Crystalline TQPP as p-type semiconductor: X-ray crystallographic investigation, OTFT device, and computational analysis of transport properties

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Highlights

- TQPP materials with thermal stability up to 370°C were synthesized.
- TQPP and TQPP-[CH₃]₄ show interplanar stacking distances of 3.4 Å using X-ray crystallography.
- OTFT field-effect mobilities of 10⁻³ cm²/V s for TQPP and 10⁻⁵ cm²/V s for TQPP-[CH₃]₄.
- Modeling confirms higher electronic coupling constants for TQPP than TQPP-[CH₃]₄.

Abstract

Two p-type semiconducting azapyrenoacene materials, quinoxalino[2',3':9,10]phenanthro[4,5-abc]phenazine (TQPP) and 6,7,15,16-tetramethylquinoxalino[2',3':9,10]phenanthro[4,5-abc]phenazine (TQPP-[CH₃]₄), were characterized and were found to display high thermal stability and planar molecular geometry as revealed by single-crystal X-ray analysis. In bottom-gate p-channel organic thin-film transistors, field-effect mobilities of 2.5 × 10⁻³ cm²/V s and 7.5 × 10⁻⁵ cm²/V s were measured in ambient air for TQPP and TQPP-[CH₃]₄, respectively. Computational results of reorganization energies and electronic couplings indicate larger inter and intra-columnar couplings for TQPP-[CH₃]₄ in comparison to TQPP and predict the suitability of both semiconductors for hole as well as electron transporters.

Introduction

Extended, nitrogen-containing heteroacenes are derivatives of extended acene systems and have gained momentum due to their potential toward applications in liquid-crystalline materials [1,2], materials with the ability to self-assemble [3–5], as sensors as well...
as dyes [6–9], and as n-type semiconductors [10,11]. The latter aspect was extensively reviewed by Bunz et al. [12–14] and analyzed in a computational study by Winkler and Houk [15]. A sub-class of these materials comprise pyrene-fused pyrazacenes, as reviewed by Mateo-Alonso, which combine the ease of synthetic versatility, using condensation between tetraketopyrene and diamine of choice, with high thermal stability and interesting materials’ properties [16,17]. Alkylthio-substituted pyrene-fused pyrazacenes TQPP-[SC12X]4 have previously been studied in a computational study by Winkler and Houk [15]. A sub-class of these materials comprise pyrene-fused pyrazacenes, as reviewed by Bunz et al. [12–14] and Mateo-Alonso, which combine the ease of synthetic versatility, using condensation between tetraketopyrene and diamine of choice, with high thermal stability and interesting materials’ properties [16,17]. Alkylthio-substituted pyrene-fused pyrazacenes TQPP-[SC12X]4 have previously been studied in a computational study by Winkler and Houk [15].

Materials and methods

Synthesis

Tetraketopyrene (1) was prepared using a literature procedure [20], diamines 2, e.g., 1,2-phenylenediamine (2a) and 4,5-dimethylphenylenediamine (2b) were acquired from commercial sources and used as received.

General procedure for the synthesis of TQPP- [X]4 (X = H, CH3)

A solution of 150 mL ethanol: acetic acid (1:1) was added to a mixture of tetraketopyrene (1) (2.67 mmol) and diamine 2 (5.34 mmol). Scheme 1. The reaction mixture was stirred at 120 °C for 24 h, cooled in an ice bath and then filtered to yield a yellow solid. The solid was purified by Soxhlet extraction using toluene and was then recrystallized from 1,2-dichlorobenzene to yield TQPP- [X]4 (X = H, CH3).

Quinoxalino[2,3'-9,10]phenanthro[4,5-abc]phenazine [21] (TQPP)

Yellow solid. 1.00 g (92%), mp > 300 °C (Lit. >420 °C) [21]. 1H NMR (TFA-d, 300 MHz): δ 9.949 (d, J = 8.1 Hz, 4H), 8.619 (t, J = 8.1 Hz, 2H), 8.542 (s, 4H), 2.831 (s, 12H). HRMS-EI (m/z): [M]+ calcd for C32H22N4, 462.18445; Found, 462.18232.

UV–Vis absorption

Approx. 1 mg of compound was weighted out and dissolved in spectrophotometry-grade o-dichlorobenzene (50 mL) under heating to 70 °C and sonication. Absorbance was recorded in triplicate.

Thermal gravimetric analysis (TGA)

The thermal stability of TQPP and TQPP-[CH3]4 was probed by thermal gravimetric analysis (TGA) under nitrogen at a heating rate of 2 °C/min. Decomposition temperatures are given as the temperature at which 0.1 wt% loss.

Device fabrication

Bottom-gate, organic thin-film transistors (TFTs) were fabricated using a heavily doped silicon wafer as the substrate and common gate electrode. The silicon surface was thermally oxidized in dry oxygen to obtain a 100-nm-thick layer of silicon dioxide. Onto the SiO2 surface, an 8-nm-thick layer of aluminum oxide was deposited by atomic layer deposition at a substrate temperature of 250 °C. The substrate was then immersed into a 2-propanol solution of tetradeclylphosphonic acid (OCI Synthesis) for about 1 h to allow a 1.7-nm-thick self-assembled monolayer (SAM) of the alkylyphosphonic acid to form. Thus, the gate dielectric is a combination of 100-nm-thick SiO2, 8-nm-thick AlOx and a 1.7-nm-thick SAM, having a total thickness of about 110 nm and a capacitance per unit area of 34 nF/cm2. Onto this gate dielectric, a semiconductor layer with a thickness of 30 nm was deposited by sublimation in vacuum. Finally, 30-nm-thick Au source and drain contacts were deposited on top of the semiconductor by thermal evaporation in vacuum through a shadow mask. All TFTs have a channel length of 100 µm and a channel width of 200 µm. All electrical measurements were performed in ambient air at room temperature without encapsulation. The field-effect mobility was calculated in the saturation regime (VDS = −40 V) from the slope of the forward sweep of the measured transfer curve (VDS vs. ID), and since it varies with the gate-source voltage, it has been plotted for each data point along the transfer curve.

Scanning electron microscopy

The thin-film morphology was imaged using a Zeiss Merlin field-emission scanning electron microscope using an acceleration voltage of 5 kV, a magnification of 50,000, and an in-lens detector.

Results and discussion

Synthesis

Two discoids TQPP and TQPP-[CH3]4 were synthesized as outlined in Scheme 1. While the structure and melting point of TQPP was reported by Vollmann et al. [21] no further characterization data is available for this compound in the literature. Tetraketopyrene 1 was prepared using a literature procedure [20] and was condensed with the 1,2-phenylenediamine 2a or 4,5-dimethylphenylene-1,2-diamine 2b (both commercially available) to yield TQPP and TQPP-[CH3]4, respectively. This condensation proceeded with good yields (>80%), but gave compounds with an innate insolubility in most common organic solvents. Purification was achieved by triturating the obtained solids with boiling toluene via Soxhlet extraction for 6 h followed by recrystallization from 1,2-dichlorobenzene. The low solubility made it difficult to collect 13C NMR spectra for TQPP-[CH3]4 and electrochemical data on both compounds. Both, TQPP and TQPP-[CH3]4 sublime so that electronic-grade purity was achieved.

Thermal and spectroscopic properties

Thermogravimetric analysis (TGA) showed the onset of weight loss (attributed to decomposition) of both compounds at approximately 370 °C under an air atmosphere. This observed stability is markedly higher in comparison to tetraazaoctacene, characterized by two additional fused phenyl units along the long axis of the molecule, which starts to decompose at 325 °C even under a nitrogen atmosphere [7]. The UV–vis spectra of TQPP and TQPP-[CH3]4 are shown in Fig. 1. TQPP-[CH3]4 showed characteristic absorption bands at 309, 326, 355, 376, 396, and 420 nm. An average 3 meV bathochromic shift is observed for the longest wavelength absorption bands. This shift is ascribed to the electron-releasing effect of the methyl groups [22] expected to lower the HOMO energy level of TQPP-[CH3]4 as compared to the parent TQPP.

Single crystal X-ray crystal structure analysis

The molecular structures of TQPP and TQPP-[CH3]4 were determined by single-crystal X-ray crystal structure analysis. The structures are shown in Supplementary data, Fig. S1. The molecules are planar with deviations from planarity in the 0.004–0.008 Å range for the individual rings in TQPP and 0.002–0.008 Å for TQPP-[CH3]4 while the dihedral angles range from 1.11(3)–1.70(3)° and 0.96(5)–1.53(5)°, respectively, see Supplementary data, Table S4.

Single crystal X-ray crystallography was used to study the extended structures of these materials in the solid state and to determine whether the discotic-based columns are vertical or inclined. Furthermore, the nature of intermolecular interactions between the discoid mesogens and the degree of aromatic overlap between the stacking molecules can be used to gain insight into their ability of transporting charge carriers along the column axis of the stacks [23].

For TQPP and TQPP-[CH3]4, interplanar π-stacking distances of 3.42 Å and 3.45 Å were observed, respectively, which is well in agreement with the π–π stacking distance of 3.3–3.6 Å for TQPP-[SC12H25]4 [19]. Packing motives of interleaved stacked sheets for

The charge transfer rate between two adjacent molecules k12 can be expressed in first approximation in the hopping regime within the semi-classical Marcus formalism as Eq. (1): [24]

\[
k_{12} = \frac{2\pi}{h} |t_{12}|^2 \sqrt{\frac{1}{4\pi \lambda k_B T}} e^{-\frac{\Delta G^0 + \lambda}{k_B T}}
\]

- λ is the total reorganization energy, which reflects the changes in the geometry of the molecules and the changes in the electronic and nuclear polarization of the medium between the initial and final states.
- ΔG0 is the free enthalpy of the reaction, whose value is zero for a self-exchange process, in the absence of an electric field.
- τ12 is the electronic coupling between the initial and final states.

The simplest approach to calculate the transfer integral (i.e., electronic coupling) is to estimate it as half the splitting of the HOMO [LUMO] levels in a neutral dimer for hole [electron] transport [25]. However, for non-centrosymmetric structures, this approach is often biased by electrostatic effects, which create an initial offset of the electronic levels before they start to interact. This offset does not contribute to the transfer efficiency. In line with our recent theoretical works, we calculated the transfer integral values directly using a fragment approach at the Density Functional Theory (DFT) level using the B3LYP functional with a
triple zeta polarized (TZP) basis set within the Amsterdam Density Functional (ADF) package [26].

The estimated internal reorganization energies (at the DFT B3LYP/6-31G* level) [27] for TQPP and TQPP-[CH₃]₄ are attractive compared to compounds with high charge mobilities such as oligoacenes, see Table 1. We have next calculated the electronic coupling between molecules in the same column (intra) which is expected to be the largest. This yields values of 62.4 meV and 14.5 meV for holes and electrons, respectively, in TQPP while values of 8.6 meV and 18.6 meV are obtained for TQPP-[CH₃]₄. In contrast, the electronic coupling in tetracene, pentacene, and rubrene are on the order of 70, 85, and 83 meV, respectively [29].

We have also estimated the electronic couplings for the major inter-columnar paths that are represented in Figs. 4 and 5. Note that for each path (A, B, C), the charge can be transferred either to the molecule in the plane located above that of the initial site or to a molecule in the lower plane (i.e., to the two closest neighbors), Table 2. This leads to two possible jumps along each path (A and A’ for example). The results show that the transport is mostly one-dimensional for holes in TQPP since the electronic

![Fig. 2. π-Stacking distances for TQPP (left) and TQPP-[CH₃]₄ (right). The N...N interplanar distances are indicated in the figures.](image)

![Fig. 3. Scanning electron microscopy images of 30-nm-thick films of the semiconductors TQPP (top) and TQPP-[CH₃]₄ (bottom), vacuum-deposited onto Si/SiO₂/Al₂O₃/SAM substrates.](image)

![Fig. 4. Inter-columnar coupling paths for TQPP.](image)

![Fig. 5. Inter-columnar coupling paths for TQPP-[CH₃]₄.](image)

<table>
<thead>
<tr>
<th></th>
<th>TQPP</th>
<th>TQPP-[CH₃]₄</th>
<th>Tetracene</th>
<th>Anthracene</th>
<th>Pentacene</th>
</tr>
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<tbody>
<tr>
<td>$\gamma_i$ (holes), eV</td>
<td>0.118</td>
<td>0.114</td>
<td>0.113</td>
<td>0.137</td>
<td>0.097</td>
</tr>
<tr>
<td>$\gamma_i$ (electrons), eV</td>
<td>0.080</td>
<td>0.085</td>
<td>0.160</td>
<td>0.196</td>
<td>0.132</td>
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</table>
Electronic coupling of TQPP and TQPP-(CH$_3$)$_4$ for the different paths.

<table>
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<tr>
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<th>HOMO</th>
<th>LUMO</th>
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<tbody>
<tr>
<td>TQPP</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intra</td>
<td>503</td>
<td>117</td>
</tr>
<tr>
<td>A</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>A'</td>
<td>9</td>
<td>10</td>
</tr>
<tr>
<td>B</td>
<td>43</td>
<td>1</td>
</tr>
<tr>
<td>B'</td>
<td>120</td>
<td>69</td>
</tr>
<tr>
<td>TQPP-(CH$_3$)$_4$</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Intra</td>
<td>69</td>
<td>150</td>
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<tr>
<td>A</td>
<td>29</td>
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<td>A'</td>
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<td>2</td>
</tr>
<tr>
<td>C'</td>
<td>17</td>
<td>23</td>
</tr>
</tbody>
</table>

Performance in OTFT device geometry

In order to evaluate the potential of the new organic semiconductors for electronic applications experimentally, organic thin-film transistors (OTFTs) in a bottom-gate, top-contact device structure were fabricated and characterized; see Fig. 6 and Table 3.

The electrical measurements show that the charge-carrier mobility in thin films of TQPP is a factor of 35 larger than the charge-carrier mobility in thin films of TQPP-(CH$_3$)$_4$. Fig. 7. This illustrates the significant impact on the charge transport as created by the methyl groups at the periphery of the molecule. The semiconductor without any substitution, TQPP, gives the larger mobility (0.0025 cm$^2$/V s) whilst a mobility of 7x10$^{-5}$ cm$^2$/V s is found in the methyl-substituted semiconductor TQPP-(CH$_3$)$_4$.

Among others, possible origins for the observed differences include different orientation of the molecules with respect to the substrate surface, grain size as well as charge transfer rates as evidenced by electronic coupling. As was observed by SEM, Fig. 3, the methyl substitution has a large effect on the morphology of the semiconductor films. In particular, the size and orientation of the crystalline regions and the density of grain boundaries among others are effected [30,31].

In addition, the observed difference in mobilities may substantially also be rationalized by our computational simulations. According to Eq. (1), the mobilities scale with the square of the electronic coupling $|32|$. Indeed, the highest electronic coupling for TQPP-(CH$_3$)$_4$ is 69 cm$^{-1}$, a very low value compared to electronic couplings computed for TQPP (503 cm$^{-1}$ along the stacks, and a value of 120 cm$^{-1}$ for one inter-columnar coupling). Hence, the ratio between the intra-columnar couplings (~7) is consistent with the ratio between mobilities (~35).

Conclusions

In summary, both TQPP and TQPP-(CH$_3$)$_4$ exhibit p-type semiconducting properties. Particularly, TQPP exhibits more favorable hole transport properties compared to TQPP-(CH$_3$)$_4$ in OFET geometry. Based on computational calculations, the electronic coupling largely dominates between adjacent molecules lying in the same column. In contrast, a two-dimensional character prevails for holes in TQPP-(CH$_3$)$_4$ where inter-columnar and intra-columnar hopping processes appear to be similarly efficient.
couplings are larger for TQPP than for TQPP-[CH$_3$]$_4$, especially for intra-columnar couplings. Inter-columnar couplings differ less among the two systems. TQPP shows mostly one-dimensional hole transport, while TQPP-[CH$_3$]$_4$ transports holes almost equally along two directions (2D transport).

Acknowledgements

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Appendix A. Supplementary material

Experimental parameters and data tables for X-ray crystallography of TQPP and TQPP-[CH$_3$]$_4$ are available online at http://www.sciencedirect.com. CCDC 1022119 – 1022120 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.molstruc.2015.03.057. These data include MOL files and InChiKeys of the most important compounds described in this article.

References