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Unexpected Photooxidation of H-Bonded Tetracene

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ABSTRACT

In our attempts of tuning the molecular packing of tetracene with H-bonding, we found that tetracenediamide was much more vulnerable to photooxidation than tetracene in crystals despite their similar sensitivity to photooxidation in solution. Unexpectedly photooxidation of tetracenediamide in solution and in crystals show different regioselectivities. To explain the regioselectivity, a mechanism involving H-bonding is proposed. This study indicates that molecular packing in solid state can play an important role in solid−gas reactions.

Organic field effect transistors (OFETs) offer promising applications in large-area, flexible, and low-cost electronics.[1] However, degradation of device performance when operated in the presence of oxygen and moisture remains a critical challenge for the development of OFETs.[2] One key factor that leads to the device performance degradation of OFETs is the oxidation of organic semiconductor molecules in ambient air. Pentacene and tetracene and their derivatives are an important family of organic semiconductors applied in OFETs[3] but suffer from the atmospheric instability toward photooxidation in air.[4,5]> One widely accepted mechanism for such photooxidation is that the photoexcited acene molecule sensitizes the formation of singlet oxygen,[5,6] which then reacts with ground-state acene to generate endoperoxide.[7–9] In our attempts to modulate the molecular packing of tetracene with H-bonding, we found that yellow crystals of tetracenediamide (structure shown in Scheme 1) underwent photooxidation with the color faded and the crystallinity not destructed when they were exposed to ambient air and light. Our unexpected findings are that molecular packing in solid state plays an important role in photooxidation of tetracenediamide, showing effects not only on the reaction rate but also on the product regioselectivity (shown in Scheme 1).

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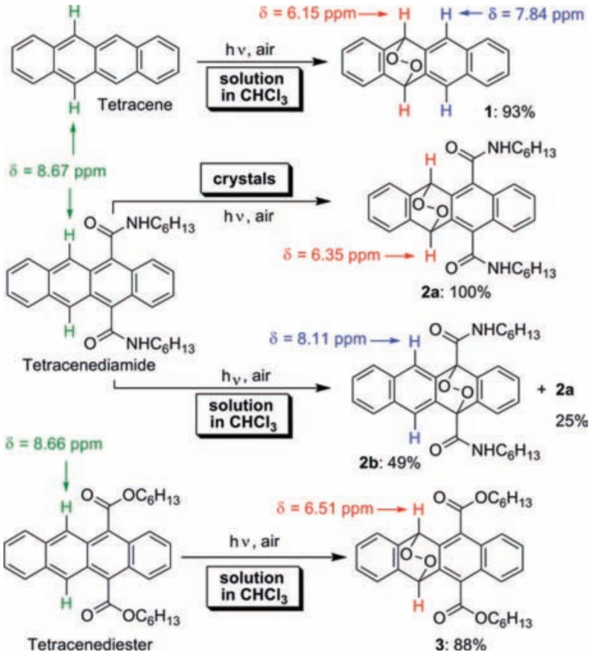
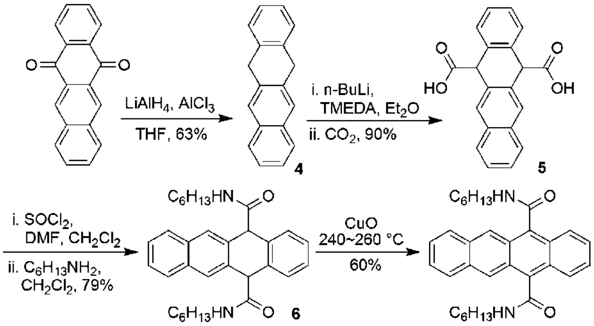
Scheme 1. Photooxidation of Tetracene and Its Derivatives



Scheme 2. Synthesis of Tetracenediamide



The study below details synthesis and unexpected photooxidation of tetracenediamide.

This work was initiated by our attempts to better understand the relationship between molecular packing and electrical properties, which is another key question in the research of OTFTs.[10] In our study on tuning molecular packing of tetracene, we designed *N*,*N′*-dihexyl-5,12-tetracenedicarboxamide, which equips tetracene backbone with amide groups for formation of H-bonds[11] and alkyl groups for better solubility. Due to lack of direct ways to functionalize tetracene at C5 and C12,[12] dihydrotetracene[13] **4** was used as shown in Scheme 2 so that the two internal rings of tetracene backbone could be differentiated. Treatment of **4** with *n*-BuLi at the presence of TMEDA yielded the dianion of tetracene, which was quenched with CO_2 to yield dicarboxylic acid **5**. Diamide **6** happened to be inert to attempted dehydrogenation by DDQ or Pd/C. The dehydrogenation step was finally achieved by heating **6** with CuO.[14]

The yellow crystals of tetracenediamide turned colorless after being exposed to ambient air and light for 24 h. In contrast, the crystals were stable in ambient air but in the dark. As indicated by ^{1}H NMR and HRMS, the resulting colorless crystals only contained peroxide **2a** (shown in Figure 1), indicating that the photooxidation of tetracenediamide was complete. The photooxidation of tetracenediamide in crystals was monitored by microscopy with the crystals being exposed to ambient air and the light from the halogen lamp of microscope. As shown in Figure 1a, no change on the crystal shape is observed during the progress of photooxidation. The polarized light micrographs for crystals of tetracenediamide shown in Figure 1b were viewed between crossed polarizers during the progress of photooxidation and clearly display birefringent crystals of the photooxidation product. These facts indicate that the photooxidation occurs in molecular crystals of tetracenediamide without destruction of crystallinity and suggest that only small motions of atoms are involved during photooxidation. In contrast, crystals of tetracene showed no observable changes after being exposed to the ambient air and the same light for 24 h.

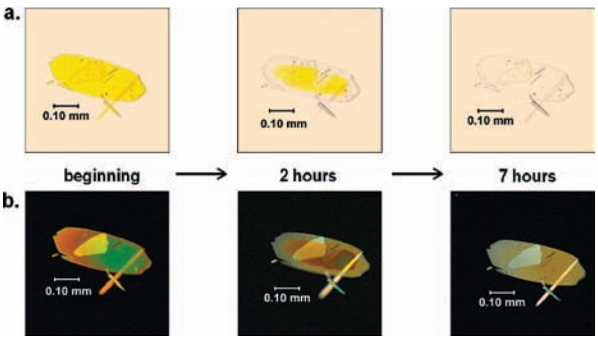


Figure 1. Photooxidation of tetracenediamide in crystals monitored by microscopy: (a) viewed with normal light; (b) viewed with polarized light between two crossed polarizer.

Thin films of tetracenediamide that were deposited by thermal evaporation behaved as semiconductors in OFETs initially but turned insulating after being exposed to air and ambient light for several hours with the yellow films turning colorless. The device degradation is apparently due to photooxidation of tetracenediamde.

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Photooxidation of tetracenediamide and tetracene in solution was investigated. As shown in Figure 2a, the solutions of tetracene and tetracenediamide in $CHCl_3$ have similar UV−vis absorption spectra showing the longest wavelength absorption at 475 and 488 nm, respectively, which decreases with the progress of photooxidation because conjugation of tetracene backbone is broken in the products. Therefore the decrease in the absorbance of tetracene at 475 nm and that of tetracenediamide at 488 nm as a function of time was used to monitor the progress of photooxidation. As shown in Figure 2b, tetracene and tetracenediamide in solutions have similar stability to photooxidation. To characterize the photooxidation products, solutions of the two compounds at higher concentrations were open to air and subject to irradiation with a 500W tungsten lamp, and the two major products **2a** and **2b** were isolated by column chromatography in a yield of 25 and 49%, respectively, as shown in Scheme 1. The structures of **2a** and **2b** were determined by comparing their ^{1}H NMR spectra with that of **1** (the photooxidation product of tetracene).[9]

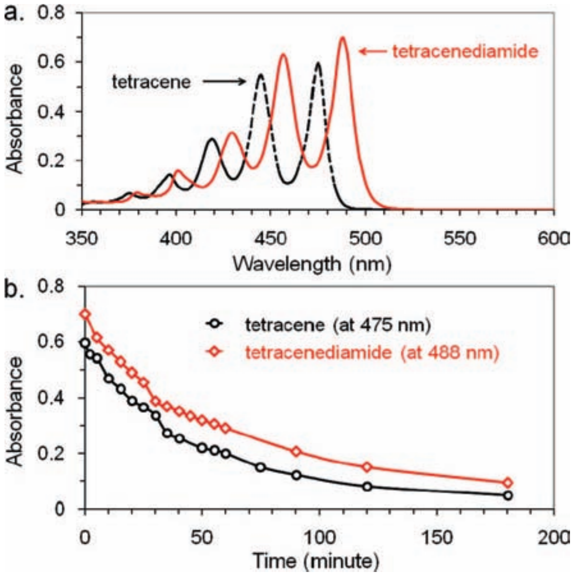

Figure 2. (a) UV−vis absorption of 0.05 mM solutions of tetracenediamide and tetracene in $CHCl_3$; (b) the absorbance as a function of time for the solutions of tetracenediamide and tetracene (0.05 mM in $CHCl_3$) exposed to ambient light.

The above studies raised two questions: why tetracenediamide is much more vulnerable to photooxidation than tetracene in the crystal state although the two compounds have similar stability in solution and why photooxidation of tetracenediamide shows different regioselectivity in solution and in crystals. The similar stabilities of tetracene and tetracenediamide in solutions reflect the chemical properties of isolated molecules because no association was observed at the concentration used in those experiments. It has been reported that ethynyl[5] and pentafluorophenyl[7] substituents at C6 and C13 can increase the stability of pentacene toward photooxdiation in solution because they lower the energy level of lowest unoccupied molecular orbital (LUMO) of pentacene. Such stabilizing effect of amide substituent appears to be very small in tetracenediamide not only due to the weak electron-withdrawing nature of amide but also because the unfavorable interactions between amide groups and H atoms of the adjacent rings prevent effective conjugation between amide and tetracene core.

To answer the first question, the molecular packing of tetracenediamide has to be considered. Unfortunately, crystals of tetracenediamide grown from solutions were not suitable for X-ray crystallography. On the other hand, the crystal structure of its smaller analogue, N,N'-dihexyl-9,10-anthracenediamide (**7**), is solved and shown in Figure 3. Crystal structure of **7** clearly shows H-bonds between the amide groups, which are out of the aromatic plane with N−H atoms on the opposite sides. The closest H-to-C and C-to-C distances between anthracene backbones are 2.99 Å and 3.56 Å respectively indicating a loose packing of anthracene backbones in comparison with the herringbone packing of unsubstituted anthracene, which has the closet intermolecular H-to-C and C-to-C distances of 2.53 and 3.51 Å, respectively.[15] We assume that tetracenediamide has a similar packing motif in solid state as its anthracene analogue with H-bonds between amide groups and a loose packing of tetracene backbones. Such assumption is supported by the UV−vis absorption of tetracenediamide in thin films. The longest wavelength absorbance of tetracenediamide (shown in Figure S-1 in Supporting Information), essentially does not change on going from solution to a thin film while that of tetracene shifts to the red by approximately 45 nm on going from solution (475 nm) to a thin film (520 nm). The red shift of tetracene can be attributed to electronic delocalization due to aromatic interactions[16] whereas the absence of red shift in tetracenediamide suggests weak interactions between aromatic backbones due to loose packing. The high reactivity of tetracenediamide to photooxidation can thus be

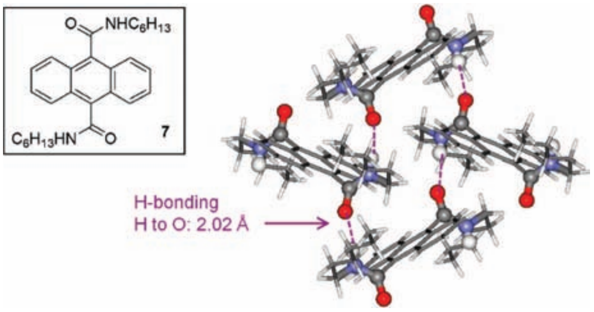

Figure 3. Molecular and crystal structure of *N*,*N*′-dihexyl-9,10-anthracenediamide with amide groups highlighted as balls and sticks and the other parts displayed as fine sticks.

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attributed to its loose molecular packing, which allows diffusion of O_2 into the crystal lattice. On the other hand, the condensed packing of tetracene prevents O_2 diffusion.[4,5]

To explain the regioselectivities for photooxidation of tetracenediamide in crystals and in solution, we propose a mechanism involving H-bonds between photosentisized singlet O_2 and tetracenediamide.[17] As might be expected, we found two locally stable geometries with almost equal energy for tetracenediamide in density funcitonal theory (DFT) optimization with B3LYP/6-31G(d) method.[18] As shown in Figure 4a, one geometry has the N−H atoms of amide groups on the same side of the tetracene core (syn) and the other has the N−H atoms on opposite sides (anti). We propose that the syn conformer of tetracendiamide can bind O_2 with a pair of H-bonds as shown in Figure 4b in a similar manner as 1,3-benzenediamde binds halide anions.[19] Such cooperative H-bonds guide O_2 to access the substituted ring resulting peroxide **2b**. In contrast, the anti conformer has amide N−H atoms on the opposite sides so that such pair of H-bonds to O_2 can not form. As a result, the anti conformer has oxygen added to the unsubstituted ring, which should be electron-richer and less sterically hindered, yielding peroxide **2a**. Because the two conformers of tetracenediamide can convert to each other during the reaction in solution, the conformer that reacts faster should yield the major product. Because the syn conformer reacts faster with assistance of the H-bonds between O_2 and itself, **2b** is the major product when photooxidation occurs in solution. On the other hand, tetracenediamide is assumed to adopt the anti conformation exclusively in crystals as its anthracene analogue (**7**) does (shown in Figure 3). Thus photooxidation of the anti conformer in crystals yields **2a** as the only product.

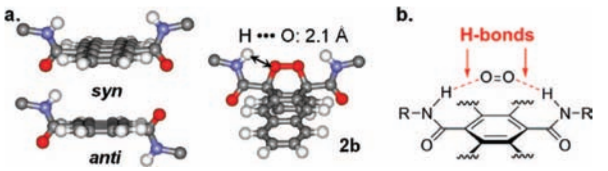

Figure 4. (a) DFT optimization models of tetracenediamide (syn and anti) and peroxdide **2b** with hexyl chains simply shown as a carbon atom for clear view; (b) proposed H-bonds between syn tetracenediamide and O_2.

The proposed mechanism is supported by several experimental facts. Photooxidation of tetracenediester (shown in Scheme 1), an analogue of tetracenediamide that can not form H-bonds, occurred in solution yielding peroxide **3** as the major product in an isolated yield of 88%. Meanwhile solids of tetracenediester showed no observable changes after being exposed to the ambient air and light for 24 h. The second evidence comes from photooxidation of tetracenediamide in solution at the presence of DMSO, a H-bond acceptor that can compete with O_2. Upon adding 40 μL of DMSO-d_6 to a 10 mM solution of tetracenediamide in 0.5 mL of $CDCl_3$, the photooxidation product ratio **2a**:**2b** changed from 1:2.7 to 1.7:1 as monitored by ^{1}H NMR. The two experiments above suggest that H-bonds play an important role in the photooxidation of tetracenediamide in solution. Moreover the energy minmized model of **2b** displayed in Figure 4a shows N−H atoms of both amide groups at the same side forming H-bonds to bridge oxygen atoms. In contrast, intramolecular H-bonds are not observed in energy minimized model of **2a**. In fact ^{1}H NMR spectra of **2a** and **2b** at the same concentration (10 mM) in $CDCl_3$ show chemical shifts of N−H at 5.97 ppm and 6.40 ppm respectively. Moreover, adding 100 mM of DMSO-d6 to these solutions leads to downfield shift of N−H of **2a** to 6.60 ppm while causing almost no change on chemical shift of N−H of **2b** (6.43 ppm). These NMR studies indicate that N−H and bridge O of **2b** form intramolecular H-bonds, which are the trace of intermolecular H-bonds between syn tetracenediamide and O_2.

In summary, the unexpected photooxidation of tetracenediamide highlights the important role of molecular packing in solid−gas reactions. This study suggests that selective oxidation of organic substrates by photosentisized singlet O_2 can be achieved in crystals, where molecular conformations are fixed.

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Supporting Information Available: Experimental details of photooxidation and synthesis, crystallographic information file for **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(17) To the best of our knowledge, amide binging O_2 via H-bonds was not reported. For an example of hydroxyl group binding singlet O_2 via H-bonds, see: Adam, W.; Peters, E. M.; Peters, K.; Prein, M.; von Schnering, H. G. *J. Am. Chem. Soc.* **1995**, *117*, 6686–6690.

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