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Bisthiadiazole-Fused Tetraazapentacenequinone: An Air-Stable Solution-Processable n-Type Organic Semiconductor

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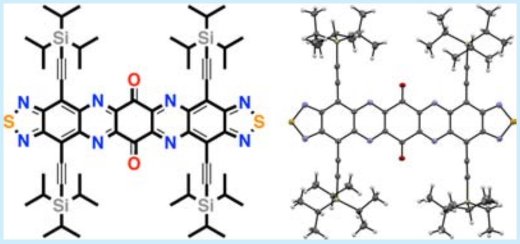
Supporting Information

ABSTRACT: The synthesis and characterization of a tetraazapentacenequinone fused to two thiadiazoles is reported. This linear derivative constituting seven fused rings shows a very low LUMO level (−4.46 eV) and a low HOMO−LUMO gap (1.77 eV). Its high solubility, endowed by four triisopropylsilyl groups, allows the fabrication of air-stable field-effect transistors by liquid deposition methods that show electron mobilities up to 2.42×10^{-3} cm^2 V^{-1} s^{-1} without any device optimization.



In the past several years, organic semiconductors have witnessed a spectacular increase in their performance.[1] This is in part due to synthetic organic chemistry that has become a fundamental tool for tailoring the optoelectronic properties and processability of organic materials. Because of their high HOMO levels and their optimal packing in the solid state, chemically modified *n*-acenes[2] have been investigated as p-type semiconductors in field-effect transistors[3] as well as different types of solar cells[4] and of light-emitting devices[5] with remarkable results. However, for some applications electron-transporting materials with the same level of performance are also highly desirable.[6] A useful approach to prepare electron-transporting acene derivatives consists of exchanging the C atoms of their aromatic framework for more electronegative heteroatoms such as N.[7] However, an important aspect that must be taken into account when designing n-type organic semiconductors is their stability. This is because negatively charged species tend to react with H_2O and O_2. As a general rule, n-type semiconductors with LUMO levels below −3.7 eV are required to avoid H_2O reduction[8] and below −4.0 eV to reduce O_2 trapping.[6f]

Along these lines, 2,1,3-benzothiadiazoles[9] have been introduced in semiconducting molecular and polymeric materials as electron-deficient components in field-effect transistors, solar cells, and light emitting diodes. Similarly, electron-deficient benzoquinone derivatives have been introduced in field-effect transistors,[9b,10] used as electron acceptors in artificial photosynthetic reaction centers,[11] and also have attracted much attention as materials for energy storage.[12] Herein, we report the synthesis and characterization of compound **1** that combines a tetraazapentacenequinone with two thiadiazoles in a linear array of seven fused rings. Compound **1** shows a very low LUMO level (−4.46 eV), a narrow HOMO−LUMO gap (1.77 eV), and high thermal stability (up to 305 °C). In addition, the high solubility of **1**, endowed by four triisopropylsilyl (TIPS) groups, allows the fabrication of field-effect transistors by liquid deposition methods. The devices exhibit electron mobilities up to 2.42×10^{-3} cm^2 V^{-1} s^{-1} under ambient conditions without any device optimization.

The synthesis of **1** is achieved in two steps (Scheme 1) from diamine **2**. The latter was synthesized following a reported procedure in five steps from *o*-phenylenediamine.[7e] The cyclocondensation between 2.2 equiv of diamine **2** and 1,2,3,4,5,6-hexaketonecyclohexane **3** in refluxing acetic acid provided a mixture of the dihydro- **4** and the tetrahydro- **5** linear bisdiazanaphthothiadiazoles in moderate yields (21% and 14% respectively). The formation of **4** and **5** is favored, even in the presence of 3.3 equiv of diamine **2** with no sign of the tricyclocondensed adduct **6** detected. Oxidation of the hydrogenated compounds **4** and **5** in the presence of MnO_2 yielded compound **1** in good yields (87%).

Because of the four TIPS substituents, compound **1** and the intermediates **4** and **5** were perfectly soluble in a wide variety of solvents; CH_2Cl_2, $CHCl_3$, and chlorobenzene were the most representative.

Slow evaporation of a chlorobenzene solution of **1** yielded crystals suitable for X-ray diffraction that, upon analysis, provided definitive proof of the molecular structure as well as insight into molecular packing (Figure 1). The aromatic framework of **1** is essentially flat while two of the TIPS-

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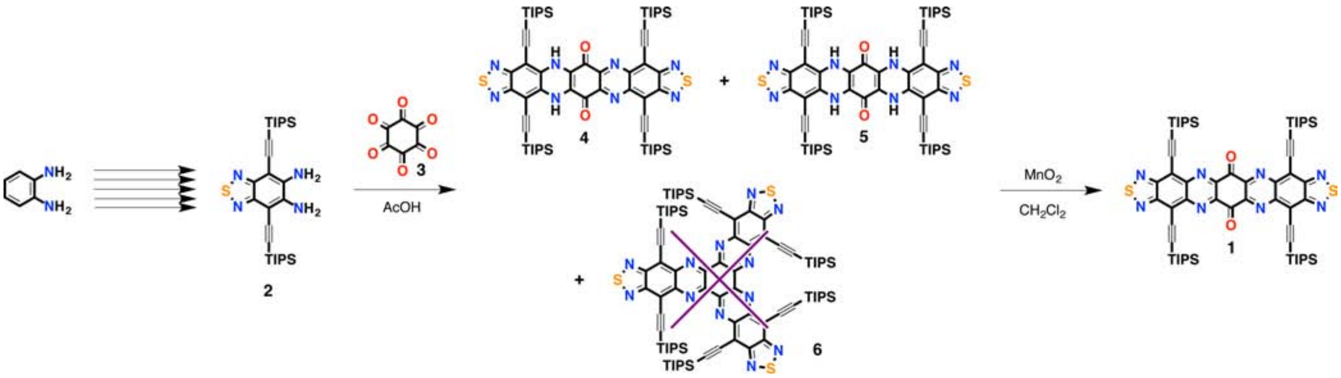
Scheme 1. Synthetic Route for Compound 1



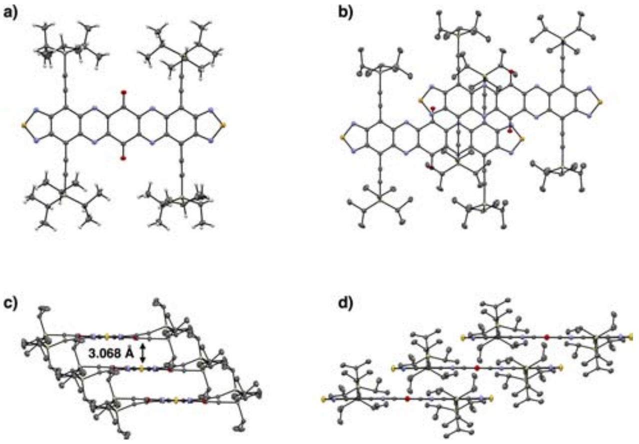


Figure 1. X-ray crystal structure of compound **1**.

acetylene substituents are slightly out of plane (Figure 1a). Compound **1** piled-up into 1D slipped stacks in which the acetylenes of one molecule sit at 3.068 Å on top of the π-core of an adjacent molecule (Figure 1b–d) suggesting the existence of a π–π interaction between them.

Compound **1** is dark green both in the solid state and in solution. The absorption spectrum in CH_2Cl_2 shows intense absorption bands in the UV and less intense bands in the violet, blue, yellow, orange, and red regions of the visible with peaks at 267, 282, 387, 448, 478, 599, and 646 nm (Figure 2). The photoluminescence spectrum of **1** in CH_2Cl_2 obtained by excitation at 620 nm shows a featureless band centered in the NIR at 725 nm with a shoulder at around 810 nm (Figure 2).

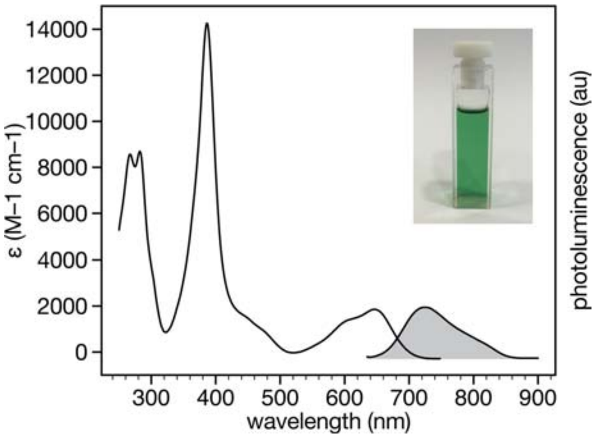


Figure 2. Absorption (white) and emission (gray) spectrum of compound **1** in CH_2Cl_2. Inset shows a solution of **1** in CH_2Cl_2.

The redox chemistry of **1** was investigated by cyclic voltammetry. The voltammograms show four reduction processes (Figure 3), while no oxidations were detected. The reduction waves show half-wave potentials at $E_{1/2}$ = −0.44, −0.75, − 1.43, and −1.63 V versus the ferrocene/ferrocinium couple. A small current was detected at −1.02 V on the reverse scan in between the second and third reduction waves, which was ascribed to the lack of reversibility of one of the reduced species. The low $E_{1/2}$ illustrates the high electron affinity of **1**.

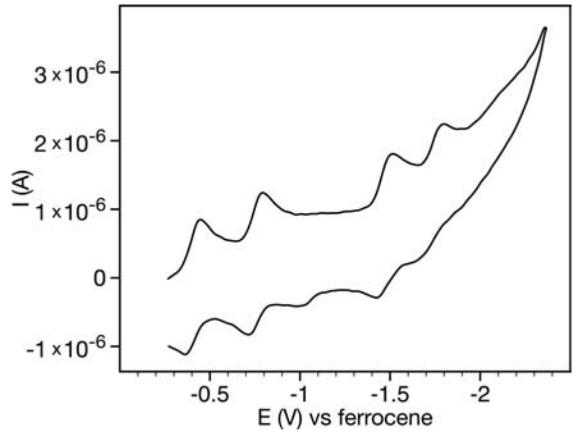


Figure 3. Cyclic voltammogram of **1** in a 0.1 M solution of nBu_4NPF_6 in CH_2Cl_2.

The HOMO–LUMO gap of **1** (E_{gap} = 1.77 eV), estimated from the absorption onset, is in the same range as pentacene (E_{gap} = 1.90 eV) and tetraazapentacene (E_{gap} = 1.86 eV) derivatives[2,7b,c] and wider than that of diazaheptacene[13] (E_{gap} = 1.33 eV), which shows the same number of rings. This illustrates that cross-conjugation at the benzoquinone residue reduces the linear conjugation to some extent. The LUMO level was estimated from the potential onset of the first reduction wave (E_{LUMO} = −4.46 eV), which is substantially lower than that observed for diazaheptacene[13] (E_{LUMO} = −4.01 eV) and for pentaceno(thiadiazole)dione[9b] (E_{LUMO} = −3.44 eV). The HOMO level (E_{HOMO} = −6.23 eV) was calculated from the difference of the optical gap and the electrochemical LUMO. DFT calculations (B3LYP-CH_2Cl_2-6-311g+(d2,p)) predicted a HOMO–LUMO gap (1.78 eV), HOMO (−6.16 eV), and LUMO (−4.38 eV) levels that follow the same trends as the experimental values. The computed HOMO and HOMO

− 1 are almost degenerate (their energy differs by 40 meV) and show a large density on the benzene ring of the benzothiadiazole residues. While the LUMO and LUMO + 1 are delocalized over the whole aromatic framework, the LUMO + 2 is mostly located over the quinone residue (Figure 4).

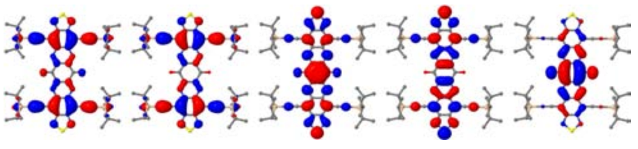


Figure 4. Frontier orbitals at the B3LYP-CH_2Cl_2-6311g+(d2,p) level. From left to right: HOMO − 1, HOMO, LUMO, LUMO + 1, and LUMO + 2.

The thermal properties of compound **1** were investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). TGA of **1** shows very high thermal stability under nitrogen up to 305 °C (Figure S7) in contrast to *n*-heptacene[14] and *n*-azaheptacene[13] derivatives that decompose readily at ambient conditions. This enhanced stability was attributed to cross-conjugation at the benzoquinone ring. In addition DSC shows a phase transition at 96 °C (Figure S8).

By taking advantage of the enhanced solubility of compound **1**, field-effect transistors were fabricated by introducing the semiconducting layer by liquid deposition. Solutions of **1** in $CHCl_3$ and chlorobenzene were spin-coated in a glovebox on bottom-contact bottom-gate transistors. These devices were fabricated on Si/SiO_2 substrates on top of which gold source and drain electrodes were evaporated. Before the semiconducting layer was spin-coated, the SiO_2 surface was treated with a layer of hexamethyldisilazane (HMDS). All the devices were characterized before and after 30 min of annealing at different temperatures (50, 80, and 100 °C) inside a glovebox. The devices showed the typical n-type behavior. Representative transfer and output curves are given in Figure 5. The best results were obtained for devices deposited from chlorobenzene solutions that exhibited electron mobilities (μ_e) up to 2.42×10^{-3} cm^2 V^{-1} s^{-1} and on/off ratios ($I_{on/off}$) up to 10^3 for the best performing transistors (Table S1). On average $\mu_e = 0.83 \times 10^{-3}$ cm^2 V^{-1} s^{-1} and $I_{on/off} = 10^2$ were obtained (Table S1). While an increase of the average μ_e was observed on the devices fabricated from $CHCl_3$ upon annealing, in the case of the devices deposited from chlorobenzene, no significant changes were observed with annealing temperature. AFM studies revealed little information owing to the high surface roughness of the films. Given the low LUMO level of **1** ($E_{LUMO} = -4.46$ eV), we tested if the devices were stable in air. The measurements carried out in ambient conditions on the best performing devices show reproducible results in terms of μ_e.

To conclude, we have reported the synthesis of the bisthiadiazole-fused tetraazapentacenequinone **1** that has been obtained in seven steps. X-ray characterization provided unequivocal proof of the molecular structure and confirmed that **1** piles-up into 1D slipped stacks. Absorption spectroscopy revealed a low HOMO−LUMO gap (E_{gap} = 1.77 eV) comparable to state-of-the-art pentacene and tetraazapentacene derivatives. Cyclic voltammetry illustrated that **1** is a highly electron-deficient material with a very low LUMO level (E_{LUMO} = −4.46 eV). The optoelectronic and electrochemical characterization is consistent with DFT simulations. The high solubility of **1** allowed the fabrication of field-effect transistors by liquid deposition methods. These devices show electron mobilities up to 2.42×10^{-3} cm^2 V^{-1} s^{-1} without any optimization, and most importantly, they are stable under ambient conditions with no changes in mobilities. These results show that the linear combination of tetraazapentacenequinone and two thiadiazoles provides stable n-type organic semiconductors with great potential not only for field-effect transistors but also for other applications in which electron-deficient organic semiconductors are required.

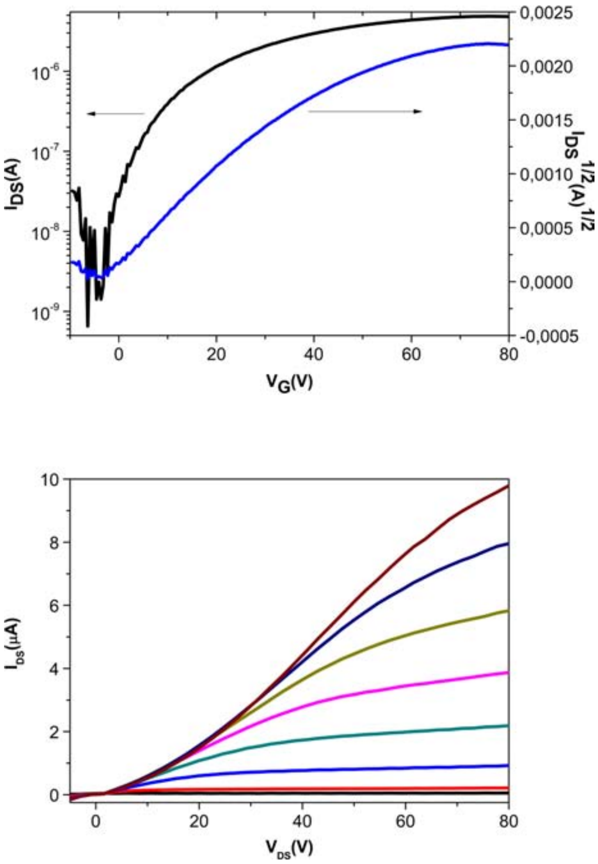


Figure 5. Representative transfer (top) and output 0−60 V (bottom) curves of thin films of **1** (L20 × W10000).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.5b03099.

Full synthetic procedures, details on the characterization and theoretical predictions for **1** (PDF)
Crystallographic data for **1** (CIF)

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Notes

The authors declare no competing financial interest.

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