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Efficient Synthesis of a Novel, Twisted and Stable, Electroluminescent "Twistacene"

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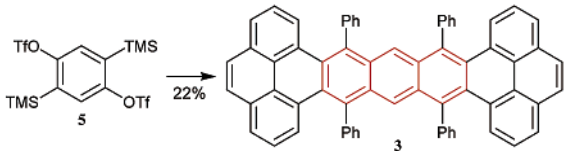
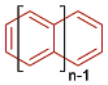
ABSTRACT



5 3

A twistacene, 6,8,15,17-tetraphenyl-1.18,4.5,9.10,13.14-tetrabenzoheptacene (3), was synthesized using a mild and novel bisbenzyne precursor. It was characterized by X-ray crystallography, NMR, UV–vis, and IR spectroscopies, as well as cyclic voltammetry and DFT calculations. The heptacene derivative possesses a nonpropeller twist topology and is unusually stable for a highly conjugated oligoacene. In addition, it is fluorescent, with a quantum efficiency of 15%. Distortion from planarity, mostly due to the phenyl substituents, causes only marginal changes in electronic properties and is beneficial for redox reversibility, which is required for efficient OLED devices.

The linear polyacenes **1**, members of a family of polycyclic aromatic hydrocarbons (PAHs), are linearly fused benzenoid hydrocarbons that in the recent past have been of interest from fundamental and applied perspectives.[1] Currently, pentacene ($n = 5$) is the most widely studied and promising organic semiconductor candidate for field effect transistor (FET) applications and organic photodiodes.[2] Longer acenes are expected to exhibit a smaller band gap, which should make them potentially more interesting materials for molecular electronics. However, it is well documented that the preparation of these linearly extended benzenoid molecules is plagued by facile photooxidation, insolubility, and most detrimental, dimerization and polymerization.[3] Thus far, the longest isolated known system with only moderate stability is hexacene ($n = 6$).[4]



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Twisted PAHs are topologically interesting molecules that have been studied in detail, mostly by Pascal,[5] who has designed, synthesized, and characterized many of these contorted molecules up to "pentacene" **2** (Figure 1).[5] We postulated that the added rigidity inherent in the twisted

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(2) (a) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99. (b) Dimitrakopoulos, C. D.; Mascaro, D. J. *IBM J. Res. Dev.* **2001**, *45*, 11. (c) Meng, H.; Bendikov, M.; Mitchell, G.; Helgeson, R.; Wudl, F.; Bao, Z.; Siegrist, T.; Kloc, C.; Chen, C.-H. *Adv. Mater.* **2003**, *15*, 1090. (d) Hegmann, F. A.; Tykwinski, R. R.; Lui, K. P. H.; Bullock, J. E.; Anthony, J. E. *Phys. Rev. Lett.* **2002**, *89*, 227403. (e) Tokumoto, T.; Brooks, J. S.; Clinite, R.; Wei, X.; Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *J. Appl. Phys.* **2002**, *92*, 5208.

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(4) (a) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: London, 1964; Vols. 1, 2. (b) Biermann, D.; Schmidt, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 3163.

(5) (a) Smyth, N.; Engen, V. D.; Pascal, R. A., Jr. *J. Org. Chem.* **1990**, *55*, 1937. (b) Pascal, R. A., Jr.; McMillan, W. D.; Engen, V. D.; Eason, R. G. *J. Am. Chem. Soc.* **1987**, *109*, 4660. (c) Schuster, I. I.; Cracium, L.; Ho, D. M.; Pascal, R. A., Jr. *Tetrahedron* **2002**, *58*, 8875. (d) Zhang, J.; Ho, D. M.; Pascal, R. A., Jr. *Tetrahedron Lett.* **1999**, *40*, 3859. (e) Qiao, X.; Ho, D. M.; Pascal, R. A., Jr. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 1531.

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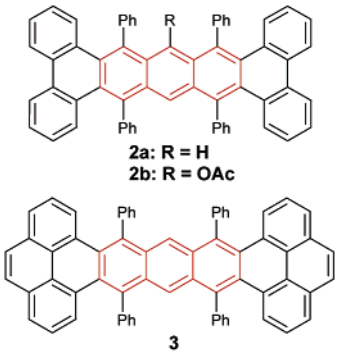
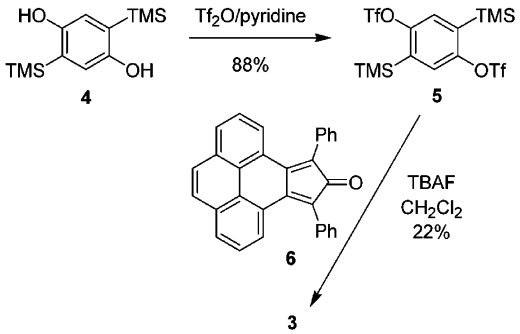


Figure 1. "Pentacene" derivatives **2**[5c,d] and "heptacene" derivative **3**.

topology, together with strategically located phenyl substituents (perpendicular to the acene plane), could serve as a viable strategy to obtain stable polyacenes. These features should inhibit substantially the dimerization observed with the larger oligoacenes such as heptacene,[3] ultimately allowing full characterization in the solid state. More importantly, to serve as functional materials in OLEDs, the electronic properties should be retained even under moderate twisting. Here we report the synthesis of a "twistacene" **3** (Figure 1) through a very mild bisbenzyne generation and demonstrate its favorable electronic properties and high thermal stability. Further, it was gratifying to learn, in collaboration with our colleagues in the School of Engineering, that indeed **3** affords excellent light-emitting diodes (white light, low turn-on voltage, high luminance).[6]

In analogy with the synthesis of **2**,[5c] compound **3**[7] was assembled using benzyne-trapping chemistry. Bisbenzyne precursor **5** was prepared by triflate formation of hydroquinone **4** in pyridine, Scheme 1.[8,9] Sequential aryne formation from precursor **5** triggered by TBAF (tetrabutylammonium fluoride),[10] followed by trapping with 2 equiv of the pyrano-diphenylcyclopentadienone **6**, cleanly afforded **3** as a bright orange powder.

Scheme 1



(6) Yang, Y.; Xu, Q.; Duong, H. M.; Wudl, F. Manuscript is in preparation.

Several "double-barrel" bisbenzynes that are based on benzobistriazole,[11] 1,4-dihalobenzene,[12] and iodonium-triflate salt[13] have been reported. Despite their high reactivity with furan, arynes generated from benzobistriazole and 1,4-dibromobenzene precursors were incompatible with **6**. We are aware of only one other bisbenzyne produced through a fluoro-desilylation mechanism of a phenyl-[2,4,5-tris(trimethylsilyl)phenyl] iodonium triflate salt. However, that particular hypervalent iodine aryne precursor involves a two-step process with isolation of a synthetic intermediate (where one of the remaining TMS groups is a latent iodonium ion),[13] whereas in our case, the bisbenzyne is generated in one pot from precursor **5**.

Considering the limited number of 1,4-benzadiyne precursors known, generation of bisbenzyne from **5** requires extremely mild conditions, especially for a "double-barrel"[14] system. In a recent report, the preparation of **2a** was successfully demonstrated through biscycloaddition between a phenanthrene-derived cyclone (similar to **6**) and the bisbenzyne derived from a bisiodonium-carboxylate precursor.[5c] Unfortunately, the chromatography-mediated isolated yield of the corresponding "pentacene" derivative was only 1.2%, likely as a result of the high temperature required to generate the aryne. In comparison, the bisbenzyne precursor **5**, based on benzotrimethylsilyl triflate, afforded "heptacene" **3** directly in 22% yield.

The X-ray crystal structure of **3** (Figure 2)[8] shows a twisted topology that is unique and quite different from the reported

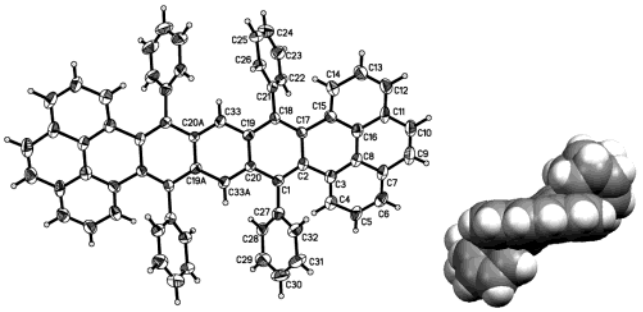


Figure 2. X-ray structure of **3**; (right) space filling representation viewed from the longitudinal axis of pyrene.

twisted PAHs[5a,b] and essentially identical to the phenanthrene analogue **2a**.[5c] In the molecular unit the terminal pyrene (penanthrene[5c]) moieties are **coplanar** (see space filling

(7) Characterization of **3**: ^{1}H NMR (ODCB, 400 K, 500 MHz) δ 8.56 (s, 2H), 7.98 (d, 4H, J = 7.93 Hz), 7.71 (s, 4H), 7.68 (d, 4H, J = 7.93 Hz), 7.33−7.41 (m, 20H), 7.24 (t, 4H, J = 7.93 Hz); elemental analysis found C 95.12, H 4.76; calcd C 95.39, H 4.61; MALDI-TOF MS found 830.2940, calcd 830.2974.

(8) For details, see Supporting Information.

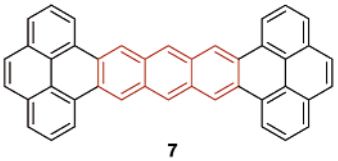
(9) For preparation of **4**, see: Bock, H.; Nick, S.; Ruppert, K. *Z. Naturforsch.* **1995**, *50*, 595.

(10) Bisbenzyne precursor **5** is a modification from the benzyne motif of: Himeshima, Y.; Sonoda, T.; Kobayashi, H. *Chem. Lett.* **1983**, 1211.

(11) Hart, H.; Dong, O. *J. Org. Chem.* **1986**, *51*, 979.

(12) Netka, J.; Crump, S. L.; Rickborn, B. *J. Org. Chem.* **1986**, *51*, 1189.

model in Figure 2), while the central anthracene component (red in Figure 1), is twisted out of plane, adopting a nonpropeller conformation. The twist conformation of **3** is more dramatic than that reported for the parent **7**.[15] The torsional angles measured at C1−C2−C3−C4 and C14−C15−C17−C18 in **3** are 20.6° and 23.0°, respectively, Figure 2. The same torsional angles for **7** were reported to be only 4.0° and 6.2°. The C2−C3 and C15−C17 bonds in **3** (Figure 2) are significantly longer (1.48 Å) than the rest of the C−C bonds. In both molecules, the twist is induced by steric encumbrance stemming from the phenyl substituents (at C1) and hydrogen atoms (at C4) in **3** and hydrogen atoms at C1 and C4 in **7**. However, since **3** has four phenyl substituents, the hydrogen-to-arene effect is more pronounced than the hydrogen-to-hydrogen effect observed in **7**. Hence, not unexpectedly, the degree of deformation for **3** is more dramatic. In the ^{1}H NMR, spectrum the C33 protons resonate at 8.56 ppm, while the C9 (C10) protons resonate at 7.71 ppm, similar to the corresponding protons in phenanthrene (7.69 ppm) and **6** (7.62 ppm).



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To shed more insight into the structure of **3**, we performed DFT (B3LYP) calculations using the 6-31G(d) basis set.[8] The fully optimized structure of **3** (C2−C3 = 1.484 Å, C1−C2−C3−C4 = 21.6°) is very similar to the X-ray structure, indicating that twisting is an intrinsic property of **3** and not due to crystal packing. Pascal et al.[5c] also reached similar conclusions for compound **2a**. The twist observed in **3** is somewhat counterintuitive. We anticipate the phenyl substituents to favor π-stacking, and as a result they would point toward the same general direction, inducing a propeller conformation. Indeed, the twisted conformer exhibited in the X-ray structure is not a global minimum. Another conformer of **3**,[16] where the entire acene skeleton is twisted in one direction, leading to a nearly perpendicular arrangement of a terminal pyrene unit (C9−C10−C9′-C10′ = 86°), is 2.8 kcal/mol lower in energy.

The absorption spectrum of **3** (Figure 3) was measured in *o*-dichlorobenzene (ODCB) and 1,2,4-trichlorobenzene (TCB). The spectra in both solvents are nearly identical, displaying a longest absorption λ_{max} at 530 nm. Despite (or perhaps due to) the significant twisting in **3**, the absorption is approximately 24 nm red-shifted compared to its parent **7** (λ_{max} = 506 nm in TCB).[15a] The bathochromic effect is most likely a result of a combination of the phenyl substituents and

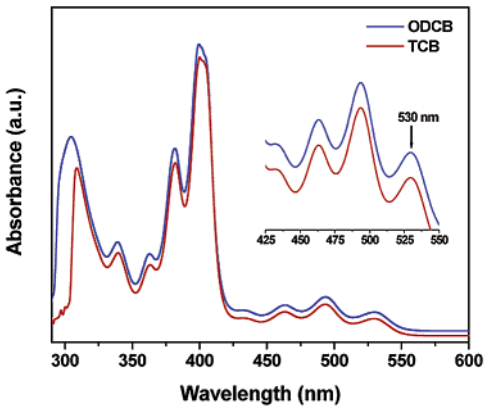

Figure 3. UV−vis spectrum of **3**; inset is a magnified view of the 425−550 nm region.

twisting of the π system. Overall, the λ_{max} of **3** falls between tetracene (475 nm) and pentacene (582 nm), i.e., considerably longer wavelength than anthracene, the longest, non-cross-conjugated moiety in **3**. In addition, **3** is strongly fluorescent with 15% quantum efficiency and essentially zero Stokes shift.[8]

Cyclic voltammetry (CV) of tetrabenzoheptacene **3**, measured in 0.1 M tetrabutylammonium perchlorate (TBAP)/ODCB showed that the oxidation and reduction processes are chemically and electrochemically reversible (Figure 4).

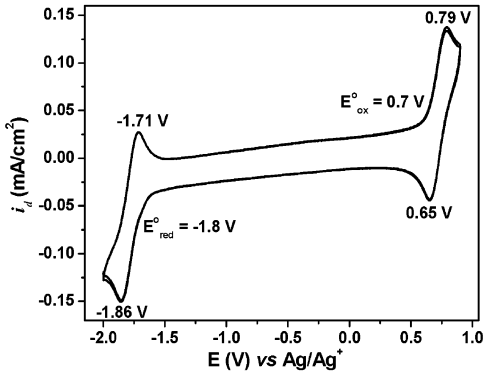

Figure 4. Cyclic voltammogram of 10^{-5} M **3** in 0.1 M TBAP/ODCB (three cycles).

From the CV experiment, the HOMO−LUMO gap, $\Delta E_{HOMO-LUMO}$, is 2.5 eV, in agreement with the value of 2.3 eV derived from the UV−vis data. These values also agreed well with the calculated result [2.6 eV, B3LYP/6-31G(d)]. Furthermore, both calculation and experimental results placed the HOMO−LUMO gap of **3** right between tetracene (calcd 2.8 eV, exptl 2.6 eV) and pentacene (calcd 2.2 eV, exptl 2.1 eV). The HOMO of **3**, at −4.7 eV, is 0.2 eV higher than the HOMO of tetracene, while both the LUMO of **3** and tetracene are located at −2.1 eV. The

(13) Winling, A.; Russell, R. A. *J. Chem. Soc., Perkin Trans. 1* **1998**, 3921.

(14) This notation refers to bisbenzyne precursor where both arynes are promoted in one reaction.

(15) (a) Clar, E. *Polycyclic Hydrocarbons*; Academic Press: London, 1964; Vol. 2, p 200. (b) Ferguson, G.; Parvez, M. *Acta Crystallogr.* **1979**, *B35*, 2419.

(16) See **3a** in Supporting Information.

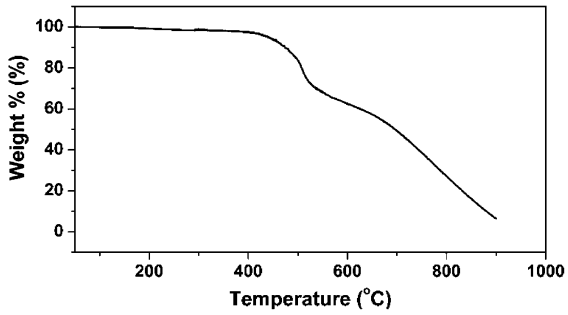

Figure 5. TGA of **3**.

combined photoluminescence and CV results bode well for a luminescent hole-transporting layer in OLEDs.

The nonpropeller twisting motif of **3** is favorable in two ways. First, fusing the pyrenyl terminal units onto an anthracene moiety decreased the $\Delta E_{\mathrm{HOMO-LUMO}}$ of the central acene π-system by approximately 130 nm. This is broken down to about 60 nm per pyrene, calculated using anthracene (375 nm), 1.14,4.5-dibenzopentacene (442 nm),[8] and tetrabenzoheptacene **7** (506).[4] Second, the phenyl substituents shield the central anthracene portion from degradation. This is evident by the fact that **3** showed no sign of decomposition after 3 years of storage at ambient laboratory conditions. Thermogravimetric analysis performed under nitrogen showed a remarkable thermal stability, with weight loss observed only beyond 410 °C (Figure 5). Differential scanning calorimetry also showed no sign of decomposition or melting up to 400 °C.

In conclusion, we developed a swift synthesis of a new heptacene derivative using a bisbenzyne approach. Like its phenanthrene analogue,[5c] the new acene possesses a nonpropeller twist topology that is unusually stable. Distortion from planarity causes only marginal changes in electronic properties and is beneficial for redox stability, required in OLEDs. Taking into account the exceptional stability of our relatively short twistacene, we are extending this approach for syntheses of longer "oligotwistacenes"

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Supporting Information Available: Experimental details for synthesis of **3** and **5**, their characterization, and DFT calculations; structure of **3** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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