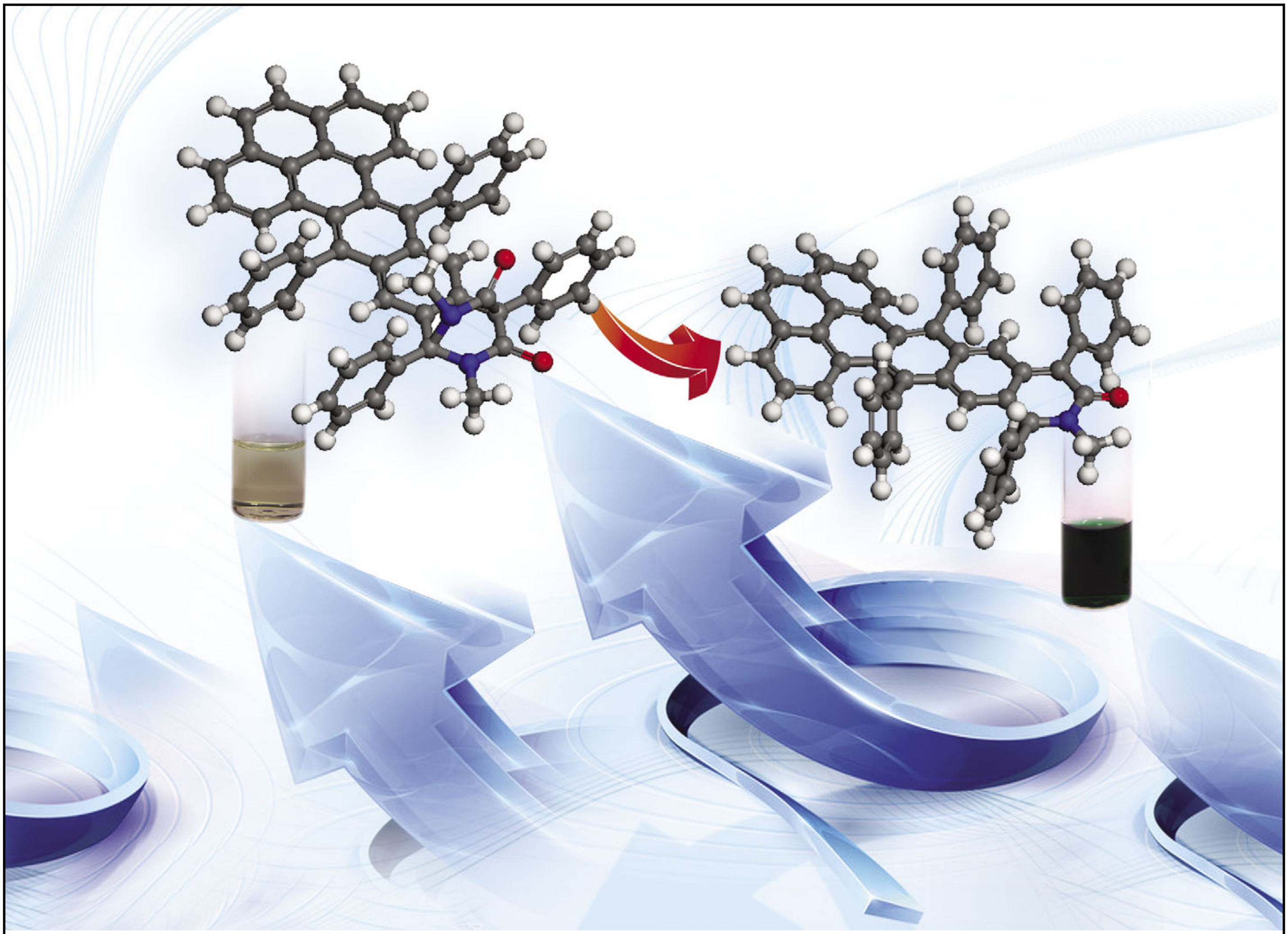

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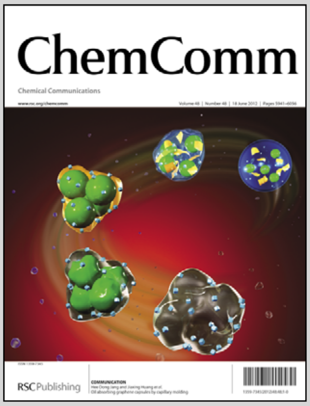

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Approaching a stable, green twisted heteroacene through "clean reaction" strategy†

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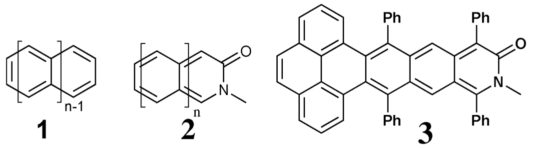
A new, longest, stable, green twisted heteroacene 2-methyl-1,4,6,13-tetraphenyl-7:8,11:12-bisbenzo-anthro[*g*]isoquinolin-3(2*H*)-one (3) was synthesized by employing a "clean reaction" strategy based on thermally eliminating lactam bridges. Calculation shows that the HOMO–LUMO bandgap is in good agreement with experimental data.

Heteroacenes, analogs of oligoacenes **1** (Scheme 1), have at least one heteroatom such as N, P, O and S in their conjugated frameworks.[1] Recently, heteroacenes have attracted much attention both in fundamental research (theoretical studies and synthetic challenges) and potential technological applications.[2,3] The replacement of carbon atoms in oligoacenes **1** by heteroatoms not only leads to very interesting electronic properties (*e.g.* position changes for the HOMO and LUMO, HOMO–LUMO gap, UV-Vis absorption) but also affects the arrangement of conjugated frameworks (*e.g.* π–π stacking, hydrogen bonding, S···S interaction).[4] One member of the heteroacene family, isoquinolinones **2** (Scheme 1) have been widely studied in biological systems.[5] However, as potential candidates for electronics, their remarkable electronic structures have not caught scientists' attention. Although higher conjugated isoquinolinones might have similar ground states (open shell singlet or singlet polyradical character) as predicted in larger acenes,[6] experimental data related to these predictions are rare. In addition, we have already demonstrated that the HOMO–LUMO gaps of isoquinolinones **2** (n = 2, and 3) are close to those of tetracene and pentacene,[7] but the longer isoquinolinones **2** ($n > 3$) remain unknown. This gap in knowledge strongly encourages us to explore the larger isoquinolinones.

Recently, Pascal, Wudl, and our group have already proved that the twisted topology can serve as a protective motif to aid synthesis of the larger stable polyacenes.[7,8] Surprisingly, the moderately twisted structures did not affect the electronic properties. Employing this concept, we anticipated that we could prepare the longer, highly conjugated, twisted isoquinolinones. Furthermore, 1,4-cycloaddition involving isoquinolinones (n = 1, 2 and 3), demonstrated by our group and others,[7,9] proved that they were valuable diene intermediates in the construction of larger oligoacene frameworks. The soluble 1,4-cycloaddition lactam-bridged adducts (oligocene precursors) were key elements in the "clean reaction" strategy to produce the corresponding acenes through thermally eliminating lactam bridges (a retro-Diels–Alder reaction, Scheme 2). The amazing advantage for this strategy was that the target products can be readily obtained in pure state with nearly 100% yield and tedious separation will be avoided. Employing this method, we have successfully synthesized several conjugated compounds such as 5,7,14,16-tetraphenyl-8:9,12:13-bisbenzo-hexatwistacene and 3-(2*H*)-isoquinolinone.[7] It was our continuous interest in this field to employ the "clean reaction" strategy to prepare larger conjugated isoquinolinones. Herein, we report the synthesis, physical properties and theoretical study of a novel, stable, green twisted compound 2-methyl-1,4,6,13-tetraphenyl-7:8,11:12-bisbenzo-anthro[*g*]-isoquinolin-3(2*H*)-one (**3**).

Although many routes have been reported in the literature for preparing various isoquinolinone derivatives,[5] the practical methodology to achieve larger isoquinolinones ($n > 2$, Scheme 1) was recently established by employing a "clean reaction" strategy based on thermally eliminating lactam bridges from soluble precursors through a retro-Diels–Alder reaction. In this report, the soluble precursor **6** was obtained through



Scheme 1 The structure of oligoacenes (**1**), isoquinolinones (**2**) and 2-methyl-1,4,6,13-tetraphenyl-7:8,11:12-bisbenzo-anthro[*g*]isoquinolin-3(2*H*)-one (**3**).

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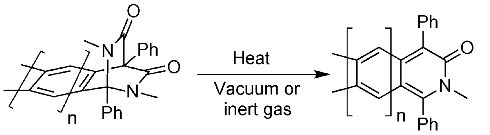
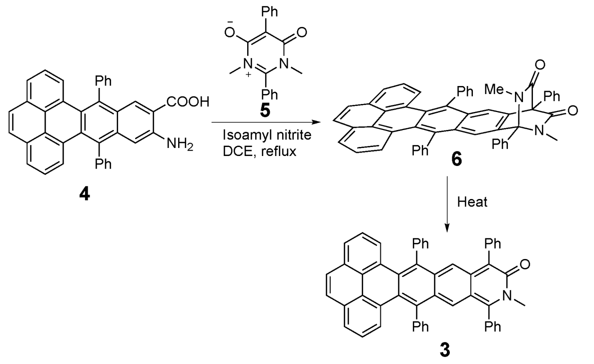


Scheme 2 "Clean reaction" strategy to approach higher acenes.

a [4 + 2] cycloaddition involving *in situ* arynes as dienophiles (from precursor **4** reacting with isoamyl nitrite)[8a] and meso-ionic pyrimidine **5**[9] as a diene (Scheme 3). Compound **3** was obtained in quantitative yield from precursor **6** through thermal elimination of lactam bridges at 220 °C in the solid state or in tetrahydronaphthalene solvent.

Besides full characterizations of spectral data of precursor **6**, good crystals suitable for single-crystal X-ray diffraction analysis were obtained in a mixed solution of CH_2Cl_2–methanol (1 : 1) through slow evaporation. The solved structure of precursor **6** with atomic labeling is shown in Fig. 1. Although we were able to grow single crystals of compound **3** upon slow cooling of a tetrahydronaphthalene solution of **3** in a sealed tube from 250 °C to room temperature, unfortunately, we could not solve the crystal structure due to the small size and poor quality. It is noted that these crystals were very stable in air for more than 15 days without any protection. Thermogravimetric analysis (TGA) analysis of compound **3** shows that it is stable up to 390 °C (Fig. S10, ESI†). The as-prepared compound **3** was further characterized by ^{1}H NMR, ^{13}C NMR, MS-ESI, HiResMALDI-TOF and FT-IR, differential scanning calorimetry (DSC) and elemental analysis.

The absorption spectrum of **3** in dichloromethane (DCM) displayed an absorption λ_{max} at 665 nm with a shoulder at 710 nm (Fig. 2a). We were very surprised by the fact that compound **3** with its relatively small π-framework had an optical band gap at 1.86 eV, which is a similar HOMO–LUMO gap to that of hexacene, but the twisted heteroacene **3** was more stable. We observed no obvious change in the UV-Vis absorption of **3** in *o*-dichlorobenzene (ODCB) solution in 6 h even without degassing and shielding of light. Cyclic voltammetry (CV) of **3**, measured in 0.1 M tetrabutylammonium perchlorate (TBAP)–ODCB, showed that the oxidation and reduction processes were chemically and electrochemically reversible (Fig. 2b). The HOMO–LUMO gap calculated from the difference between the half-wave redox potentials ($E_{1/2}{}^{ox}$ = +0.40 eV and $E_{1/2}{}^{red}$ = −1.50 eV) is 1.90 eV. This value was in good agreement with the optical band gap, 1.86 eV, calculated from UV-Vis data (665 nm).



Scheme 3 Synthetic route to 2-methyl-1,4,6,13-tetraphenyl-7:8,11:12-bisbenzo-anthro[*g*]isoquinolin-3(2*H*)-one (**3**).

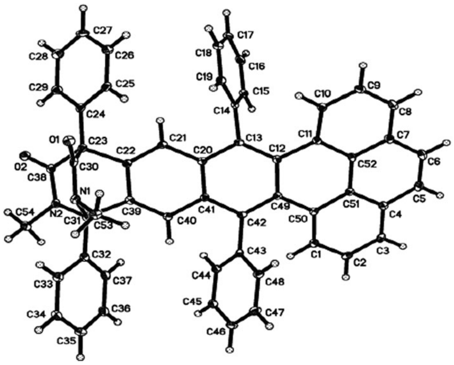


Fig. 1 The crystal structure of precursor **6**.

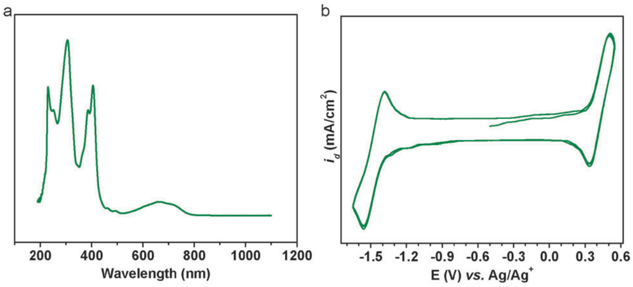


Fig. 2 UV-vis spectrum of **3** in DCM (a) and cyclic voltammogram of **3** in 0.1 M TBAP–ODCB (b).

The electronic states of compound **3** were also strongly governed by the pyridone end unit. The two possible major contributing resonance structures in compound **3** are the neutral polyene state and the charge-separated state (meso-ion state).[7b] Either electronic state can be readily favoured through the appropriate choice of solvents together with Lewis acid or strong acid. When strong Lewis acids such as anhydrous $ZnCl_2$ were added into aprotic solvents (for example dichloromethane as shown in Fig. 3), the longest absorption maxima centre was blue-shifted to 510 nm with a 603 nm shoulder (similar phenomena have been reported previously[10]). The same phenomenon was also observed in strong acidic solvents (for example trifluoroacetic acid (TFA), shown in Fig. 3) and the absorption spectrum was drastically blue-shifted to 509 nm. It is believed that strong Lewis acids or strong organic acids can shorten the N–CO bond through protonation.[7b] As to a relatively weaker acid (*e.g.* acetic acid (AcOH) shown in Fig. 3), the absorption peak (λ_{max} = 610 nm) fell between that in dichloromethane and that in trifluoroacetic acid, which indicates that compound **3** is partially protonated.[7b]

Density function theory (DFT) at B3LYP/6-31G(d,p) [11] was applied to optimize the geometry of heterotwistacene **3**, which was fully relaxed using the Gaussian 09 code[12] 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 structure of **3** was a local minimum since there were no imaginary frequencies in harmonic vibrational analyses carried on 6-311+G(d,p) basis set. The HOMO–LUMO band gap was 2.1 eV, corresponding to the π–π* type transition as shown in Fig. 4, which was in good agreement with the experimental data (1.9 eV). In addition, the calculation demonstrated that C=O and the pyrene unit showed a genuine contribution to the HOMO–LUMO gap.

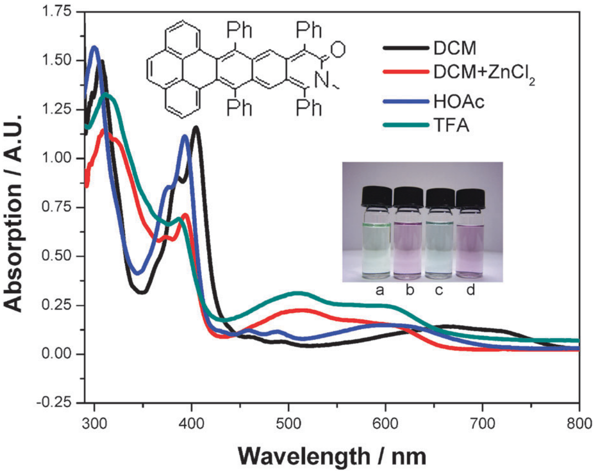


Fig. 3 UV-vis spectrum of **3** in different solvents (2.2×10^{-5} M): (a) DCM (b) DCM + $ZnCl_2$ (c) AcOH and (d) TFA. The inset shows the colour changes in the different solvents.

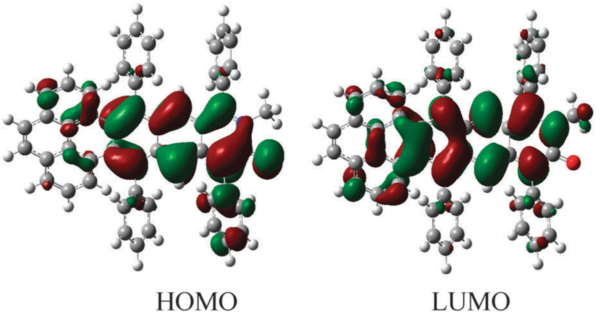

HOMO LUMO

Fig. 4 Wave functions for the HOMO and LUMO of **3**.

In conclusion, we developed a "clean reaction" strategy to approach a novel, longest, stable, green heterotwistacene 2-methyl-1,4,6,13-tetraphenyl-7:8,11:12-bisbenzo-anthro[*g*]-isoquinolin-3(2*H*)-one (**3**). The fact that it had a low HOMO–LUMO gap, which could be compared with that of hexacene, makes it a potential candidate for electronics. In addition, we believed that the as-prepared heterotwistacene (**3**) could act as a scaffold towards the construction of larger twisted polycyclic compounds. Further work to form highly-conjugated twisted polycyclic compounds is still under investigation.

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