

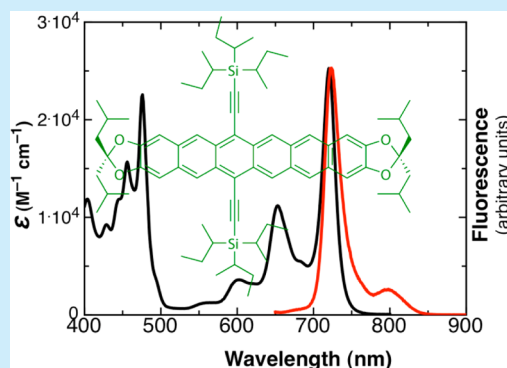
Synthesis and Optical Properties of Dioxolane-Functionalized Hexacenes and Heptacenes

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Supporting Information

ABSTRACT: The synthesis of dioxolane-functionalized hexacenes and heptacenes is reported. While heptacenes were too reactive to be successfully isolated, hexacenes showed higher stability and characteristic long-wavelength fluorescence both in solution and in the solid state as crystalline powders.



Acenes are among the most highly investigated aromatic semiconductor materials in organic electronics, leading to the development of functionalization strategies to increase their solubility, alter their crystal packing, and enhance their semiconducting properties. Although acenes as large as nonacene have been synthesized,¹ pentacene and its derivatives dominate studies of semiconductor device performance due to the diminishing chemical stability of the larger acenes. Several years ago, we developed dioxolane-functionalized pentacenes and noted the enhanced fluorescence relative to pentacene.² The addition of ethyl substituents orthogonal to the chromophore resulted in a highly stable material with strong, solid-state fluorescence useful for the fabrication of red light-emitting diodes³ and photovoltaics.⁴ Curious whether a similar strategy could be applied to larger acenes to enhance stability and solubility while yielding emission in the near-infrared, we describe here the synthesis and basic photophysical properties of dioxolane-functionalized hexacenes and heptacenes.

Our silylthyne-functionalization strategy requires an acenequinone precursor, and the synthetic outline of our approach to the necessary quinones is shown in Scheme 1. Beginning with 6,7-dibromo-2,3-dihydroxy naphthalene,⁵ condensation with the appropriate ketone led to acetals **2a** and **2b** which were used to make both asymmetric “halves” of the acenequinones. The dialdehyde “halves” were constructed through nitriles **3a** and **3b** formed using either Pd-catalyzed⁶ or Rosenmund–von Braun cyanation conditions. Hydrolysis followed by lithium aluminum hydride reduction gave corresponding dimethanols **4a** and **4b** (Figure S1, Supporting Information), which were oxidized under Swern conditions to dialdehydes **5a** and **5b**. The corresponding hydroquinone moieties were also made from synthetic intermediates **2a** and **2b** via aryne formation and trapping with furan to give endoxides **6a** and **6b**. Ring-opening

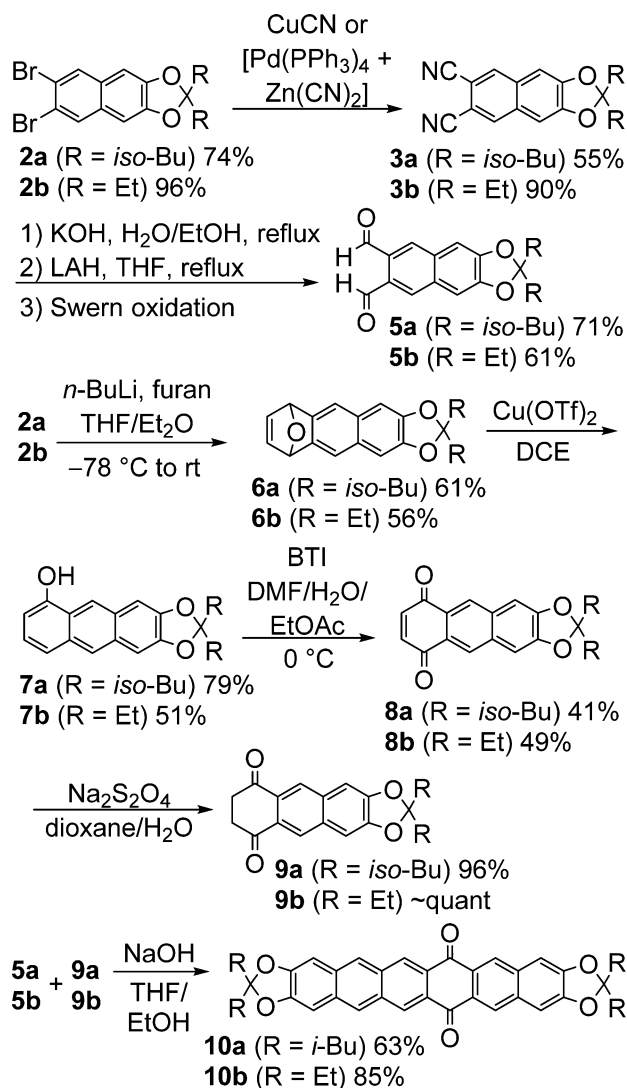
of this type of molecule is often accomplished by treatment with aqueous acid; however, this was not attempted due to the acid-sensitive acetal functional groups. We found that the Lewis acid Cu(OTf)₂ quickly accomplished this transformation to phenols **7a** and **7b**, which were then oxidized with the λ^3 -iodane reagent [bis(trifluoroacetoxy)iodo]benzene (BTI) to yield anthraquinones **8a** and **8b**.^{7,8} Reduction with sodium dithionite then gave diketones **9a** and **9b**. Although such species are frequently represented as hydroquinones, ¹H and ¹³C NMR evidence suggests these compounds were isolated as the keto tautomers shown. Precursors **5** and **9** were subjected to base-mediated aldol condensation to form quinones **10a** and **10b**. Crystals suitable for single-crystal X-ray analysis were grown from toluene, confirming their structures (Figure S2, Supporting Information). Both structures were disordered with respect to the carbonyl oxygens, a result of the pseudo inversion inherent to the asymmetric molecular structures of the quinones.

Treatment with bulky lithiated (trialkylsilyl)acetylenes followed by deoxygenation with aqueous SnCl₂ yielded the desired deep-green hexacenes (Scheme 2). Crystals of three of the hexacenes were grown, but they were not suitable for X-ray analysis. Hexacenes **11** and **12** were significantly more stable than **13** and **14**. While **11** and **12** withstood recrystallization from boiling hexanes and acetone, respectively, both **13** and **14** underwent decomposition at these elevated temperatures and purification by repeated recrystallization proved futile. These results suggest the more bulky isobutyl groups of **11** and **12** contribute to the enhanced stability relative to results **13** and **14** by hindering face-to-face dimerization.⁹

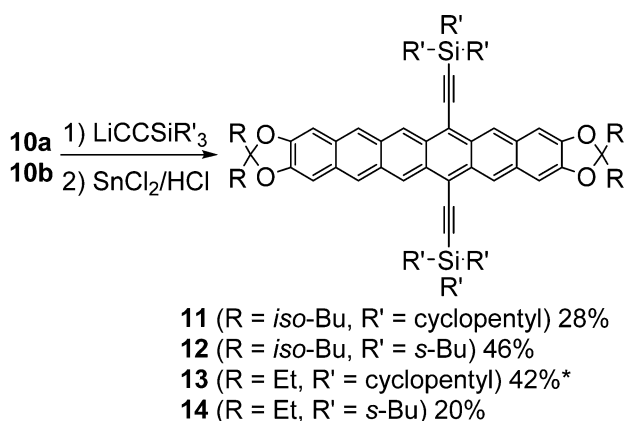
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Scheme 1. Synthesis of Hexacenequinones

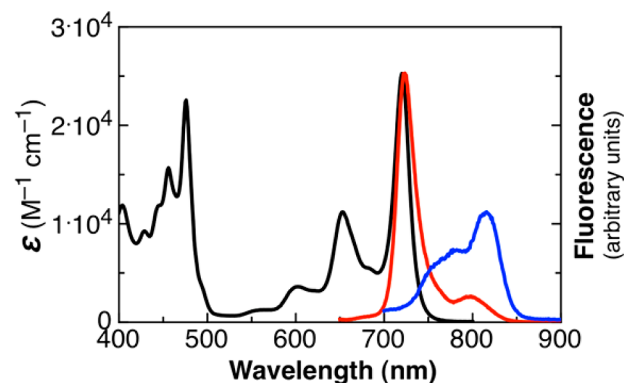


Scheme 2. Synthesis of Hexacenes



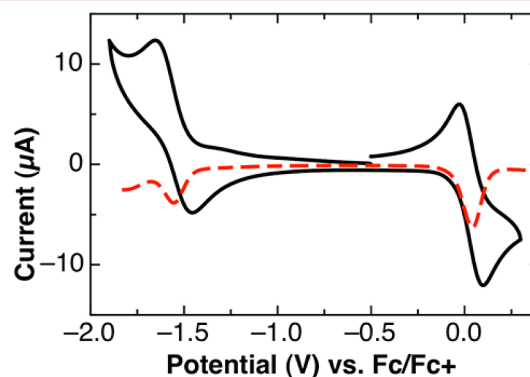
* indicates impure crystalline yield

Representative solution absorption and fluorescence as well as solid-state fluorescence spectra of dioxolane hexacene **12** are shown in Figure 1. In comparison to the solution fluorescence spectrum showing the expected mirror image of absorption, emission from powdered crystals of **12** appears anomalous. The

Figure 1. Solution absorption (black) and emission (red) spectra in hexanes and solid-state emission spectrum (blue) of hexacene **12**.

solution fluorescence shows an emission maximum at 723 nm, which corresponds to a peak-to-peak Stokes shift of only 3 nm, leading to significant reabsorption of the 0–0 vibronic emission band in the solid state. At longer wavelengths the absorbance is very low, so more intense emission is observed in spite of the smaller Franck–Condon factors. The Stokes shift observed here is similar to the analogous pentacenes, although the fluorescence quantum yields are substantially lower.

The electrochemistry of hexacene **12** was also investigated (Figure 2). Cyclic voltammetry shows reversible oxidation and

Figure 2. Cyclic and differential pulse voltammetry of **12**.

reduction corresponding to HOMO and LUMO level energies of -4.84 and -3.24 eV, respectively. Differential pulse voltammetry supports these values. The electrochemical HOMO–LUMO gap of 1.60 eV agrees well with the optically determined HOMO–LUMO gap.

In addition to hexacenes, the analogous heptacenes were prepared (Figure S3, Supporting Information). Structures of the quinones were verified by single-crystal X-ray analysis (Figure S4, Supporting Information). Standard ethynylation procedures gave a mixture of *syn*- and *anti*-diols, which were isolated chromatographically. While the corresponding heptacenes proved too reactive to isolate, we could obtain in situ visible-NIR spectra by performing deoxygenation in a cuvette. The absorption spectrum (Figure 3) shows the expected vibronic bands characteristic of acenes and is in agreement with other reported functionalized heptacenes.¹⁰

We have prepared several dioxolane-functionalized hexacenes from commercially available and inexpensive 2,3-dihydroxynaphthalene. The bulkier isobutyl substituents were found to give the hexacenes added stability. These hexacenes exhibited

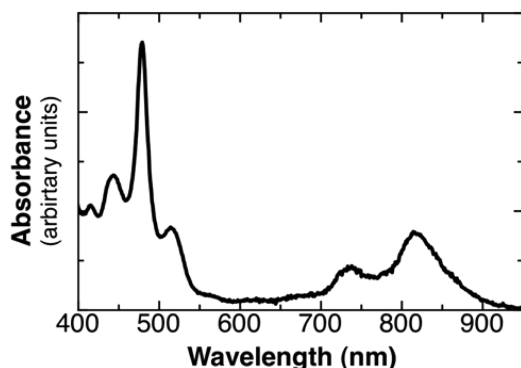


Figure 3. Visible–NIR absorption spectrum (in situ) of dioxolane heptacene 17 in THF.

long-wavelength fluorescence both in solution as well as in the solid state as powdered crystals. Dioxolane-functionalized heptacenes were also synthesized, but all attempts to isolate these materials have been unsuccessful. We are now exploring the use of these hexacenes in applications requiring hydrophobic materials with near-infrared fluorescence.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental procedures, spectroscopic data, and crystallographic CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) (a) Purushothaman, B.; Bruzek, M.; Parkin, S. R.; Miller, A.-F.; Anthony, J. E. *Angew. Chem., Int. Ed.* **2011**, *50*, 7013. (b) Kaur, I.; Jazdzzyk, M.; Stein, N.; Prusevich, P.; Miller, G. *J. Am. Chem. Soc.* **2010**, *132*, 1261.
- (2) Payne, M. M.; Delcamp, J. H.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2004**, *6*, 1609.
- (3) (a) Wolak, M. A.; Melinger, J. S.; Lane, P. A.; Palilis, L. C.; Landis, C. A.; Delcamp, J.; Anthony, J. E.; Kafafi, Z. H. *J. Phys. Chem. B* **2006**, *110*, 7928. (b) Wolak, M. A.; Melinger, J. S.; Lane, P. A.; Palilis, L. C.; Landis, C. A.; Anthony, J. E.; Kafafi, Z. H. *J. Phys. Chem. B* **2006**, *110*, 10606.
- (4) Palilis, L. C.; Lane, P. A.; Kushto, G. P.; Purushothaman, B.; Anthony, J. E.; Kafafi, Z. *Org. Electron.* **2008**, *9*, 747.
- (5) Cammidge, A. N.; Chambrier, I.; Cook, M. J.; Garland, A. D.; Heeney, M. J.; Welford, K. *J. Porphyrins Phthalocyanines* **1997**, *1*, 77.
- (6) For alternative conditions, see: Iqbal, Z.; Lyubimtsev, A.; Hanack, M. *Synlett* **2008**, 2287.
- (7) Peng, F.; Fan, B.; Shao, Z.; Pu, X.; Li, P.; Zhang, H. *Synthesis* **2008**, 3043.
- (8) Wu, A.; Duan, Y.; Xu, D.; Penning, T. M.; Harvey, R. G. *Tetrahedron* **2010**, *66*, 2111.
- (9) Purushothaman, B.; Parkin, S. R.; Anthony, J. E. *Org. Lett.* **2010**, *12*, 2060.
- (10) (a) Payne, M. M.; Parkin, S. R.; Anthony, J. E. *J. Am. Chem. Soc.* **2005**, *127*, 8028. (b) Chun, D.; Cheng, Y.; Wudl, F. *Angew. Chem., Int. Ed.* **2008**, *47*, 8380. (c) Kaur, I.; Stein, N. N.; Kopreski, R. P.; Miller, G. P. *J. Am. Chem. Soc.* **2009**, *131*, 3424. (d) Qu, H.; Chi, C. *Org. Lett.* **2010**, *12*, 3360. (e) Mondal, R.; Tönshoff, C.; Khon, D.; Neckers, D.; Bettinger, H. *J. Am. Chem. Soc.* **2009**, *131*, 14281.