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“Clean Reaction” Strategy to Approach a Stable, Green Heptatwistacene Containing a Single Terminal Pyrene Unit

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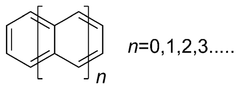
Acenes, first introduced by Clar to describe the family of hydrocarbons with linear annellation of benzene rings (Scheme 1),[1] can be considered as one piece of carbon nanotube or graphene, and have received a lot of attention as active elements in organic semiconducting devices.[2–4] Although polycyclic aromatic hydrocarbons (PAHs) can be found in heavy oil or be generated from petroleum asphaltenes,[5] higher conjugated acenes are not observed owing to their high reactivity, such as easy oxidation and photodimerization. Natural rarity or non-existence of higher conjugated oligoacenes together with the theoretical interest[6] (e.g. in the gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO–LUMO gap) and electronic properties) gave scientists more reasons to synthesize them. Unfortunately, the extreme instability, poor solubility, and tedious purification of higher conjugated oligoacenes make the synthetic work more challenging. Although several groups have reported the photospectroscopic characterization and the study of electronic structure of higher acenes ($n \geq 7$),[7] there are only five examples of higher acenes ($n \geq 7$) characterized by X-ray single-crystal structures.[8]



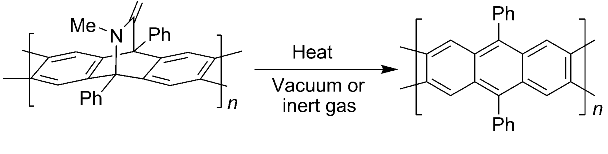
Scheme 1. The structure of oligoacene.

By facing above-mentioned problems, we aim at a “clean reaction” to prepare the higher acenes from their precursors in pure state and in quantitative yield. The “clean reaction” strategy is based on thermally eliminating lactam bridges from soluble acene precursors through a retro-Diels–Alder reaction (Scheme 2). In fact, a similar method has been reported by our group and other groups.[7h,9]

Because of the poor solubility and extreme instability of higher acenes, several types of protecting groups (e.g. phenyl, fluoride, aryl thio, silylethyne) have been successfully employed to enhance their solubility and stability.[7e,f,8b,c,d,e] Interestingly, the nonbonded interactions between the phenyl substituents and the benzo unit of pyrene can cause PAHs to twist.[4e,f,10] Such a twist together with strategically located phenyl substituents nearly perpendicular to the acene plane might substantially inhibit the dimerization and oxidation observed in larger acenes. Previously, we reported a novel, twisted 6,8,15,17-tetraphenyl-1:18,4:5,9:19,13:14-tetrabenzoheptacene containing two terminating pyrene units, which was shown to be remarkably stable.[8b] The stability is attributed to the protection gained from the rigid terminal pyrenes as well as the strategically installed phenyl substituents.[8b] This exciting result, together with the promise of increasing device performance in thin-film transistors (TFTs) using a narrow HOMO–LUMO gap acene as observed when going from tetracene to pentacene,[11] prompted us to investigate larger conjugated PAHs.

The system containing rigid terminal pyrenes (or phenanthrenes) can be divided into two types:[1,8a,10] double-terminal pyrenes (or phenanthrenes, type I) and single-terminal pyrene (or phenanthrene, type II, Scheme 3). In type II, the longest member which has been reported in the literature is 1:16,4:5-bisbenzohexacene **1** (Scheme 3), whose absorption is similar to pentacene.[12] The result leads us to synthesize the next benzolog, 1,2,3,4,6,8,15,17-octaphenyl-9:10,13:14-bisbenzoheptacene (**2**, Scheme 4), whose HOMO–LUMO gap is similar to that of hexacene.[13]

The desired precursor 6,17-dihydro-1,2,3,4,6,815,17-octaphenyl-9:10,13:14-bisbenzo-20-methyl-6,17-(iminomethano)-heptacene-19-one (**3**) was obtained in 40% yield through the cycloaddition reaction between 2-methyl-1,4,6,7,8,9-hex-



Scheme 2. “Clean reaction” strategy to approach higher acenes.

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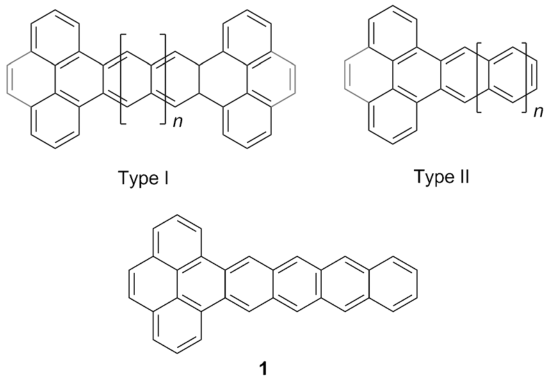
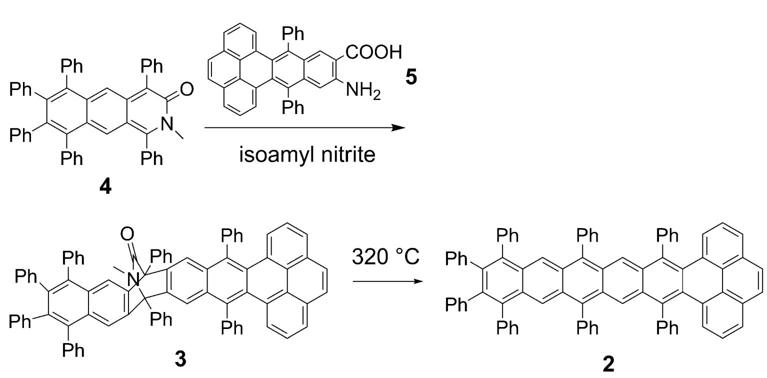


Scheme 3. Types of twistacenes.



Scheme 4. Synthesis of 1,2,3,4,6,8,15,17-octaphenyl-9:10,13:14-bisbenzoheptatwistacene (**2**).

aphenyl-benz(g)-isoquinolin-3(2H)-one (**4**)[9f] and the aryne generated from 3-amino-5,12-diphenyl-6:7,10:11-bisbenzotetracene-2-carboxylic acid (**5**, Scheme 4).[4e]

Thermogravimetric analysis (TGA) of **3** showed about a 5% weight loss starting at approximately 330 °C (Figure S1 in the Supporting Information). The observed weight loss is closely in line with the calculated weight percent for a methyl isocyanate unit (5.1%). Obvious decomposition of **2** is observed in the thermogram if the sample temperature is higher than 375 °C. Therefore, the temperature to remove the lactam bridges should carefully be controlled. Eliminating the bridge in diphenyl ether (sealed tube at 320 °C, Scheme 4) proved to be an efficient, better way to form compound **2** (which can moderately dissolve in hot 1,3,5-trichlorobenzene to form a green solution; Figure 1a). Slow cooling of the diphenyl ether solution afforded plate-like green crystals of **2** (Figure 1b). The structure of compound **2** was confirmed by ^{1}H NMR spectroscopy, elemental analysis, and mass spectrometry. A clean ^{1}H NMR spectrum, recorded in CD_2Cl_2 at 500 MHz, is shown in Figure 1c. The signals observed at $\delta = 8.42$ (s, 2H), 7.76 (d, 2H), 7.66 (d, 2H), and 7.23 ppm (t, 2H) are from protons belonging to the pyrene system. The singlets at $\delta = 8.07$ (2H) and 7.80 ppm (2H) are assigned to the protons residing on the pentacene framework. Proton signals corresponding to the phenyl substituents observed at $\delta = 7.42$ (m, 4H), 7.34 (m, 16H), 7.11 (m, 10H), and 6.86 ppm (m, 10H). The remaining small impurities at 7.00 and 7.10 ppm are the result of residual diphenyl ether. The compound is very stable, and the CH_2Cl_2 solution of it in open air did not show obvious bleaching in three days (Figure S2 in the Supporting Information).

High-quality single crystals (Figure 1b, CCDC number: 846054) suitable for X-ray structural analysis are stable in air for more than 10 days without any protection. As predicted, compound **2** displays a twisted structure with a twist angle of 23.49°, and π–π stacking (3.24 Å) only happens by the pyrene units (Figure 2). The pentacene unit, which has a main contribution to electronic properties, is involved in no π–π interaction at all. Such an arrangement makes compound **2** more stable.

The UV/Vis spectrum of **2** (1.0×10^{-6} M, measured in CH_2Cl_2), with the longest absorption λ_{max} at 683 nm (1.82 eV), is shown in Figure 3a. The "finger" peaks in the range of 550–720 nm are characteristic of the acene family (Figure 3a). Cyclic voltammetry (CV) of **2**, measured in 0.1 M tetrabutylammonium perchlorate (TBAP)/1,2-dichlorobenzene (ODCB), showed that the oxidation and reduction processes are chemically and electrochemically reversible (Figure 3b). The HOMO–LUMO gap calculated from the difference between half-wave redox potentials ($E_{1/2}^{ox} = +0.37$ eV and $E_{1/2}^{red} = -1.55$ eV) is 1.92 eV. $\Delta E_{HOMO-LUMO}$ corroborates the value of 1.82 eV derived from the UV/Vis data. Furthermore, these results placed the HOMO–LUMO gap of **2** right in

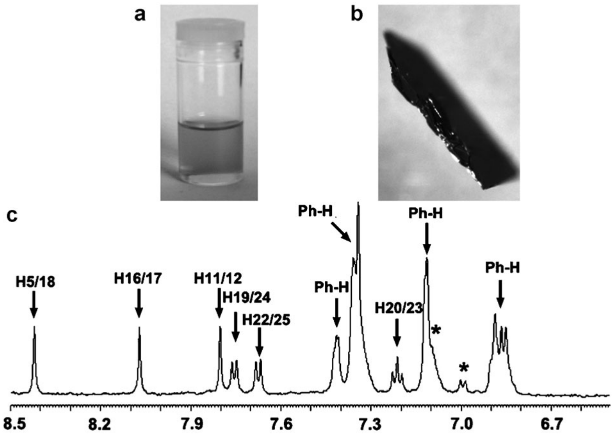


Figure 1. a) Solution of **2** in ODCB. b) Single-crystal image of **2**. c) ^{1}H NMR spectrum in CD_2Cl_2 (the peaks with * are from solvent diphenyl ether).

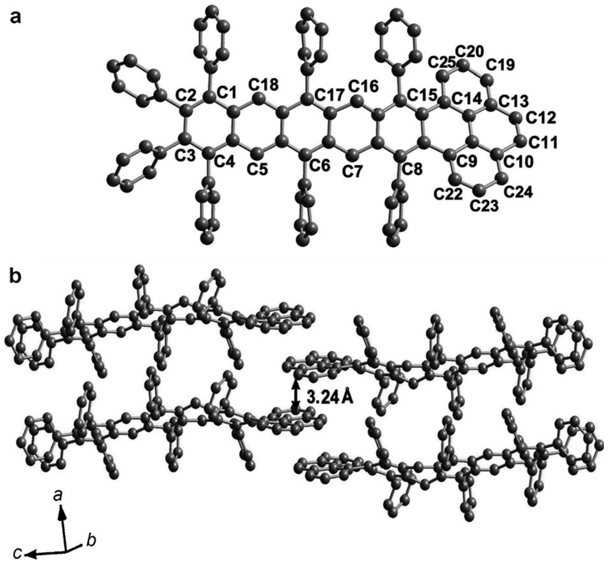


Figure 2. Single-crystal analysis of **2**. a) One molecule unit. b) Molecular stacking.

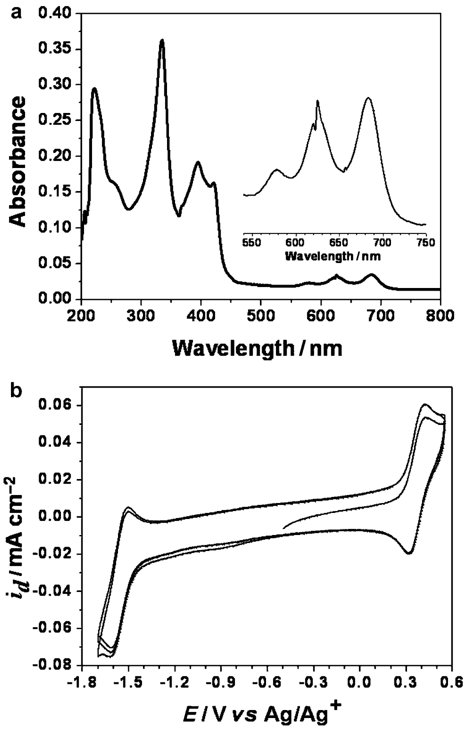


Figure 3. a) The UV/Vis absorption of **2** (1.0×10^{-6} M) in CH_2Cl_2. b) Cyclic voltammogram of **2** in ODCB using tetrabutylammonium perchlorate as electrolyte.

the region of hexacene (exp. 1.84 eV),[8a] which is lower than that of pentacene (exp. 2.1 eV).[14]

Density function theory (DFT) at the B3LYP level of theory[15,16] (which includes the gradient-corrected exchange and correlation functionals along with the exact exchange) with double-ζ quality basis functions 6-31G(d,p) (augmented with polarized function for all atoms) was applied to optimize the geometry of **2**. The geometry of **2** is fully relaxed using Gaussian 09 code[17] with a convergence criterion of 10^{-3} a.u. on the gradient and displacement and 10^{-6} a.u on energy and electron density. Harmonic vibrational analyses show no imaginary frequency, thus indicating that the structure of **2** is a local minimum. The dipole-allowed vertical excitation in the gas phase is calculated by the time-dependent density functional theory (TD-DFT) approach[18] using the same basis set. The first absorption peak with an excitation energy of 1.64 eV is the electron excitation from HOMO to LUMO and corresponds to the π–π* type transition as shown in Figure 4, which is in good agreement with the experimental data (1.8 eV). In addition, the calculation demonstrates that the pyrene unit does contribute to the HOMO–LUMO gap.

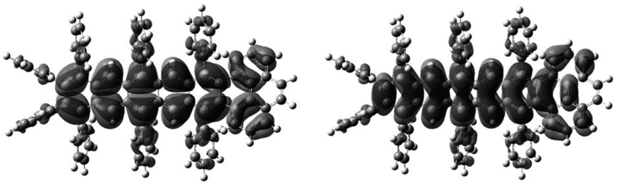


Figure 4. Plots of wave functions for HOMO (left) and LUMO (right) of **2**.

In conclusion, we developed a "clean reaction" method to approach a novel heptatwistacene. The novel, stable, green twistacene **2** possesses a low HOMO–LUMO gap, which is close to that of the reported hexacene. Crystallographic analysis revealed the presence of the conjugated heptacene chromophores with a twisted shape. Using our strategy, we are synthesizing longer oligotwistacenes.

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Keywords: density functional theory · physical properties · polycycles · structure elucidation · twistacenes

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