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Synthesis and Characterization of 7,8,15,16-Tetraazaterrylene

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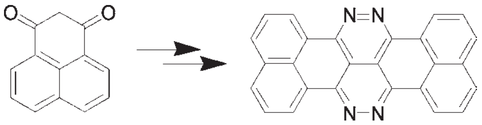
ABSTRACT



A facile three-step synthesis of 7,8,15,16-tetraazaterrylene (TAT) from phenalene-1,3-dione, with potential application in organic electronics, is reported. Single crystal structure analysis shows one-dimensional columnar stacks with an interplanar distance of 3.352 Å.

Organic charge-transporting materials based on rylene derivatives have attracted considerable attention due to their high thermal stability and unique electronic structure.[1] Rylene derivatives, particularly perylene-diimides,[2] have been extensively studied and, in a number of cases, exhibit high electron mobilities due to their excellent photochemical/oxidative stability, high electron affinities, and crystal packings. However, the higher rylene (terrylene, quaterrylene, etc.) derivatives have only recently been investigated and their fundamental properties are still not well explored.[3]

Rylene derivatives are typically employed as electron-transport semiconductors with application in organic photovoltaic (OPV) cells[4] and n-channel organic field-effect transistors (OFETs).[5] The lowest unoccupied molecular orbital (LUMO) levels of these materials could be tuned by appending strong electron-withdrawing functional groups such as fluoro, cyano, acyl, or the most popular tetracarboxylic diimide to the conjugated cores. On the contrary, modification of the rylene skeleton itself to tune electronic properties is rarely reported. In that context, the simplest member of the family, the azaperylenes, have also been a rarity in the arsenal of organic electronics.[6]

Here we report the facile synthesis of a new rylene derivative, 7,8,15,16-tetraazaterrylene (TAT). This compound is

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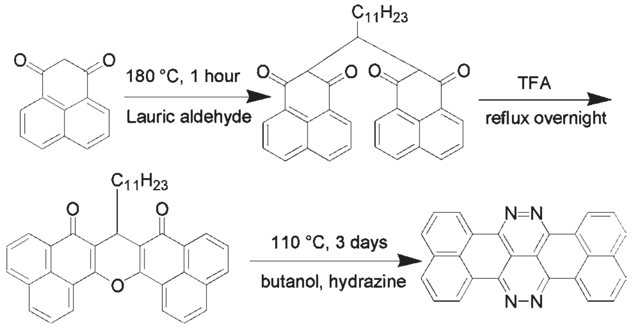
expected to yield a high electron affinity, due to its four doubly bonded nitrogen atoms. Compared to rylene diimides with their bulky solubilizing groups on the imide nitrogen atoms, TAT has no insulating, sterically demanding solubilizing groups. This should enable strong intermolecular interactions in the solid state that are favorable for efficient charge transport in semiconductor materials.[7]

Scheme 1. Synthesis of TAT



The synthetic route to TAT is shown in Scheme 1. The synthesis started with the dimerization of phenalene-1,3-dione,[8] followed by an intramolecular cyclodehydration reaction in TFA solution, terminated by a domino reaction with hydrazine. The first step was carried out under neat conditions. Dodecanal was deliberately used in the reaction to increase the solubility of the dimer and the cyclized compound. It should be noted that aliphatic aldehydes are required for the formation of such a tetraaza-compound in high yield since aromatic aldehydes tend to lead to *N*-aminoacridinediones.[9] The reaction mechanism for the domino reaction has been proposed by Tu,[9] and it is proposed to involve initial formation of a dihydrodiazepine, followed by a 3,3*s* shift resulting in the crucial transannular C–C bond formation concomitant with a cyclopropane ring formation and cleavage of the diazepine's N–N bond. This proposal has not been independently tested.

The isolation of TAT involved precipitation from butanol solution and collection by filtration as a maroon solid. The aromatic heterocycle shows very poor solubility in common organic solvents, and its FI-MS spectrum exhibited one main peak at 380.09 Da (Calcd 380.11 Da), indicating the formation of tetraazaterrylene. This material was further confirmed by ^{1}H NMR in deuterated trifluoroacetic acid. Two doublets (δ = 9.44 and 8.74 ppm) and one triplet (δ = 8.23 ppm) were observed in the aromatic region, as expected for such a highly symmetric structure. No additional peaks were observed in the aliphatic region, indicating the absence of the long alkyl chain.

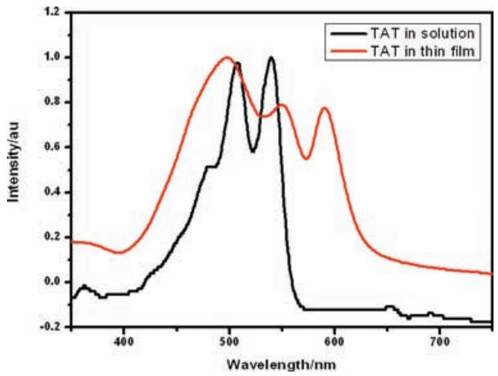


Figure 1. UV/vis absorption spectra of compound TAT in chloroform and in the solid state.

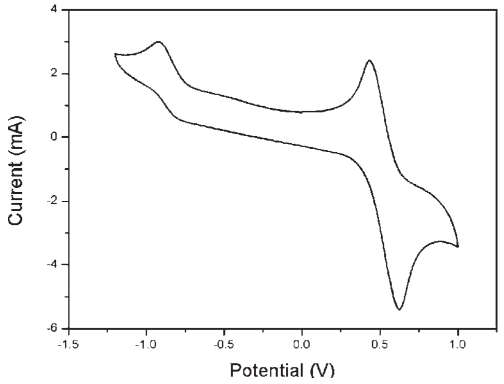


Figure 2. Cyclic voltammogram of TAT on Pt working electrode. Scan rate = 100 mV/s. Wave at ca. 0.5 eV is the internal Fc/Fc$^+$ reference.

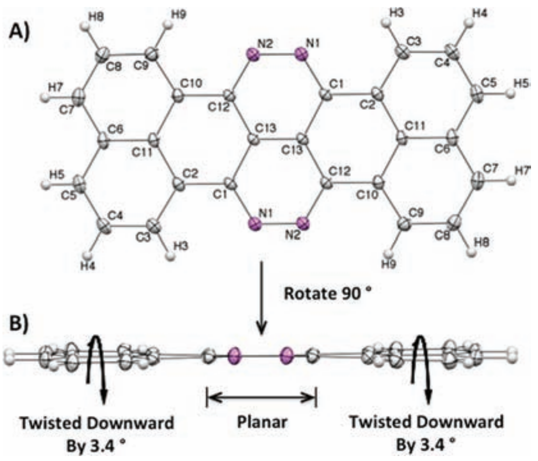


Figure 3. (A) Crystal structure of TAT and (B) 90° rotation of TAT showing the 3.4° downward torsional angle twisting of the outer "wings."

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The UV/vis spectrum of TAT in the solid state (Figure 1) shows an onset optical absorption at around 625 nm to yield an optical band gap of ~1.98 eV.

The electrochemical properties of TAT were examined by cyclic voltammetry (Figure 2). The electrochemical reduction potential in the solid state of the first wave vs SCE is −0.8 V. The LUMO value of TAT was calculated from the reduction potential onset, yielding a value of −3.50 eV, whereas the HOMO value of −5.48 eV was determined from the difference between the LUMO and the optical band gap.

In order to determine the molecular packing, a single crystal of TAT was grown by physical vapor transport and analyzed using X-ray crystallography. TAT forms a monoclinic unit cell, space group $P2_1/c$, with unit cell dimensions $a = 3.7429$ Å, $b = 15.815$ Å, $c = 13.990$ Å, $\alpha = 90.00°$, $\beta = 93.947°$, $\gamma = 90.00°$ and an R-Factor of 4.43%. As shown in Figure 3, X-ray crystallographic analysis revealed a structure in which the backbone of TAT is nearly planar with a dihedral angle between the outer aromatic "wings" and the central planar pyridazinopyridazine ring of ~3.4°. The heterocycles are held together by intermolecular C–H···N hydrogen bond interactions [(C5···N2) = 3.44 Å; (C5–H5–N2) = 158°] to afford a 2D network in the *bc*-plane (Figure 4A). Furthermore, shown in Figure 4B, the TAT molecules pack face-to-face in one-dimensional stacks along the crystallographic *a*-axis with interplanar distances of 3.352 Å (C1···C13) and 3.380 Å (C10···C11) (Figure 4C). UNI field force calculations were carried out using Mercury crystallographic software to determine the intermolecular potential between molecules. A value of −32.3 kcal/mol was determined at their center of inversion of two TAT molecules. These short intermolecular contacts may provide an efficient pathway for charge transport.

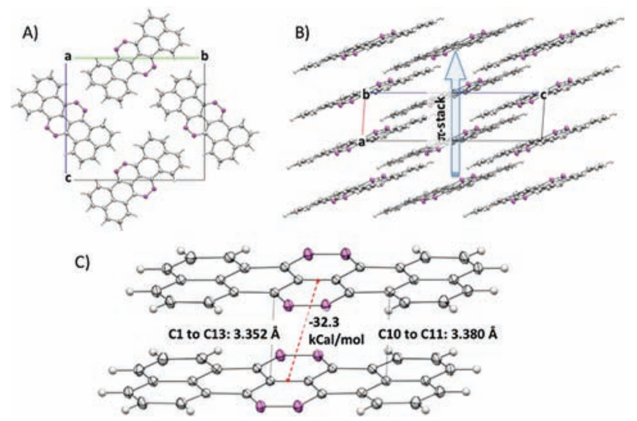

Figure 4. View down crystallographic (A) *a*-axis, (B) *b*-axis, and (C) the shortest contacts between C1···C13 (3.352 Å) and C10···C11 (3.380 Å). The red dashed line at the center of inversion indicates the intermolecular potential calculated by the 'UNI' force field.

In conclusion, the novel rylene derivative, 7,8,15,16-tetraazaterrylene, was prepared by a very short synthesis. This approach is versatile and should be applicable to the generation of higher members of the TAT family as well as the 3,4,11,12-tetracarboxylic acid and its derivatives. The low-lying LUMO of TAT indicates this compound is a good electron acceptor and the stacked crystal structure augurs well for applications in organic electronics.

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Supporting Information Available. Detailed synthetic procedures and characterization, and general procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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