

Incorporating TCNQ into Thiophene-Fused Heptacene for n-Channel Field Effect Transistor

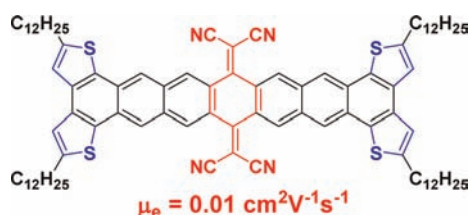
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ABSTRACT



Incorporation of electron-deficient tetracyanoquinodimethane (TCNQ) into electron-rich thiophene-fused heptacene was successfully achieved for the purpose of stabilizing longer acenes and generating new n-type organic semiconductors. The heptacene-TCNQ derivative **1** was found to have good stability and an expected electron transporting property. Electron mobility up to $0.01 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ has been obtained for this novel material in solution processed organic field effect transistors.

Acenes are a category of organic semiconductors which have attracted intensive attention due to their intriguing photophysical and electronic properties and potential use as novel charge transporting materials.¹ The intrinsic electron-rich character of acenes, on one hand, favors hole transporting property but, on the other hand, hampers the stability of longer acenes. By attaching electron-withdrawing groups, such as imides, the cyano group, and fluorine atom, the stability of longer acenes can be greatly enhanced² while, at the same time, the charge transporting

behavior can be inverted with electron transporting observed for some of these derivatives.³

7,7,8,8-Tetracyano-*p*-quinodimethane (TCNQ) based molecules have been widely applied to the preparation of charge transfer complexes and organic conductors.⁴ Due to their high electron affinity, TCNQ derivatives, especially π -extended derivatives, have been tested as novel n-type organic semiconductors.⁵

We are particularly interested in incorporating TCNQ into longer acenes in hopes of solving the stability issue and

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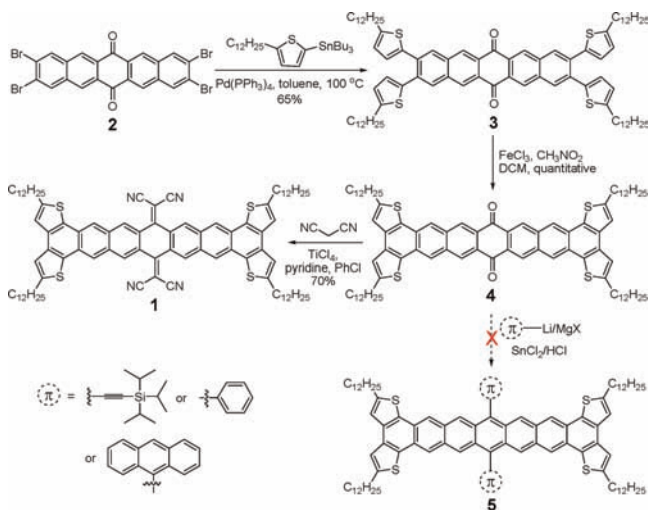
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creating novel n-type organic semiconductors. The strong electron affinity of TCNQ is believed to be beneficial for both purposes. So far the longest acene-TCNQ derivative reported to date is based on pentacene.⁶ Herein, we would like to report a heptacene based TCNQ derivative, 19,19,20,20-tetracyano-7,16-tetra(5'-dodecylthieno)[a,c,p,r]-heptacenequinodimethane (**1** in Scheme 1), with good stability and the desired n-type charge transporting behavior observed. Fusion of four 2-dodecyl thiophene groups to the two outmost benzene rings of the heptacene unit is supposed to afford sufficient solubility for the target compound and also further enhance the stability of the heptacene.

Scheme 1. Synthesis of Compound 1



The synthesis of compound **1** is shown in Scheme 1. The 2,3,9,10-tetrabromopentacenequinone **2** was prepared according to Anthony's procedure.⁷ Stille cross-coupling between **2** and tributyl(5-dodecylthiophen-2-yl)stannane under standard conditions afforded 2,3,9,10-tetra(5'-dodecylthienyl)-6,13-pentacenequinone (**3**) in 65% yield. The subsequent oxidative cyclization was attempted with an FeCl₃/CH₃NO₂/CH₂Cl₂ protocol which was reported to be successful for similar substrates.⁸ With 4 equiv of ferric chloride used at room temperature, no desired cyclization product was observed and only the starting material

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was recycled. This is possibly due to the presence of the electron-withdrawing quinone group, which retards the generation of a radical cation intermediate. However, when the reaction was carried out with addition of more FeCl₃ (15 equiv) and a prolonged time (1 h), the cyclized product 7,16-tetra(5'-dodecylthieno)[a,c,p,r]heptacenequinone (**4**) was generated in nearly quantitative yield. Such an oxidant quantity-dependent and high-yield cyclization is quite interesting, and we ascribed it to two reasons: first, the quinone deactivates both pentacene and the thienyl parts, and thus a large excess of oxidant is required to generate a radical cation on the thiophene rings to initialize the intramolecular ring cyclization and also a longer reaction time is needed to complete all new C–C bond formation; second, the much lower solubility of the product in CH₂Cl₂ and the presence of the quinone group prevent any further side reactions such as chlorination on the product. The target compound **1** was then obtained in 70% yield by a Knoevenagel condensation reaction⁹ between compound **4** and malononitrile in the presence of strong Lewis acid TiCl₄ and Lewis base pyridine. Compound **4** showed a very strong tendency of aggregation in solution which made the detailed NMR characterization unsuccessful. However, after replacing the carbonyl groups with malononitrile groups, compound **1** was found to have good solubility and a well-resolved NMR spectrum with sharp aromatic peaks (see Supporting Information (SI)), indicating that the planarity of the molecule would be sacrificed after attachment of mononitrile groups. It was reported that the anthracene-TCNQ derivative adopted a butterfly conformation.^{4a,10} The heptacene-TCNQ derivative **1** was thus envisaged to have a similar distortion from planarity (*vide infra*).

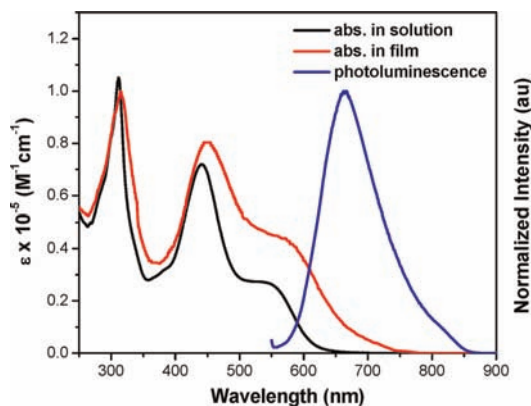


Figure 1. Absorption spectrum of **1** in chloroform, its normalized absorption spectrum in thin film, and its photoluminescence spectrum ($\lambda_{\text{exc}} = 540$ nm) recorded in chloroform.

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The synthesis of thiophene ring-fused heptacene derivatives **5** was also attempted by using standard acene chemistry from quinone **4**. The nucleophilic 1,2-addition onto the carbonyl groups in **4** with various types of organolithium reagents or Grignard reagents, however, was hampered by undesired 1,4-addition (Michael addition), and inseparable isomeric products were obtained. We presume that the extended conjugation of the quinone system would be the cause of an unselective addition reaction, and similar phenomena were observed for other extended quinones as previously reported by us.¹¹

The heptacene-TCNQ derivative **1** has good solubility in common organic solvents (~30 mg/mL in chloroform), and its chloroform solution was stable for weeks upon exposure to ambient air and light conditions. The UV-vis absorption and photoluminescence spectra of **1** recorded in dilute chloroform solution and thin films are shown in Figure 1. In solution, compound **1** mainly absorbs at 300 and 450 nm, with a shoulder at 550 nm. In the thin film state, there is no significant change in the vibronic structure, while the lowest energy absorption onset is red-shifted by ca. 85 nm, indicating the strong tendency of aggregation of compound **1** in the solid state. Compound **1** showed a weak photoluminescence peak centered at 665 nm (Figure 1), most possibly due to its intramolecular charge transfer nature (*vide infra*).

The electrochemical properties of heptacene-TCNQ derivative **1** were investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). The measurement was carried out in dry dichloromethane (DCM) at room temperature, and the results are shown in Figure 2. Compound **1** showed one reversible reduction wave with a half-wave potential $E_{1/2}^{\text{red}}$ at -1.22 V (vs Fc⁺/Fc). The LUMO energy level of **1** was estimated to be -3.67 eV based on the onset potential of the first reduction wave. Two irreversible oxidation waves were observed with half wave potentials $E_{1/2}^{\text{ox}}$ at 0.75 and 0.90 V, respectively. The HOMO energy level was estimated to be -5.46 eV for **1**, and the electrochemical energy gap was therefore determined to be 1.79 eV.

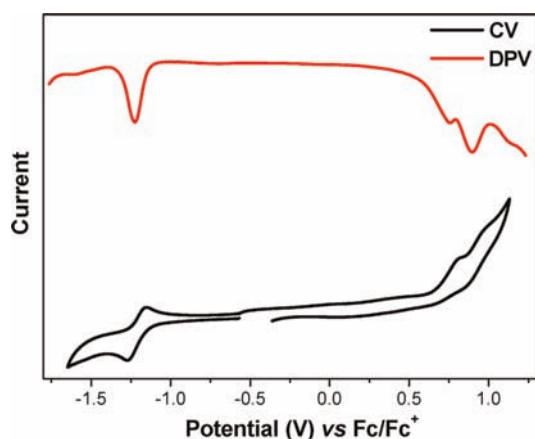


Figure 2. Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) of compound **1** in dry DCM with 0.1 M Bu₄NPF₆ as supporting electrolyte.

Time-dependent density function theory (TD DFT at B3LYP/6-31G*) calculations were conducted for compound **1** to understand its geometric structure, electronic property, and optical property (see SI for details). Due to steric congestion between the zigzag edges of the heptacene and the four -CN groups, two possible conformers, denoted as “up-up” with all four CN groups bent to the same side (a) and “up-down” with two CN groups bent upward and the other two CN groups bent down with respect to the heptacene unit (b), were evaluated (Figure 3). Calculations predicted that the “up-up” conformer (a) with a butterfly conformation has a much lower energy (10.7 kcal/mol) than the “up-down” conformer (b), which has a more planar conformation for the heptacene unit. That means molecule **1** likely adopts a bent structure in the ground state. While the HOMO is homogeneously distributed through the two side parts of the TCNQ unit, the LUMO is mainly localized at the central TCNQ framework. Such a partially separated frontier orbital profile also indicates significant intramolecular charge transfer character, which can explain the observed weak fluorescence from **1**. TD DFT calculations also predicted three major absorption bands at 315 nm ($f = 1.1901$, dominated by a HOMO-1 to LUMO+4 transition), 458 nm ($f = 1.0588$, dominated by a HOMO-2 to LUMO+1 transition), and 572 nm ($f = 0.4071$, HOMO to LUMO). The band shape is in good agreement with the experimental data.

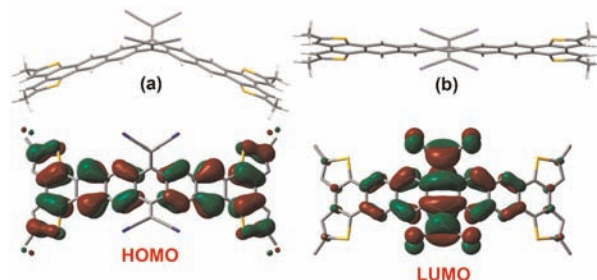


Figure 3. Structure of two conformers of **1** optimized by DFT (B3LYP/6-31G*) calculations, and the HOMO and LUMO molecular orbital profiles of the conformer (a). The dodecyl groups are replaced by methyl groups during the calculation.

Field effect transistors (FETs) of **1** were fabricated on p+-Si/SiO₂ substrates by solution processing. The SiO₂ dielectric was treated with octadecyltrimethoxysilane (OTMS),¹² and the thin film was spin-coated from a CHCl₃ solution of **1** onto the substrates and then vacuum annealed at 200 °C for 30 min. Au (or Al) source/drain electrodes (80 nm) were patterned on the organic layer through a shadow mask to afford a bottom-gate top-contact device. All devices were characterized in a N₂ atmosphere or in air.

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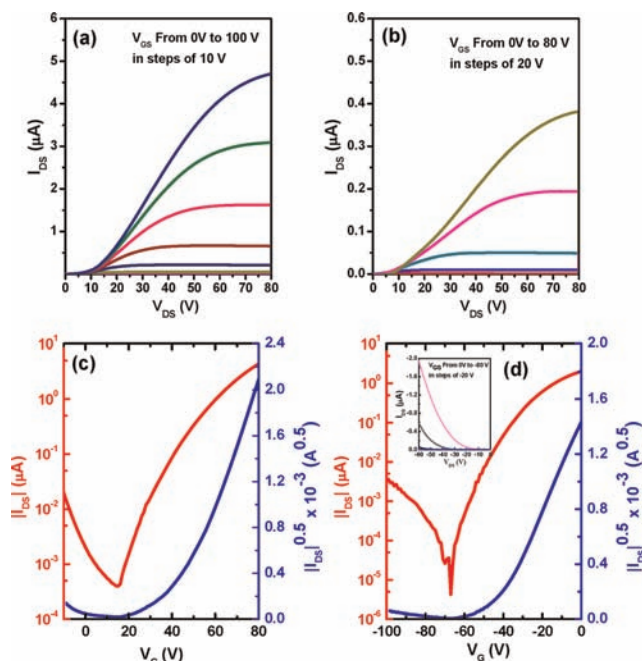


Figure 4. Output and transfer characteristics of FET devices fabricated by spin coating of **1** on OTMS-treated substrate followed by annealing at 200 °C, measured under N₂ conditions: output characteristics for a Au-contact device (a) and an Al-contact device (b) and transfer characteristics for n-type (c) and p-type (d) operation. Inset is the corresponding output curve for p-channel operation.

The typical transfer and output curves measured in N₂ are shown in Figure 4. Large contact resistance which ascribes to the large injection barrier between the work function of Au and the LUMO energy level of **1** was observed in output characteristics at low source–drain voltage. All devices based on Au contacts exhibited ambipolar behavior and revealed an average mobility of up to 0.01 cm² V⁻¹ s⁻¹, a threshold voltage of 44 V, and a current on/off ratio of 10⁴ for n-type behavior, while only a low FET hole mobility of about 10⁻⁵ cm² V⁻¹ s⁻¹ was achieved

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for p-type behavior. In order to reduce the energy barrier and improve the device performance, an Al contact was used to act as the source–drain contact. However, a five times lower performance (~ 0.002 cm² V⁻¹ s⁻¹) was observed compared to Au based devices, which may be due to oxidation of the Al electrode.¹³ When the thin films were exposed to air, the electron mobility decreased to 5×10^{-4} cm² V⁻¹ s⁻¹ as a result of the relative lower electron affinity, which makes the radical anion unstable toward O₂ and water in the ambient conditions.¹⁴ The hole mobility was maintained at $\sim 10^{-5}$ cm² V⁻¹ s⁻¹.

Thin film morphology and solid state microstructure were characterized by tapping-mode atomic force microscopy and 2D X-ray diffraction (see SI). The thin film exhibited large plate-like crystals when annealed at 200 °C and gave a surface roughness of 9.89 nm. The XRD measurements of thin film of **1** on OTMS treated substrates exhibited the primary peak at $2\theta = 4.1^\circ$ which corresponds to a *d* spacing of 21.6 Å. A lamellar packing structure was deduced from the diffraction peaks. The ordered layer-like packing of **1** in thin films allows effective charge transport between the source and drain electrodes.

In summary, a thiophene-fused heptacene-TCNQ derivative **1** was synthesized, which represents the largest acene-TCNQ derivative reported so far. By careful design, both the solubility and stability problems of heptacene have been solved and an FET electron mobility up to 0.01 cm² V⁻¹ s⁻¹ has been achieved for this novel material by simple solution processing. More effort will be carried out to better understand the nucleophilic addition reaction on π -extended quinones in the future, and the synthesis of even longer acene-TCNQ derivatives is underway in our laboratories.

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Supporting Information Available. Synthetic procedures and characterization data for all new compounds. Calculation data for compound **1**. Device fabrication and characterization details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

The authors declare no competing financial interest.