/jo500760c | *J. Org. Chem.* 2014, 79, 5858−5860

as an insoluble red solid that was purified by vacuum sublimation.

According to density functional theory (DFT) calculations at the B3LYP/6-31G(d) level, PBDTQ is completely planar (see the Supporting Information). Its HOMO−LUMO gap (2.6 eV) is reduced relative to that of isoelectronic homoanalogue heptacene-7,16-dione (3.0 eV). This gap reduction can be traced to the peripheral thiadiazole rings in PBTDQ, which stabilize the LUMO energy (−3.49 eV), greatly improving the electron-accepting character (and electron-transporting character; see below) of the molecule. Despite the presence of highly polar carbonyl and thiadiazole moieties, calculations revealed an unexpectedly low electron-transfer reorganization energy of 0.10 eV, similar to that of the benchmark pentacene semiconductor (0.094 eV for hole-transfer[15]).

Cyclic voltammetry of a PBTDQ thin film revealed quasireversible reduction at −1.36 V vs ferrocene (Figure 1a), from which a LUMO energy of −3.44 eV can be estimated.[16] This value is very close to that of the previously studied octafluoropentacenequinone semiconductor (E_{LUMO} = −3.51 eV[12]). Solid-state UV/vis absorption of PBTDQ studied in thin films showed a broad spectrum with peaks in the visible range at 452, 508, and 541 nm (Figure 1b). The band gap calculated from the onset of absorption is ~2.15 eV.

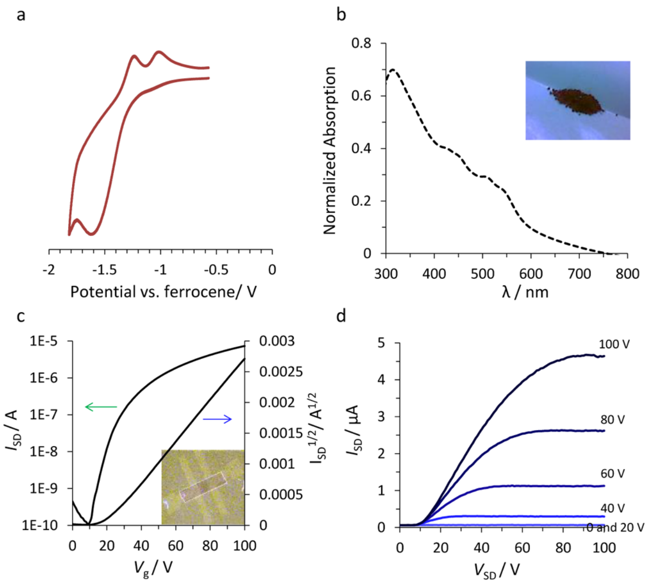


Figure 1. (a) Cyclic voltammogram (0.2 M Bu_4NPF_6 in CH_2Cl_2, 100 mV/s) of a PBTDQ film vacuum-deposited on an ITO electrode. (b) UV/vis absorption spectrum of PBTDQ. (c) Transfer and (d) output characteristics of single-crystal field-effect transistors fabricated using PBTDQ.

Field-effect transistors were prepared in order to assess the charge transport properties of PBTDQ. Thin-film transistors fabricated by vacuum sublimation of PBTDQ revealed n-channel behavior with average electron mobility $\mu_e = 1.4 \times 10^{-3}$ cm^2 V^{-1} s^{-1}, threshold voltage V_T = 30 V, and on−off ratio of 10^4 in the unoptimized devices (see the Supporting Information). The single-crystal[17] OFET devices also showed n-channel (only) characteristics with maximum electron mobility μ_e = 0.11 cm^2 V^{-1} s^{-1} (average = 0.09 cm^2 V^{-1} s^{-1}) and reduced threshold voltage (V_T = 20 V) and slightly improved on−off ratio (10^5) compared with the thin film devices. The slight deviation in linearity observed in the output characteristics (Figure 1d) likely resulted from thickness-dependent resistance in the single crystals and was not present in the thin-film devices.

In conclusion, we have prepared the new heteroacenequinone semiconductor PBTDQ with seven linearly fused rings. Electron-deficient thiadiazole groups on the molecular periphery drastically reduce the LUMO energy compared with the parent heptacenequinone, leading to enhanced electron-acceptor ability. The fused-ring structure of PBTDQ ensures molecular planarity and leads to a small electron reorganization energy, conducive to charge transport. Single-crystal field-effect transistors exhibited n-type characteristics with a maximum measured electron mobility of 0.11 cm^2 V^{-1} s^{-1}, demonstrating the merit of extended acenequinones as functional n-type organic semiconductors.

■ EXPERIMENTAL SECTION

5,6-Dimethyl-[2,1,3]benzothiadiazole (2).[18] Thionyl chloride (1.75 g, 14.7 mmol) was added dropwise to a CH_2Cl_2 solution of **1** (1.00 g, 7.34 mmol) and triethylamine (3.74 g, 37.0 mmol), and the mixture was refluxed for 5 h. After the solvent was removed under reduced pressure, water (70 mL) was added, and then concentrated HCl was added to achieve a final pH of 1. The mixture was extracted with CH_2Cl_2 (3 × 20 mL), and the product was purified by column chromatography on silica gel (10:1 hexane/ethyl acetate). Yield: 0.96 g, 80%. Mp: 83−85 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.73 (s, 2H), 2.44 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.3, 140.6, 119.8, 20.8. HRMS (APCI-TOF) calcd for $C_8H_9N_2S$ [M + H]$^+$ 165.0481, found 165.0482.

5,6-Bis(bromomethyl)[2,1,3]benzothiadiazole (3). Compound **3** was prepared following the literature procedure, albeit in higher yield.[18] A mixture of **2** (0.50 g, 3.04 mmol), NBS (1.08 g, 6.07 mmol), and benzoyl peroxide (30 mg, 0.12 mmol) in CCl_4 (50 mL) was refluxed overnight. The suspension was cooled and filtered, and the filtrate was evaporated to give the product as a brown solid (0.76 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.05 (s, 2H), 4.85 (s, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 154.5, 138.2, 123.5, 30.1.

[2,1,3]Benzothiadiazole-5,6-diylbis(methylene) diacetate (4). A solution of compound **3** (0.50 g, 1.55 mmol) and NaOAc (1.0 g, 12.2 mmol) in AcOH (5 mL) was refluxed overnight. The resulting suspension was cooled and evaporated to remove most of the acetic acid, and then water (30 mL) was added. The mixture was extracted with ethyl acetate (3 × 20 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), concentrated in vacuo, and purified by chromatography (10:1 hexane/ethyl acetate) to provide the product as a white solid (0.37 g, 85%). Mp: 88−90 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.03 (s, 2H), 5.31 (s, 4H), 2.15 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 170.4, 154.3, 136.2, 121.3, 63.5, 20.9. HRMS (ESI-TOF) calcd for $C_{12}H_{12}N_2NaO_4S$ [M + Na]$^+$ 303.0410, found 303.0416.

[2,1,3]Benzothiadiazole-5,6-diyldimethanol (5). A solution of compound **4** (1.10 g, 3.92 mmol) and NaOH (16 mg, 0.39 mmol) in methanol (100 mL) was stirred at room temperature for 4 h, and then acidic ion-exchange resin (732) (2.0 g) was added. The mixture was stirred for 1 h and then filtered. The filtrate was evaporated to give the product as a white solid (0.62 g, 81%). Mp: 130−132 °C. ^{1}H NMR (300 MHz, DMSO-d_6) δ: 7.99 (s, 2H), 5.25 (s, 2H), 4.69 (s, 4H). ^{13}C NMR (75 MHz, DMSO-d_6) δ: 153.9, 143.5, 116.8, 60.0. HRMS (ESI-TOF) calcd for $C_8H_8N_2NaO_2S$ [M + Na]$^+$ 219.0199, found 219.0199.

[2,1,3]Benzothiadiazole-5,6-dicarbaldehyde (6). To a dry 100 mL two-necked flask were added oxalyl chloride (0.78 g, 6.1 mmol) and CH_2Cl_2 (20 mL) under dry nitrogen. The reaction mixture was cooled to −78 °C, and a solution of DMSO (0.62 g, 12.4 mmol) in CH_2Cl_2 (2 mL) was added dropwise. The resulting solution was stirred for 5 min, and then compound **5** (0.50 g, 2.6 mmol) dissolved in a 2:1 CH_2Cl_2/DMSO mixture (3 mL) was added dropwise. The reaction was allowed to continue for 0.5 h, and then Et_3N (10 mL) was slowly added at −78 °C. The reaction mixture was allowed to stir for 10 min and then slowly warmed to rt. Ice-cold water (30 mL) was added, and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were washed with brine, dried ($MgSO_4$), concentrated in vacuo, and purified by chromatography (2:1 hexane/ethyl acetate) to provide the product (0.26 g, 53%) as a yellowish solid. Mp: 163−165 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 10.62 (s, 2H), 8.63 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 191.5, 155.6, 136.1, 127.5. HRMS (ESI-TOF) calcd for $C_8H_5N_2O_2S$ [M + H]$^+$ 193.0066, found 193.0074.

Pentaceno[2,3-*c*:9,10-*c*′]bis([1,2,5]thiadiazole)-6,13-dione (PBTDQ). To a stirred solution of compound **6** (0.20 g, 1.0 mmol) and 1,4-cyclohexanedione (58 mg, 0.52 mmol) in ethanol (50 mL) at 60 °C was added dropwise a solution of potassium hydroxide (32 mg) in ethanol. A brown precipitate was immediately observed. After 1 h of stirring at the same temperature, the reaction mixture was cooled to room temperature. The resulting solid was filtered off, washed with ethanol, and dried in air to yield the product as a brownish-red powder (0.15 g, 68%). Mp: >320 °C. The ^{1}H NMR spectrum was not recorded because of low solubility. ^{13}C CP-MAS NMR (100 MHz, solid) δ: 180.7, 151.8, 133.3, 129.0, 122.4, 117.4. MS (MALDI) *m*/*z*: 425 ([M + H]$^+$). HRMS (APCI-TOF) calcd for $C_{22}H_9N_4O_2S_2$ [M + H]$^+$ 425.0161, found 425.0177. Elemental analysis calcd for $C_{22}H_8N_4O_2S_2$: C, 62.25; H, 1.90; N, 13.20; S, 15.11. Found: C, 62.52; H, 1.71; N, 12.96; S, 15.04.

Transistor Device Fabrication. All of the devices were fabricated in the bottom-gate top-contact configuration using Au source and drain electrodes and a 200 nm SiO_2 layer (C_i = 17.2 nF cm^{-1}) thermally grown on heavily n-doped (Sb) Si ($\rho \approx 0.01\ \Omega$ cm) as the dielectric and gate electrode, respectively. Thin films of PBTDQ (50 nm) were grown at room temperature by vacuum deposition (10^{-6} mbar, deposition rate 0.2−0.4 A s^{-1}). Au electrodes (50 nm) were then patterned (W/L = 10) by evaporation through a shadow mask at pressures of <10^{-6} mbar. For single-crystal devices, the SiO_2 surface was first passivated with a thin polystyrene layer by spin-coating (10 mg/mL toluene, 6000 rpm). Thin crystals of PBTDQ were prepared via physical vapor transport under a flow of Ar (∼50 mL/min) at ambient pressure by heating to ∼300 °C. The chosen crystals were picked by the tip of a needle and laminated onto the polystyrene surface. A shadow mask was carefully placed over the crystals, and the Au source and drain electrodes were patterned by thermal evaporation. The device width and length were determined by the crystal size and measured using an optical microscope. Typical values were W = 50−100 μm and L = 50 μm. All device characterization was performed under vacuum using a Keithley 4200 SCS instrument.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of NMR spectra, thin-film transistor device characteristics of PBTDQ, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful for the financial support from NSERC of Canada, NanoQuebec, the National Science Foundation for Fostering Talents in Basic Research of the National Natural Science Foundation of China (Grant J1103307), the program of the China Scholarships Council, and the 111 Project.

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