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Isoquinolinones

Photooxidation of a Twisted Isoquinolinone

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Abstract: Understanding the oxidation mechanism and positions of twistacenes and twistheteroacenes under ambient conditions is very important because such knowl-edge can guide us to design and synthesize novel, larger stable analogues. Herein, we demonstrated for the first time that a twisted isoquinolinone can decompose under oxygen and light at room temperature. The as-decom-posed product 1 was fully characterized through conven-tional methods as well as single-crystal structure analysis. Moreover, the physical properties of the as-obtained prod-uct were carefully investigated and the possible formation mechanism was proposed.

Acenes are one type of polycyclic conjugated hydrocarbons with six-membered aromatic rings annulated in one row.[1–4] Since they can be applied as active elements in low-cost, large-area, and flexible electronic devices, acenes have re-ceived wide interests from both fundamental studies (theoreti-cal simulation and synthetic approaches) and technological applications such as organic photovoltaic cells (OPVs), organic field-effect transistors (OFETs), and light-emitting diodes (OLEDs).[5–9] However, considering their potential applications in optoelectronic devices, these materials still have some limitations (e.g. poor stability/solubility, unsatisfied physical properties, unmatched band gap/band position). Thus, it is highly desirable to develop some new methods to enhance their properties and address these issues. One widely-used method to modify their charge-transport or optical properties is to introduce heteroatoms (S, O, N,B, P) onto the frameworks of oligoacenes (so-called “doping”).[10–19] Comparing with plain oligoacenes, heteroacenes would provide more chances for researchers to modify their physical properties because the energy level of HOMO/LUMO as well as the band gap of oligoheteroacenes strongly depends on the number, position, type, and valance charge of heteroatoms.[20–24] In fact, their electronic properties (e.g. the changes in UV/Vis absorption or HOMO/ LUMO position) and the arrangement of conjugated frame-works through hydrogen bonding and p–p stacking have been emphasized by several groups.[24–33]

Currently, the advancement on developing n-type (electron-transporting) organic semiconductors is much slower compar-ing with the research of p-type (hole-transporting) ones, which is mainly due to the presence of air and moisture as well as the oxygen-trapping problem.[34] Such issues have become an urgent topic that requires scientists to input their more efforts to address. However, although significant progresses have been witnessed in theoretical study, synthesis, and applications of n-type heteroacenes, the influence of oxygen on the stabili-ty of organic semiconductors is still not very clear now.[14, 35–37]

In this research, we are more interested in the oxidation of isoquinolinoenes (one type of twistheteroacenes) under ambi-ent atmosphere. As one member of heteroacene family, isoquinolinones with well-defined structural motifs, have attracted considerable attention in organic synthesis because their analogs have been widely found in many natural products to show incredible pharmacological and biological activities.[38, 39] Moreover, the remarkable electronic structures make them more promising as potential candidates for organic optoelec-tronics. Therefore, numerous approaches to construct large isoquinolinones have been developed over the past decades.[40, 41] In our effort to prepare new isoquinolinones, we have reported the synthesis of twisted isoquinolinones through a “clean reaction’’ strategy based on thermal elimination of lactam bridges.[19] However, these isoquinolinones materials were sus-ceptible to be photooxidized when exposed in air and light. To make us disappointed, such studies on the oxidation mecha-

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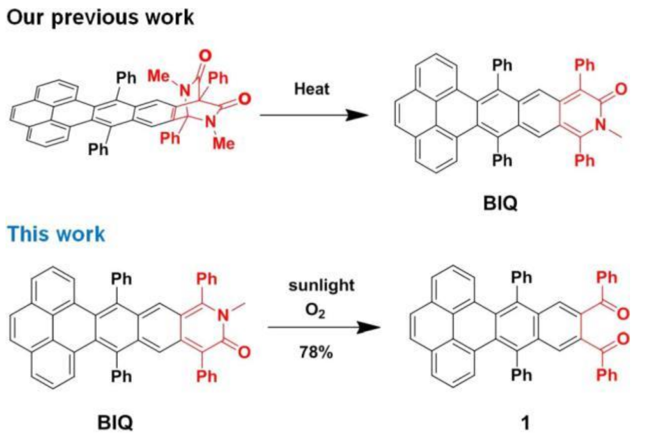
nism and positions in twistacenes and twistheteroacenes are rarely reported. This gap strongly encourages us to conduct our research in this direction.

Herein, we report the photooxidation reaction between 2-methyl-1,4,6,13-tetraphenyl-7:8,11:12-bisbenzoanthro[g] isoqui-nolin-3(2H)-one (BIQ) and oxygen gas under ambient air and light at room temperature, to offer a novel decomposed prod-uct 9,14-diphenyldibenzo[de,qr]tetracene-11,12-diyl-bis(phenyl-methanone) (1).

As shown in Scheme 1, BIQ was oxidized when its dichloromethane solution was exposed to light and oxygen under ambient condition. The color of the original solution changed from green to light yellow (Figure S8). The as-obtained decomposed product was fully characterized using ^{1}H NMR, ^{13}C NMR spectroscopy, fourier transform infrared spectroscopy (FT-IR), and high-resolution mass-spectrometry (HRMS). All data are found to be consistent with the proposed structure. Com-pound 1 can easily dissolve in common organic solvents such as tetrahydrofuran (THF), toluene, dichloromethane (DCM) and chloroform. The solubility of 1 is quite high in chloroform at room temperature (>10 mg mL$^{@1}$). Figure 1 shows the UV-vis absorption spectra of 1 in dichloromethane solution (1 0 $10^{@5}$ m). One can clearly see that 1 exhibits two distinct absorp-tion bands. The absorption band under 300 nm can be as-signed to p–p* electronic transition from pyrene units, and the other one in the range of 340–370 nm can be attributed to an intramolecular charge-transfer (ICT) transition from the pyrene unit to the carbonyl groups through the conjugated bridge. In-terestingly, upon the addition of organic acids such as tri-chloroacetic acid, 1 shows a bathochromic-shifted broad ab-sorption due to the protonation of carbonyl groups (Figure S7), which is similiar to our previously-reported results.[19] The onset absorbance in DCM was 418 nm, from which the optical band gap (E_g) is calculated to be 2.96 eV. Fluorescence spec-trum in DCM solution (Figure 1) indicates 1 has very weak fluo-rescence, which might be due to the introduction of two car-bonyl groups, leading to the quenching of emission.



Scheme 1. Synthetic route to prepare compound 1. a) Our previous work. b) This work.

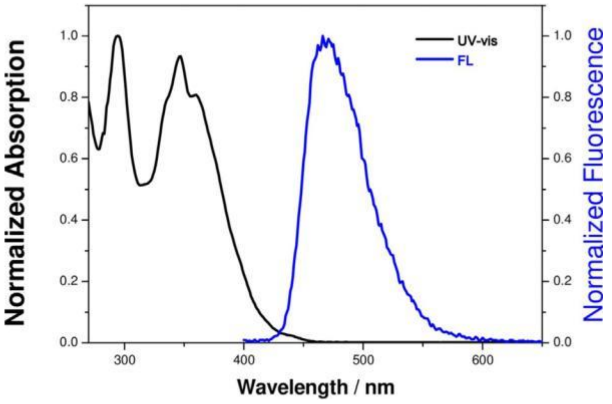


Figure 1. Absorption and emission spectra of 1 in dichloromethane solution. Concentration, 1 0 $10^{@5}$ M.

Single crystals of 1 (CCDC number: 1584780) were obtained from a mixture of solvents (CH_2Cl_2-methanol) through slow evaporation at room temperature (see crystallographic infor-mation file in the Supporting Information). The structure of 1 was clearly confirmed by single-crystal X-ray diffraction crystal-lography. As shown in Figure 2, its crystal system belongs to the monoclinic space group $P2_1/c$, with the lattice constants of a =11.50 &, b =11.82 &, and c =13.88 &. From the side view of the crystal packing of 1 (Figure 3), one can observe that the p-conjugated system in tetracene plane has some twist. The

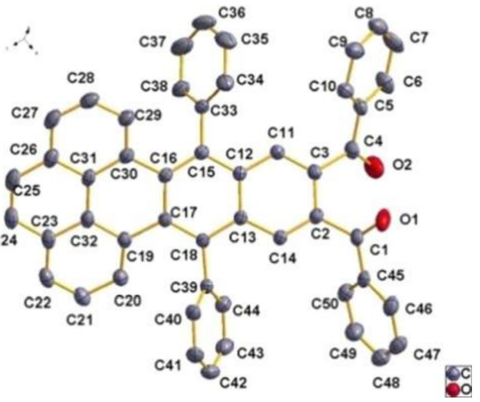


Figure 2. Crystal structure of 1.

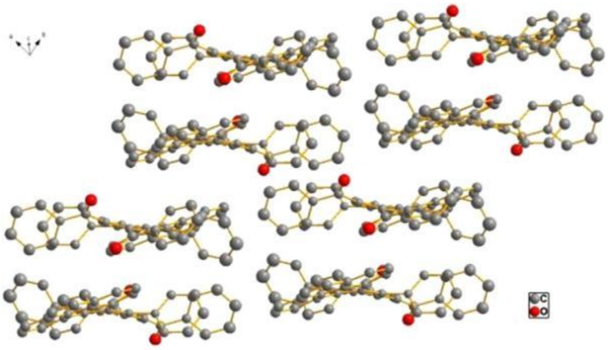


Figure 3. Packing arrangement of 1.

twist angle is about 24.498 between pyrene ring and naphthalene plane (Figure S5), which is larger than that of the tetra-cene analogue.[42] Such twist might enhance the stability of 1 due to two factors: (1) The twist can lower the potential energy of the molecule but has less effect on the conjugation; and (2) The twisted structure would made the insertion of oxygen more difficult. In addition, the crystal packing mode in-dicates that there are no apparent p–p interactions among pyrene units, and such arrangement could further stabilize 1.

Cyclic voltammetry (CV) has been employed to further investigate the electronic properties of 1. As shown in Figure 4 and Table S1, the CV exhibits one reversible reductive wave at lower potential, which might come from the reduction of carboxyl moiety. The onset potential, which is taken as the LUMO level of 1, is determined to be @1.14 V (vs. Ag/AgCl). Correspondingly, the calculated LUMO energy level of 1 is @ 3.26 eV,[43] estimated from the equation E_{LUMO} =@[E^{red}_{onset} +4.4] eV. The band gap (E_g) of 1 (2.96 eV) can be obtained from the maximum value of UV-vis spectrum. Thus, the energy level of HOMO (@6.22 eV) can be calculated from the following equation: E_{HOMO} =@(E_{LUMO} +E_g) eV. In comparison with the parent compound BIQ (E_{HOMO} =@4.8 eV), 1 shows a lower HOMO level, which reveals that 1 has a higher ionization potential, leading to a higher stability.

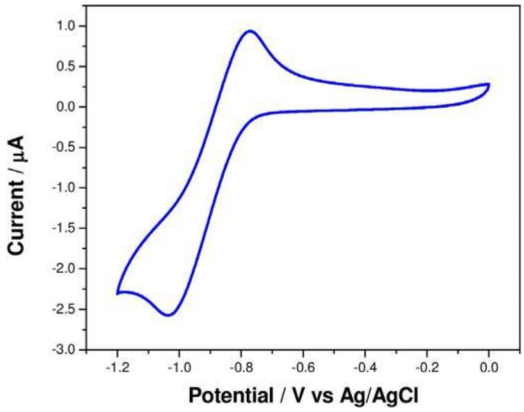
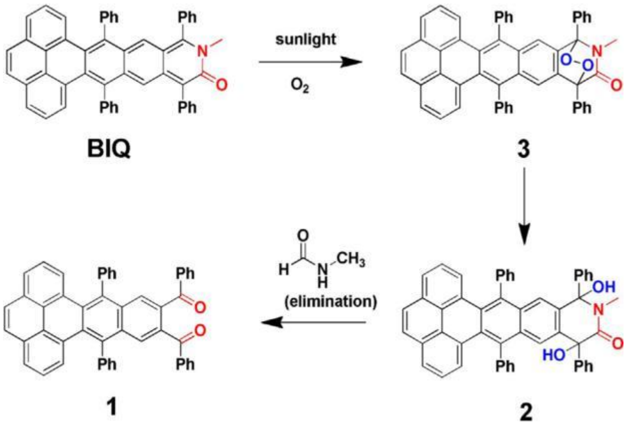


Figure 4. Cyclic voltammetry curves of 1 in dichloromethane solution containing 0.1 m Bu$_4$NPF$_6$ electrolyte. Scanning rate: 50 mV s$^{@1}$.

The proposed reaction mechanism is shown in Scheme 2. Firstly, BIQ can react with singlet oxygen under the photoirradiation through [4+2] cycloaddition to form the corresponding endoperoxide 3, which can quickly break its peroxide bridge to form a diol intermediate 2. Since 2 is not stable, it further converts into 1 through the elimination of methyl formamide.

Density functional theory (DFT) calculations were performed at the B3LYP/6-31G (d,p) level using the Gaussian 09 program.[44] The geometry of 1 is fully optimized with a convergence criterion of 10$^{@3}$ a.u. on the gradient and displacement, and 10$^{@6}$ a.u. on energy and electron density. The spatial distributions and orbital energies of HOMO and LUMO are also generated based on these calculations (Figure 5).

The HOMO orbital of 1 is mainly delocalized on the pyrene backbone, and the LUMO orbital is delocalized on the naphthalene framework through two carbonyl segments. The calculated band positions are presented in Table S2, which indicates that the calculated LUMO/HOMO energies as well as the band gap are close to the experimental results.



Scheme 2. Possible oxidation mechanism of 1.

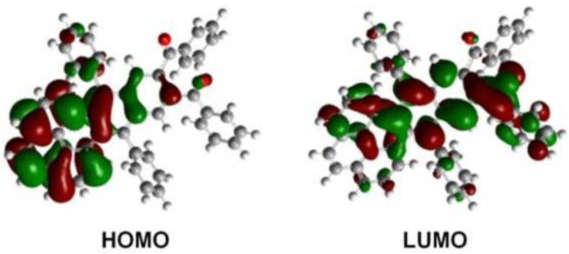


Figure 5. HOMO and LUMO visualizations for compound 1.

In summary, we have demonstrated that a twisted BIQ can be decomposed under photo-oxidization conditions through an irreversible addition with oxygen. The as-obtained decomposed product 1 has been fully characterized and its physical properties have been carefully studied through optical spectroscopy, electrochemistry and molecular simulations. Our results can provide some future guidelines for the design and synthesis of new, air-stable isoquinolinones and twistheteroacenes.

Experimental Section

Materials: All materials were purchased from Sigma–Aldrich and were used without further purification unless otherwise stated. All solvents were acquired from Tianjin Fuyu Chemical Technology Corporation. Tetrahydrofuran (THF) was carefully dried and distilled from a sodium benzophenone mixture under an argon atmosphere before use.

General procedures: ^{1}H NMR and ^{13}C NMR spectra were performed in CDCl$_3$ with TMS as internal standard on Bruker Advance 400 MHz spectrometers. Chemical shifts (d) are reported in parts per million. EI-MS measurements were performed on UK GCT-Mi-cromass or SHIMADZU G-MS-QP2010 spectrometers. HR-MS meas-urements were performed on a Bruker APEX II FT-ICRMS spectrom-eter. UV-vis spectra were recorded on a JASCO V-570 spectrometer. Cyclic voltammetry (CV) measurements were carried out on a

CHI660C analyzer in a conventional three-electrode cell setup with Pt disk as the working electrode, a platinum wire as the counter electrode, Ag/AgCl as the reference electrode and calibrated with ferrocene/ferrocenium (Fc/Fc^+) as an external potential marker in anhydrous THF solution containing 0.1 m nBu_4NPF_6 as a supporting electrolyte at a scan rate of 100 mV $s^{@1}$ under an argon atmosphere at room temperature. X-Ray diffraction (XRD) measurements of thin films were performed in reflection mode at 40 kV and 200 mA with CuK_a radiation using a 2 kW Rigaku X-ray diffractometer.

Synthesis of 9,14-diphenyldibenzo[de,qr]tetracene-11,12-diyl-bis(phenylmethanone) (1)

In a 100 mL round-bottom flask, 2-methyl-1,4,6,13-tetraphenyl-7:8,11:12-bisbenzoanthro[g]isoquinolin-3(2H)-one (BIQ) (20 mg, 0.029 mmol) and 30 mL dichloromethane were added. Then, the solution was bubbled with air and at the same time, solar-simulat-ed light was radiated for 48 hours. The color of the solution was changed from green to light yellow. After the reaction finished, the solvent was evaporated under vacuum and the residue was puri-fied by silica column chromatography (eluents: dichloromethane/ hexane). After removing solvents, light yellow solid was obtained (15 mg, yield 78 %). M.p >300 8C, ^1H NMR ($CDCl_3$, 400 MHz): d = 8.22 (s, 1 H), 7.96–7.84 (m, 5 H), 7.59–7.29 ppm (m, 9 H). ^{13}C NMR ($CDCl_3$, 125 MHz): d =196.19, 140.93, 137.45, 137.32, 136.32, 132.78, 132.12, 131.71, 131.38, 130.80, 130.39, 129.92, 129.61, 129.32,

128.98, 128.24, 128.11, 126.97, 126.59, 125.99, 124.89 ppm. FT-IR: n˜ =3458.11, 3050.77, 2922.79, 1647.41, 1445.57, 1264.94 $cm^{@1}$. MS-TOF: 662.2258 (M^+), calculated, 662.2246 (M^+).

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Conflict of interest

The authors declare no conflict of interest.

Keywords: acenes · characterization · photooxidation · pyrenes · twisted isoquinolinone

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