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Tetracene Derivatives as Potential Red Emitters for Organic LEDs

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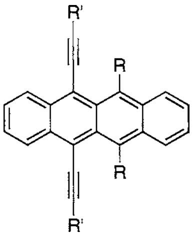
ABSTRACT



As part of our program investigating the use of ethynylated acenes in organic electronics, we have prepared a series of functionalized tetracene derivatives in search of a material with red emission suitable for use in display technologies. A number of such compounds with functionalization on the alkyne and/or the acene ring were easily prepared in one or two steps from commercially available materials. Solution fluorescence quantum efficiencies were generally good for these derivatives, which possessed emission maxima spanning the range 540–637 nm. Simple light-emitting diodes fabricated from these compounds showed that one of the derivatives did exhibit red electroluminescence.

Acenes, the series of *cata*-condensed aromatic hydrocarbons, are at the forefront of current research into organic electronic devices. Pentacene and tetracene have been used as the active layer of high-performance organic field-effect transistors[1] and have both been used as hole collectors in organic photovoltaic cells.[2] Acenes have also found use in organic light-emitting diodes (OLEDs), where the typically high fluorescence efficiency of these aromatic compounds makes them ideal emitters. Functionalized anthracene has been reported to yield efficient blue OLEDs,[3] while substituted pentacene derivatives act as a guest dye in Alq$_3$-based devices to produce red electroluminescence.[4] There are no published reports of the use of tetracene as the emissive material in OLEDs, ostensibly due to the parent compound's poor oxidative stability,[5] combined with emission (476 nm) falling outside the range considered most exploitable in display technologies.

Our research into functionalized pentacene[6] led us to consider whether functionalized tetracene could be adapted, by the addition of appropriate substituents, to become an acceptable red emitter for use in electroluminescent displays. Functionalized tetracene has several potential advantages over the larger pentacene: The smaller aromatic unit in tetracene, combined with the substituted alkyne functional groups hindering Diels−Alder reactivity on the central rings, leads to higher stability of this material over pentacene. The increased solubility of functionalized tetracenes may make

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(1) (a) Gundlach, D. J.; Nichols, J. A.; Zhou, L.; Jackson, T. N. *Appl. Phys. Lett.* **2002**, *80*, 2925. (b) Würthner, F. *Angew. Chem., Int. Ed.* **2001**, *40*, 1037. (c) Nelson, S. F.; Lin, Y.-Y.; Gundlach, D. J.; Jackson, T. N. *Appl. Phys. Lett.* **1998**, *72*, 1854. (d) Dimitrakopoulos, C. D.; Furman, B. K.; Graham, T.; Hedge, S.; Purushothaman, S. *Synth. Met.* **1998**, *92*, 47.

(2) (a) Senadeera, G. K. R.; Jayaweera, P. V. V.; Perera, V. P. S.; Tennakone, K. *Solar Energy* **2002**, *73*, 103. (b) Videlot, C.; Fichou, D.; Garnier, F. *J. Chim. Phys. Phys.-Chim. Biol.* **1998**, *95*, 1335. (c) Dahlberg, S. C.; Musser, M. E. *J. Chem. Phys.* **1979**, *71*, 2806. (d) Matsumura, M.; Uohashi, H.; Furusawa, M.; Yamamoto, N.; Tsubomura, H. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 1965.

(3) (a) Zhang, Z. L.; Jiang, X. Y.; Zhu, W. Q.; Zheng, X. Y.; Wu, Y. Z.; Xu, S. H. *Synth. Met.* **2003**, *137*, 1141. (b) Kondakov, D. Y.; Sandifer, J. R.; Tang, C. W.; Young, R. H. *J. Appl. Phys.* **2003**, *93*, 1108. (c) Danel, K.; Huang, T.-H.; Lin, J. T.; Tao, Y.-T.; Chuen, C.-H. *Chem. Mater.* **2002**, *14*, 3860. (d) Jiang, X.-Y.; Zhang, Z.-L.; Zheng, X.-Y.; Wu, Y.-Z.; Xu, S.-H. *Thin Solid Films* **2001**, *401*, 251.

(4) Picciolo, L. C.; Murata, H.; Kafafi, Z. H. *Appl. Phys. Lett.* **2001**, *78*, 2378.

(5) (a) Venedictov, E. A.; Tulikova, E. J. *Tetrahedron Lett.* **2003**, *44*, 3215. (b) Cicerone, M. T.; Ediger, M. D. *J. Phys. Chem.* **1993**, *97*, 10489.

(6) Anthony, J. E.; Eaton, D. L.; Parkin, S. R. *Org. Lett.* **2002**, *4*, 15. (b) Anthony, J. E.; Brooks, J. S.; Eaton, D. L.; Parkin, S. R. *J. Am. Chem. Soc.* **2001**, *123*, 9482.

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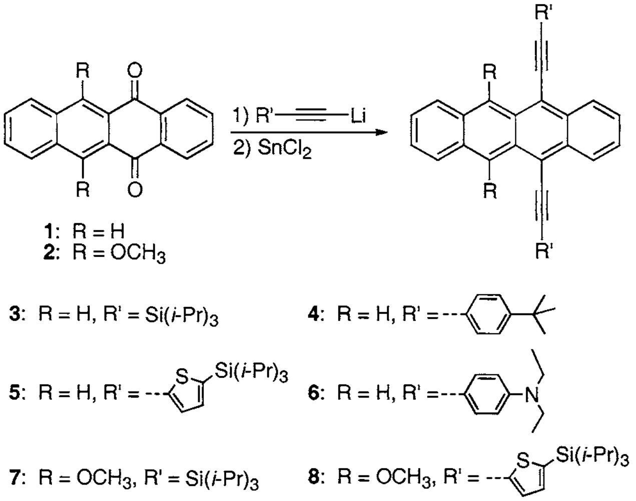
them more amenable to inexpensive solution deposition for device fabrication. Inducing bathochromic shifts using a wide variety of substituents will also allow the “fine-tuning” of the emission color. We report here the synthesis of a series of substituted tetracene derivatives, their solution absorption and emission spectra, and the electroluminescence characteristics of the derivatives with properties amenable to device fabrication.

Following the precedent of our recent work with ethynylated pentacene derivatives, we sought to prepare a series of ethynylated tetracenes with various substituents on the alkynes. The most prevalent method for the ethynylation of aromatic compounds involves Sonogashira coupling between a terminal alkyne and an aryl bromide or iodide.[7] Unfortunately, this method results in the formation of ring-fused side products when applied to halides on the *peri* position of linearly fused systems.[8] We avoid these confounding side products by adopting an alternative procedure to palladium-catalyzed coupling reactions. The addition of a lithium acetylide to an acenequinone, followed by deoxygenation with stannous chloride, provides the diethynyl acene in good to excellent yield.[9] Following this procedure, the desired ethynylated tetracenes **3**−**8** are easily prepared from 5,12-tetracenequinone **1** and 6,11-dimethoxy-5,12-tetracenequinone **2** (Scheme 1, for yields see Table 1).[10]

Scheme 1



Along with the superior solubility of these materials in common organic solvents, the most notable difference between these derivatives and the parent hydrocarbon tetracene is the generally improved oxidative stability of the alkyne-functionalized materials. While solutions of tetracene decolorize within 48 h when left exposed to light and oxygen,[11] many of the ethynylated materials were stable for months under identical conditions. This behavior mimics that observed for the silylethynylated pentacenes and is likely due to an increase in oxidation potential (Table 1).[12]

Table 1. Synthetic Yield and Spectroscopic and Electrochemical Data for Compounds **3**−**8**

compd	% yield	λ_{max}abs (nm)	λ_{max}em (nm)	Φ_{rel} (%)	λ_{max}EL (nm)	E_{ox} (mV)[a] vs SCE
tetracene		475	476			720
3	98	534	540	79	543	910
4	98	556	567	81		830
5	55	571	586	69	595	568
6	49	597	643	10		806
7	88	580	604	19	604	750
8	17	617	637	36	656	610

[a] Performed in 0.1 M solution of Bu_4NPF_6 in dichloromethane, Pt electrode, scan rate of 150 mV/s, ferrocene as internal standard.

All of the tetracene derivatives possess the characteristic strong β-band absorption at approximately 290 nm, and as expected, this band shifts only slightly with changes in substitution.[13] The long-wavelength absorptions are more sensitive to substitution and undergo significant variations upon change in functionality.[14] Simple ethynylation produces a bathochromic shift of 55−115 nm, depending on the alkyne substituent (compounds **3**−**6**). The addition of two π-electron-donating methoxy groups to the acene backbone further shifts these values by ~50 nm.[15] The sensitivity of this long-wavelength band to substitution thus allows the tuning of absorption over the range of 475 nm (unsubstituted tetracene) to 617 nm (compound **8**). Absorption spectra showing the long-wavelength region for the ethynylated tetracene derivatives **3**−**8**, along with that for unsubstituted tetracene, are represented by the black traces in Figure 1.

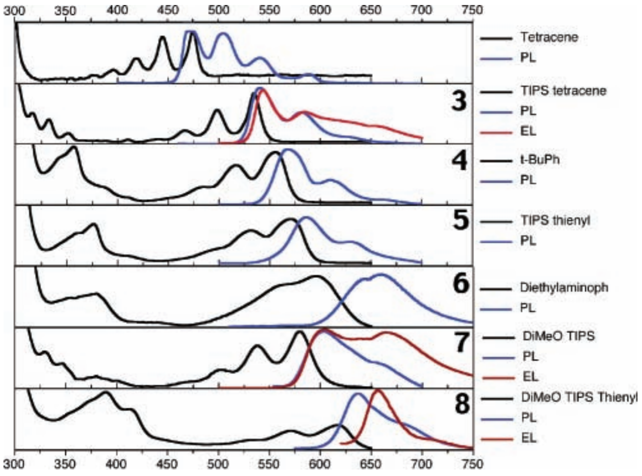


Figure 1. Absorbance (black traces), photoluminescence (PL, blue traces), and electroluminescence (EL, red traces) spectra for compounds **3**−**8**, taken in hexane.

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[7] Sonogashira, K.; Tohda, Y.; Hagihara, N. *Tetrahedron Lett.* **1975**, 4467.

[8] Dang, H.; Garcia-Garibay, M. A. *J. Am. Chem. Soc.* **2001**, *123*, 355.

[9] See e.g. Hanhela, P. J.; Paul, D. B. *Aust. J. Chem.* **1981**, *34*, 1701.

[10] Comound **8** did not crystallize readily from any solvent. To attain material pure enough for device fabrication, repeated chromatography on silica led to significant decomposition, and thus a low yield, of product **8.**

The ethynylated tetracene derivatives are all fluorescent in solution, with relative fluorescence quantum yields ranging from 10% to 81% (versus a rubrene standard).[16] Solution photoluminescence spectra, represented as the blue traces in Figure 1, showed the expected fine-structure typically mirroring the absorption features and emission $\lambda_{\max}$ ranging from 540 to 637 nm.[17] For use in a red-emitting OLED, the material should have as narrow an emission as possible, close to the low-wavelength end of the red portion of the spectrum (typically ~620 nm). Emission at wavelengths much longer than this value is less important due to the poor spectral response of the human eye at longer wavelengths. Both compounds **6** and **8** satisfy these criteria.

Determination of the electroluminescence spectra of these materials must involve the construction of a light-emitting device. Because we are interested in the color of the emission, rather than optimum device performance, we used a highly simplified device structure. While most small-molecule OLEDs incorporate Alq_3 as an electron-transport layer, electroluminescence from this compound can alter the color of the emissive layer.[18] To maintain color purity, the functionalized tetracene was used as both the emissive layer and the electron transport layer in our devices. We did find that incorporation of a lithium fluoride "buffer layer" between the cathode and the acene significantly improved device performance without altering the emission wavelength of the acene.[19] The simple device configuration is shown in Figure 2, and the specifics of device fabrication and performance are reported in the Supporting Information.

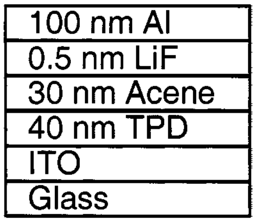

Figure 2. Configuration of simple tetracene-based devices.

To form working devices, the emissive material must be sufficiently volatile under high vacuum to be deposited onto the substrate. Unfortunately, neither of the aryl-ethynylated derivatives (**4**, **6**) evaporated before decomposing, both leaving an insoluble black residue on the evaporation boat. All of the derivatives containing the bulky tri(isopropyl)silyl group did yield homogeneous films by evaporation. Electroluminescence (EL) produced by the devices made from compound **5** (with $\lambda_{\max}$ 595 nm) was so weak that it is not shown in Figure 1.

The EL spectra for compounds **3**, **7**, and **8** are shown as the red traces in Figure 1. Derivative **3** exhibits a solid-state electroluminescence maximum at 543 nm nearly identical to the solution-state fluorescence and yields a bright orange OLED. The methoxy homologue **7** has a beautiful red-orange emission, with a maximum at 604 nm identical to the solution emission, but with an additional strong emission at 670 nm and significant tailing to longer wavelengths. Such behavior is frequently attributed to aggregation, particularly involving interaction between π-faces of adjacent molecules.[20] To further investigate the solid-state order of **7** we acquired the X-ray crystal structure of this compound. Because films formed by the thermal evaporation of acenes are typically polycrystalline, we expect a strong correlation between the order of the molecules in the thin film and the order in the single crystal.[21] As shown in Figure 3, there is indeed π-interaction between adjacent molecules in the solid state. Excimer formation arising from these interactions may be the cause of the undesired long-wavelength emission. Be-

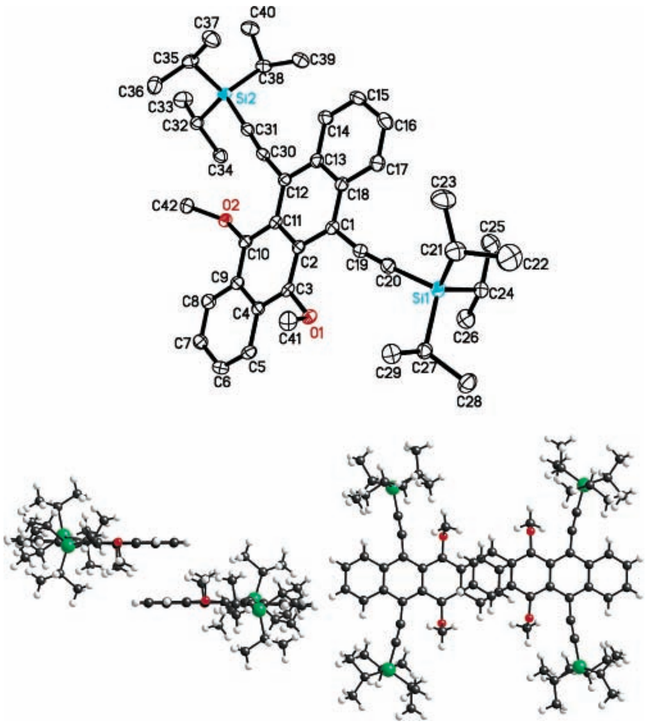

Figure 3. Crystal structure of compound **7**, showing π-interaction between adjacent molecules in the crystal.

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(11) Fritzsche, J. *Comptes Rendus Acad. Sci.* **1867**, *69*, 1035.

(12) The tetracene derivatives also exhibited a generally higher thermal stability versus tetracene, undergoing decomposition under TGA analysis (air atmosphere) at between 20 and 50 ° C higher temperature than the parent hydrocarbon.

(13) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: New York, 1970.

(14) Not surprisingly, the shifts in absorption follow the predictions made by applying the Woodward−Fieser rules to tetracene.

(15) The magnitude of this shift agrees with the empirical rules for absorption spectroscopy, each methoxy group inducing a shift of ~25 nm.

(16) Fery-Forgues, S.; Lavabre, D. *J. Chem. Educ.* **1999**, *76*, 1260. Rubrene quantum yield is essentially 1 in nonpolar solvents (all measurements done in hexane): Mattoussi, H.; Murata, H.; Merritt, C. D.; Lizumi, Y.; Kido, J.; Kafafi, Z. H. *J. Appl. Phys.* **1999**, *86*, 2642.

(17) The thin-film PL spectra of these compounds were essentially identical to EL spectra in all cases and have been omitted for clarity.

(18) (a) Troadec, D.; Veriot, G.; Moliton, A. *Synth. Met.* **2002**, *127*, 165. (b) Aziz, H.; Popovic, Z. D. *Appl. Phys. Lett.* **2002**, *80*, 2180.

cause neat films of **7** also exhibited the same long-wavelength absorption, this feature is not likely caused by interaction between **7** and the hole-transport layer (TPD).

Compound **8** shows a relatively sharp electroluminescence emission maximum at 656 nm and produces a deep red-colored emission. The solid-state electroluminescence is shifted almost 20 nm relative to the solution emission, a behavior also seen in the ethynylated pentacenes. However, there is no broadening of the emission peak characteristic of aggregate formation. The origin of this bathochromic shift in the ethynylated tetracenes and pentacenes is currently under investigation.

By careful functionalization of the tetracene backbone, it is indeed possible to tune the photoluminescence and electroluminescence emission to a significantly longer wavelength, while simultaneously improving the stability and solubility of the emissive molecule over the parent hydrocarbon. Compound **8** can be used to prepare a red-emitting diode, using a very simple device structure. Further investigation of the ethynylated acenes, to improve device performance, is currently underway.

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Supporting Information Available: Experimental procedures, characterization and crystallographic data for compound **7**, and device fabrication procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) See, for example: Shtein, M.; Mapel, J.; Benziger, J. B.; Forrest, S. R. *Appl. Phys Lett.* **2002**, *81*, 268 and references therein.