N-heteroquinones: quadruple weak hydrogen bonds and n-channel transistors†

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This study demonstrates that the easily synthesized *N*-heteroquinones, having unusual quadruple weak hydrogen bonds of a DDAA–AADD pattern, can function as n-type organic semiconductors in OTFTs with high electron mobility.

N-type organic semiconductors are the key materials that accept and transport electrons in organic electronics, such as organic phovoltaic solar cells and n-channel organic thin film transistors (OTFTs).[1,2] The development of n-type organic semiconductors has lagged behind that of p-type ones primarily due to the inherent instability of organic anions in the presence of air and water.[2a] To develop high performance n-type organic semiconductors, new designs need to be explored. Here we report the easily synthesized *N*-heteroquinones, which feature two types of electron-withdrawing moieties, quinonoid carbonyl groups and pyrazine-type nitrogen atoms,[3] function as n-type semiconductors in OTFTs. Quinones are well known as organic oxidizing reagents in organic synthesis and biological systems, but their ability to accept electrons has rarely been explored in connection with n-type organic semiconductors.[4] Nitrogen-rich heteroacenes that feature pyrazine rings are also promising n-type organic semiconductors,[5,6] but only a few of them have been tested in n-channel OTFTs.[7] In fact the reported *N*-heteroacenes are mainly p-type semiconductors.[8] Because of the electron-withdrawing quinone and pyrazine moieties, the *N*-heteroquinones have low-lying and well delocalized lowest unoccupied molecular orbitals (LUMOs), which are suitable for n-type semiconductors. Although the two *N*-heteroquinones studied here have been known for decades,[9] this study is the first time that their electronic structures, molecular packing and semiconductor properties have been investigated. Another interesting finding of this study is the unusual quadruple weak hydrogen bonds in the crystal structures of *N*-heteroquinones.

5,7,12,14-tetraaza-6,13-pentacenequinone (TAPQ) and 6,11-diaza-5,12-tetracenequinone (DATQ) were simply synthesized from very cheap starting materials by solvent-free condensation[10] and subsequent oxidation by $K_2Cr_2O_7$[6,9b] as shown in ESI.† Both TAPQ and DATQ are yellow crystalline powders, which are stable to light irradiation. As monitored by differential scanning calorimetry (DSC), TAPQ is stable up to 450 °C and DATQ melts at 320 °C with decomposition. While TAPQ is almost insoluble in common organic solvents, DATQ is soluble in several organic solvents, such as $CHCl_3$, toluene and DMF, with solubility larger than 2 mg ml^{-1}.

The electronic structures of the two molecules were studied using both experimental and computational methods. Cyclic voltammograms of TAPQ and DATQ in DMF both exhibit one reversible reduction wave. The half-wave reduction potential *vs.* ferrocenium/ferrocene is -1.02 V for TAPQ and -1.20 V for DATQ, from which the LUMO energy levels of the two molecules are estimated as -3.78 eV and -3.60 eV, respectively.[11] The UV-vis absorption spectroscopy from solutions in DMF reveals the HOMO–LUMO gap is 3.15 eV for TAPQ and 3.33 eV for DATQ based on the absorption edge. In comparison, the corresponding acenequinones have higher LUMO energy levels (-3.29 eV for 6,13-pentacenequinone and -3.39 eV for 5,12-tetracenequinone) and smaller HOMO–LUMO gaps (2.92 eV for 6,13-pentacenequinone and 2.82 eV for 5,12-tetracenequinone). The frontier molecular orbitals of TAPQ and DATQ were calculated by using the hybrid density functional method B3LYP with a 6-31+G* basis set. As depicted graphically in Fig. 1, both TAPQ and DATQ have a delocalized electron distribution in the LUMOs.

Single crystals of TAPQ and DATQ were grown using the physical vapor transport technique[12] and from a solution in DMSO, respectively. As shown in Fig. 2, X-ray crystallographic analysis‡ reveals the molecular packing of TAPQ, which consists of characteristic π–π stacking and C–H···N/O hydrogen bonds. Molecules of TAPQ form infinite stacks in two directions with a π–π distance of 3.32 Å, which is slightly shorter than the interplanar distance in graphite (3.35 Å).

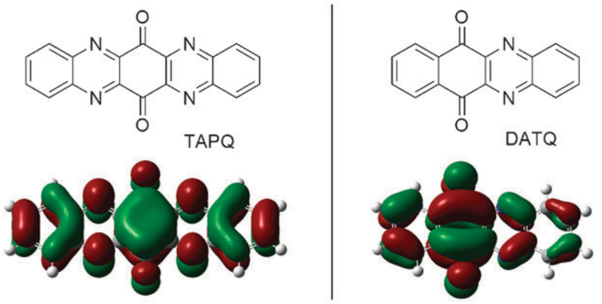

Fig. 1 Structures and calculated LUMOs of TAPQ and DATQ.

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† Electronic supplementary information (ESI) available: Synthesis and characterization of TAPQ and DATQ, CV and UV-vis for TAPQ, DATQ and acenequinones, fabrication and characterization of thin film transistors, crystal information file for TAPQ (CCDC 761663) and DATQ (CCDC 761662). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c001215g

Three C···C contacts shorter than the sum of van der Waals radii (3.40 Å) are found between two neighboring molecules in a stack (Fig. 2a). Intermolecular contacts shorter than the sum of van der Waals radii are also found between TAPQ molecules of the neighboring stacks (Fig. 2b). These short contacts are weak C–H···N/O hydrogen bonds.[13] Interestingly quadruple hydrogen bonds, which have a self-complementary DDAA–AADD pattern (D is hydrogen donor and A is hydrogen acceptor), are found between the neighboring stacks of the same direction. The close π–π stacking associated with weak hydrogen bonds between π-stacks indicates relatively strong intermolecular forces, which are consistent with the low solubility of TAPQ. Similar π–π stacking and quadruple weak hydrogen bonds are also found in the crystal structure of DATQ as shown in Fig. 2c and d. Although the C–H···O hydrogen bonds are known for benzoquinones,[13,14] the quadruple weak hydrogen bonds of a DDAA–AADD pattern found here are very unusual.[15] In these quadruple weak hydrogen bonds, the H···N and H···O distances are 2.68–2.69 Å and 2.67 Å respectively, and the C–H···N and C–H···O angles are 168–169° and 135°, respectively. TAPQ has a denser packing than 6,13-pentacenequinone in the crystals as indicated by the fact that the unit cell volume of 6,13-pentacenequinone (718.193 Å^3) is 10.4% larger than that of TAPQ (650.336 Å^3).[16] Because the π–π distance between two molecules of 6,13-pentacenequinone is 3.50 Å, only 4.5% larger than that of TAPQ, the denser packing of TAPQ must arise from not only the shorter π–π distance but also the closer contacts between the stacks, which are in good agreement with the weak hydrogen bonds found between TAPQ molecules of the neighboring stacks. Such dense molecular packing with short π–π distance and close contacts between π-stacks may enhance charge transport by increasing orbital overlap.

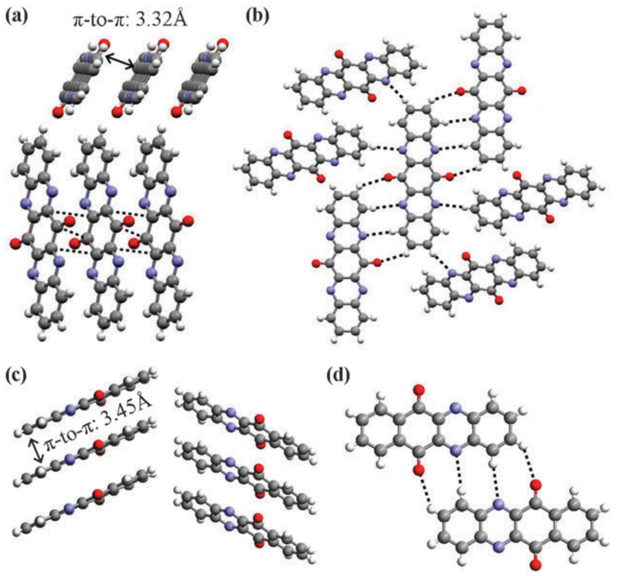

Fig. 2 Molecular packing of TAPQ and DATQ in crystals: (a) π-stacks of TAPQ in two directions, showing short intermolecular contacts within a stack; (b) weak hydrogen bonds between TAPQ molecules of the neighboring π-stacks; (c) π-stacks of DATQ in two directions; (d) quadruple weak hydrogen bonds between neighboring DATQ molecules.

To fabricate OTFTs, TAPQ was purified by the physical vapor transport technique and then deposited by thermal evaporation onto a silicon wafer. The devices had gold as the top-contact source and drain electrodes, highly doped Si as a gate electrode and a 300 nm thick layer of SiO_2 as dielectrics. When the SiO_2 dielectrics were pretreated with a self-assembled monolayer of octadecyltrimethoxysilane (OTMS)[17] and the substrate temperature was kept at 100 °C during deposition, the resulting films of TAPQ were polycrystalline as indicated by the X-ray diffraction (XRD)[18] and atomic force micrographs (shown in ESI†). These films performed as n-channel transistors with field effect mobilities of 0.04–0.12 cm^2 V^{-1} s^{-1}, which were measured under vacuum. Shown in Fig. 3 are the typical transfer *I–V* curves for such devices, from which a field-effect mobility of 0.09 cm^2 V^{-1} s^{-1} was measured in the saturation regime using the equation: $I_{DS} = (\mu WC_i/2L)(V_G - V_T)^2$ and C_i of 11 nF/cm^2 for 300 nm SiO_2.[19] The on/off ratio of the drain current obtained between 0 and 80 V gate bias was greater than 1×10^6. The relatively high threshold voltage (about 27 V) found from the transfer curve suggested a high density of charge carrier traps in the transistor.[19] When OTFTs of TAPQ were tested in the ambient air, the measured electron mobility decreased to 2×10^{-3} cm^2 V^{-1} s^{-1}. On the other hand, the n-channel OTFTs of DATQ fabricated by thermal evaporation showed a much lower electron mobility (10^{-6} cm^2 V^{-1} s^{-1}), which should be mainly attributed to the very low crystallinity of the films as found from the X-ray diffraction as shown in ESI.†

In summary, the studies above demonstrate that the easily-synthesized *N*-heteroquinones, which have low-lying and delocalized LUMOs and form close π–π stacks, can function as n-type organic semiconductors in OTFTs with high electron mobility. The crystal structures of TAPQ and DATQ reveal unusual quadruple C–H···N/O hydrogen bonds of a DDAA–AADD pattern, which may be applied as a supramolecular synthon in crystal engineering.[13] This study suggests that π-extended quinones equipped with electron-withdrawing groups would be a general design for n-type organic semiconductors. Novel molecules with such design are being studied in our laboratory.

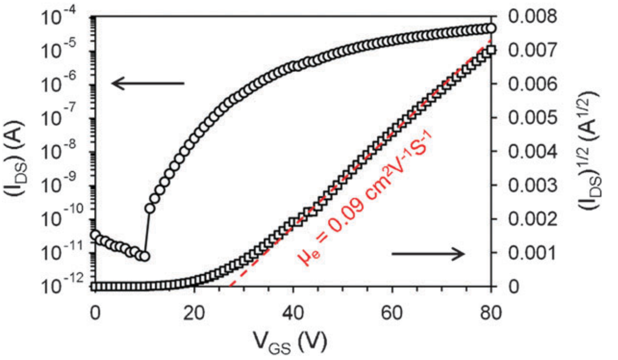

Fig. 3 Drain current (I_{DS}) *versus* gate voltage (V_{GS}) with V_{DS} = 80 V measured under vacuum from the thin film transistors of TAPQ deposited on OTMS-treated SiO_2 at substrate temperature of 100 °C with channel dimension of W = 2 mm and L = 50 μm.

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Notes and references

‡ *Crystal data* for TAPQ: $C_{18}H_8N_4O_2$: M = 312.28, monoclinic, space group $P2_1/n$, a = 3.8926(2) Å, b = 9.0707(4) Å, c = 18.4339(10) Å, α = 90°, β = 92.332(4)°, γ = 90°, V = 650.34(6) Å^3, Z = 2, 3495 reflections collected, 1088 unique (R_{int} = 0.0220). The final R was 0.0561 (all data) and wR was 0.1704 (all data). *Crystal data* for DATQ: $C_{16}H_8N_2O_2$: M = 260.24, monoclinic, space group $P2_1/c$, a = 12.1301(6) Å, b = 3.8545(2) Å, c = 24.3276(12) Å, α = 90°, β = 94.5780(10)°, γ = 90°, V = 1133.82(10) Å^3, Z = 4, 12 534 reflections collected, 2067 unique (R_{int} = 0.0378). The final R was 0.0564 (all data) and wR was 0.1315 (all data).

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