ORGANIC LETTERS

2010
Vol. 12, No. 17
3874−3877

C-9 Fluorenyl Substituted Anthracenes: A Promising New Family of Blue Luminescent Materials

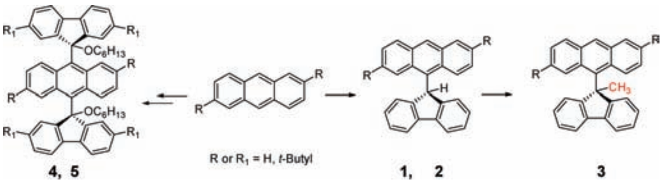
Jing Wang,[†] Wen Wan,*[,†] Haizhen Jiang,[†] Yan Gao,[†] Xueyin Jiang,[‡] Huaping Lin,[‡] Weiming Zhao,[§] and Jian Hao*[,†,||]

Department of Chemistry, Shanghai University, Shanghai, China, School of Materials, Shanghai University, Shanghai, China, Litewell Technology Inc., Dongguan, Guangdong, China, and Key Laboratory of Organofluorine Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences, Shanghai, China

wanwen@staff.shu.edu.cn; jhao@staff. shu.edu.cn

Received July 7, 2010

ABSTRACT



Syntheses, optical, and electrochemical properties of novel C-9 fluorenyl substituted anthracenes linked by a tetrahedral *sp*^{3}-hybridized carbon atom are reported for blue light emitting materials. Remarkably, an unoptimized organic light-emitting diode based on 1-fold fluorene-functionalized anthracene 3 exhibits a radiance of 4100 cd/m^2 at 12 V and a maximum EL efficiency of 1.36 cd/A with color purity CIE *x*, *y* (0.157, 0.082), which is very close to the National Television System Committee standard blue.

Since the breakthrough discovery by Tang and VanSlyke in organic light emitting diodes (OLEDs),[1] significant progress has been made because of their potential applications in full-color large displays.[2] Developing higher efficiency and purer blue light emitting materials is still a challenge due to the intrinsic wide band gap irrespective of the type of materials.[3]

Because of their high solution and solid-state photoluminescence (PL) quantum yields, research into blue-emitting materials has been focused on fluorene and anthracene derivatives in recent years.[4] In order to avoid the formation of polycrystalline films and improve thermal stability, bulky groups are often introduced to the fluorene moieties to obtain the desired spiro materials due to its specific steric configurations.[5] Terfluorenes, oligomeric fluorenes, spirofluorene-linked anthracenes, and the difuorene-indenofuorene com-

---

[†] Department of Chemistry, Shanghai University.
[‡] School of Materials, Shanghai University.
[§] Litewell Technology Inc.
[||] Chinese Academy of Sciences.

(1) Tang, C. W.; VanSlyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913–915.

(2) (a) Burrows, P. E.; Gu, G.; Bulovic, V.; Shen, Z.; Forrest, S. R.; Thompson, M. E. *IEEE Trans. Electron Devices* **1997**, *44*, 1188–1203. (b) Miyata, S.; Nalwa, H. S. *Organic Electroluminescent Materials and Devices*; Gordon and Breach Publishers: New York, 1997. (c) Wong, T. K. S. In *Handbook of Organic Electronics and Photonics*; Nalwa, H. S., Eds.; American Scientific Publishers: Stevenson Ranch, CA, 2008; Vol. 2, pp 413−472.

(3) (a) Cocherel, N.; Poriel, C.; Vignau, L.; Bergamini, J. F.; Rault-Berthelot, J. *Org. Lett.* **2010**, *12*, 452–455. (b) Goel, A.; Chaurasia, S.; Dixit, M.; Kumar, V.; Prakash, S.; Jena, B.; Verma, J. K.; Jain, M.; Anand, R. S.; Manoharan, S. S. *Org. Lett.* **2009**, *11*, 1289–1292. (c) Moorthy, J. N.; Venkatakrishnan, P.; Natarajan, P.; Huang, D. F.; Chow, T. J. *J. Am. Chem. Soc.* **2008**, *130*, 17320–17333.

(4) (a) Kim, K. S.; Jeon, Y. M.; Kim, J. W.; Lee, Ch. W.; Gong, M. S. *Org. Electron.* **2008**, *9*, 797–804. (b) Tonzola, C. J.; Kulkarni, A. P.; Gifford, A. P.; Kaminsky, W.; Jenekhe, S. A. *Adv. Funct. Mater.* **2007**, *17*, 863–874. (c) Moorthy, J. N.; Natarajan, P.; Venkatakrishnan, P.; Huang, D. F.; Chow, T. J. *Org. Lett.* **2007**, *9*, 5215. (d) Gebeyehu, D.; Walzer, K.; He, G.; Pfeiffer, M.; Leo, K.; Brandt, J.; Gerhard, A.; Stoessel, P.; Vestweber, H. *Synth. Met.* **2005**, *148*, 205–211.

(5) (a) Saragi, T. P. I.; Spehr, T.; Siebert, A.; Fuhrmann-Lieker, T.; Salbeck, J. *Chem. Rev.* **2007**, *107*, 1011–1065. (b) Gong, X.; Iyer, P. K.; Moses, D.; Bazan, G. C.; Heeger, A. J.; Xiao, S. S. *Adv. Funct. Mater.* **2003**, *13*, 325–330.

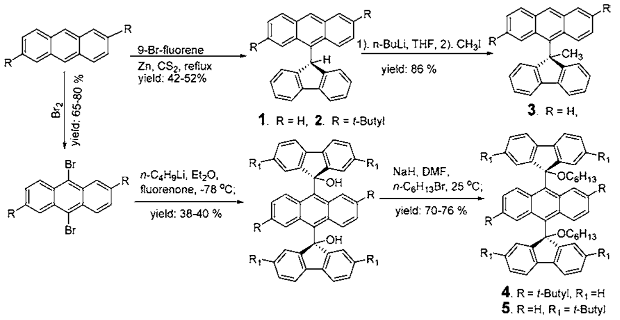
10.1021/ol101553a

pounds are generally regarded as the most promising candidates for blue OLEDs.[6]

To date, the anthracene moiety, which exhibits a highly efficient fluorescence property, with derivatives that are one of the best blue host materials, is often directly introduced to fluorene *via* aryl−aryl coupling. However, the introduction of anthracene into the C-9 position of fluorene, in which the anthracene and fluorene moieties are connected through a tetrahedral *sp*^{3}-hybridized carbon atom, has not been disclosed. The C-9 introduction of a bulky anthracene moiety is expected not only to increase molecular rigidity but also to effectively hinder close packing and intermolecular interactions, so that the tendency for molecules to crystallize should be reduced.

In this paper, we wish to report our design and preparation of two kinds of new chromophores, which contain one or two tetrahedral centers in 1-fold or 2-fold fluorene-functionalized anthracene derivatives. The tetrahedral nature of the *sp*^{3}-hybridized carbon atom (at the C-9 position of the fluorene moiety) connects the conjugated moieties of fluorene and anthracene through a σ-bond, which in turn serves as a conjugation interrupt. Thus, the desired electronic and optical properties of the corresponding chromophores combining both fluorene and anthracene's architectural specificities are expected to be preserved.[7] The photophysical, electrochemical, and electroluminescent characteristics of these chromophores in unoptimized OLED devices are also initially evaluated.

Scheme 1. Synthesis of C-9 Fluorenyl Substituted Anthracenes



As shown in Scheme 1, 9-bromofluorene was introduced into the 9-position of anthracene directly under the promotion of activated zinc powder in CS_2 solvent, affording the 1-fold fluorene-functionalized derivatives **1** and **2** with a tetrahedral center. This radical coupling of fluorene and anthracene was examined by using a variety of metals, such as Zn, Fe, Cu, Sm, in different solvents (CS_2, CCl_4, Et_2O, DMSO, NH_4Cl/MeOH) in order to improve the yields of the desired compounds **1** and **2**. It was found that the zinc-mediated radical reaction in CS_2 solvent provided a much better yield than other reaction conditions.[8] In order to increase the electrochemical stabilities of 1-fold fluorene-functionalized anthracene, the methylation of **1** was applied *via* deprotonation at the active C-9 position by *n*-BuLi and followed by an electrophilic substitution reaction with methyl idoide. The C-9 methylated 1-fold substituted derivative **3** was expected to exhibit stronger rigidity due to the existence of a steric effect of the methyl group.

The lithium−bromine exchange of 9,10-dibromoanthracene with *n*-BuLi at low temperature (−78 °C), followed by quenching with fluorenone derivatives, provided the difluorenols in moderate yields. Further alkylations with 1-bromohexane yielded the 2-fold substituted chromophores **4** and **5**, in which two tetrahedral centers were constructed simultaneously.

A single crystal of compound **2** (CCDC 765306) was cultivated from pentane and analyzed by X-ray crystallography to establish the pattern of substitution and its structure. As shown in Figure 1, the bulky fluorene moiety is nearly perpendicular relative to the anthracene ring, while two *tert*-butyl groups are at the 2,6-positions of anthracene. This conformation effectively releases the steric interactions between the anthracene and fluorene cores and prevents interchromophore interactions. Thus, the introduction of the tetrahedral *sp*^{3}-hybridized carbon atom center should break the π-stacking and prevent the excimer formation which causes the concentration quenching of fluorescence in a solid state.[9]

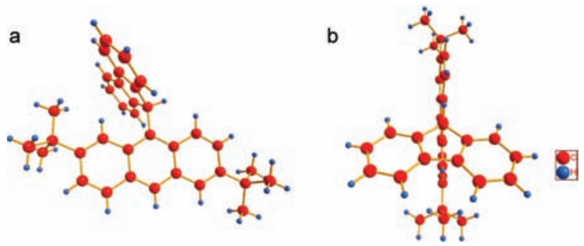


Figure 1. (a) Molecular view of X-ray structure of **2** (left). (b) Top view from the structure (right).

UV−vis absorption, photoluminescence, thermal, and electrochemical properties of these compounds are summarized in Table 1. The absorption spectra of the 1- and

---

[6] (a) Poriel, C.; Rault-Berthelot, J.; Barriere, F.; Slawin, A. M. Z. *Org. Lett.* **2008**, *10*, 373–376. (b) Horhant, D.; Liang, J. J.; Virboul, M.; Poriel, C.; Alcaraz, G.; Rault-Berthelot, J. *Org. Lett.* **2006**, *8*, 257–260. (c) Wong, K. T.; Liao, Y. L.; Lin, Y. T.; Su, H. C.; Wu, C. C. *Org. Lett.* **2005**, *7*, 5131–5134. (d) Chao, T. C.; Lin, Y. T.; Yang, C. Y.; Hung, T. S.; Chou, H. C.; Wu, C. C.; Wong, K. T. *Adv. Mater.* **2005**, *17*, 992–996. (e) Tao, S.; Peng, Z.; Zhang, X.; Wang, P.; Lee, C. S.; Lee, S. T. *Adv. Funct. Mater.* **2005**, *15*, 1716–1721.

[7] (a) Shen, W. J.; Dodda, R.; Wu, C. C.; Wu, F. I.; Liu, T. H.; Chen, H. H.; Chen, C. H.; Shu, C. F. *Chem. Mater.* **2004**, *16*, 930–934. (b) Chiang, C. L.; Shu, C. F. *Chem. Mater.* **2002**, *14*, 682–687. (c) Wu, F. I.; Dodda, R.; Reddy, D. S.; Shu, C. F. *J. Mater. Chem.* **2002**, *12*, 2893–2897.

[8] (a) Estevam, I. H. S.; Bieber, L. W. *Tetrahedron Lett.* **2003**, *44*, 667–670. (b) Lavilla, B.; Coll, O.; Bosch, J.; Orozco, M.; Luque, F. J. *Eur. J. Org. Chem.* **2001**, 3719–3729. (c) Li, C. J. *Chem. Rev.* **1993**, *93*, 2023–2035.

[9] (a) Wurthner, F.; Thalacker, C.; Diele, S.; Tschierske, C. *Chem.−Eur. J.* **2001**, *7*, 2245–2253. (b) Jenekhe, S. A.; Osaheni, J. A. *Science* **1994**, *265*, 765–768.

Table 1. Optical, Thermal, and Electrical Properties of Compounds **1**−**5**

Compd	$\lambda_{\text{max, Abs}}$ (nm)[a]	$\lambda_{\text{max, PL}}$ (nm)[a]	$\lambda_{\text{max, PL}}$ (nm)[b]	HOMO (eV)	LUMO (eV)	QE (ϕ)[c]	T_m (°C)[d]
1	261	390, 418	457	5.62	2.54	0.47	223
2	264	409, 434	435	5.56	2.64	0.59	256
3	263	387, 408	443	5.61	2.52	0.67	165
4	273	446	463	5.43	2.56	0.90	166
5	273	433	451	5.42	2.56	0.45	181

[a] Measured in CH_2Cl_2. [b] Measured in thin film solid. [c] Quantum effeciency. [d] Melting point.

2-fold fluorene-substituted anthracenes showed the characteristic vibronic patterns in the range of 330 to 400 nm (shown in Figure 2a), indicating the existence of a $\pi-\pi^*$ transition derived from the substituted anthracene backbone. All the emission maxima in CH_2Cl_2 for 1-fold functionalized derivatives **1**, **2**, and **3** lay in the region between 380 and 440 nm. A *ca.* 20−40 nm red shift in the thin film occurs (shown in Figure 2b) as compared to those in the solution state. It is noteworthy that the absorption and emission maxima shift toward the longer wavelength region by *ca.* 10−20 nm upon introduction of 2-fold functionalized anthracenes, as compared to those of 1-fold functionalized anthracenes. The photoluminescence quantum yields (ϕ) for **1**−**5** were determined in cyclohexane using quinine sulfate as a standard. The efficiencies of both 1- and 2-fold functionalized anthracenes were in the range of 0.45−0.90. The C-9 methyl substituted 1-fold functionalized derivative **3** was found to show higher photoluminescence quantum efficiency than the other 1-fold functionalized derivatives **1** and **2**.

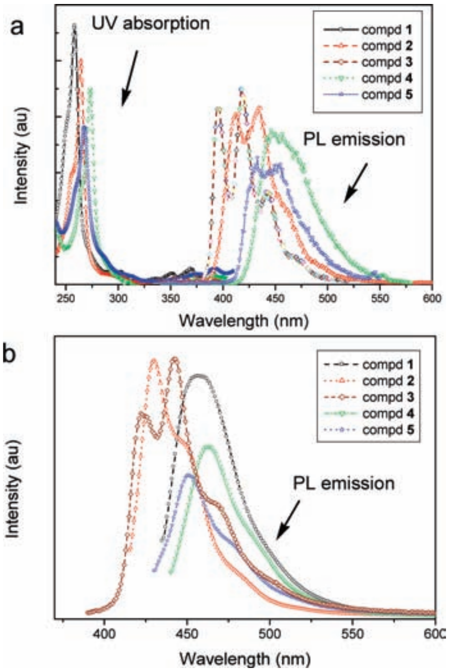


Figure 2. UV−vis absorption and photoluminescence emission spectra of compounds **1**−**5**: (a) in solution; (b) in thin film.

The thermal properties of the 1- and 2-fold functionalized derivatives were investigated by differential scanning calorimetry (DSC) under a continuous nitrogen purge. The 1-fold functionalized derivatives **1** and **2** showed an endothermic peak at 223 and 256 °C, respectively, which were much higher than in the case of the 2-fold functionalized derivatives **4** and **5**. However, the melting point of compound **3** decreased to 167 °C. It is clear that the methyl group at the C-9 position has a significant influence on the thermal stabilities of the 1-fold functionalized derivatives.

The electrochemical behaviors of **1**−**5** were also evaluated by cyclic voltammetry experiments at ambient temperature in CH_2Cl_2 (0.1 M n-Bu_4NPF_6 as a supporting electrolyte). All the compounds showed good reversibility of the oxidation potential. The values of the HOMOs for **1**−**5**, which were calculated from HOMO (eV) $= -[E_{\text{onsetox}}$ (vs SCE) $+ 4.4]$ based on an SCE energy level of 4.4 eV relative to the vacuum and the Ferrocene/Ferrocenium couple as the internal standard, were 5.42−5.62 eV. From the HOMO values and the optical band gap energy available from the UV−vis spectra, the energies of the LUMO for **1**−**5** were determined to be in the range of 2.54−2.64 eV.

Simple OLED devices as structures of ITO/MoO_x (4 nm)/NPB (20 nm)/emitting material (30 nm)/Bphen (20 nm)/LiF (0.7 nm)/Al were fabricated from compounds **1**−**5** by a thermal evaporation technique, where *N*,*N*′-bis(naphthalene-1-yl)-*N*,*N*′-bis(phenyl)benzidine (NPB) acted as a hole transporting layer, compounds **1**−**5** as an emitter, 4,7-dipheny1-l,10-phenanthroline (Bphen) as an electron-transporting layer, and LiF:Al as a composite cathode. The performance characteristics (EL maximum, brightness, luminance efficiency, and CIE coordinates) of these devices are summarized in Table 2. As can be seen, the emission was almost fixed in the sky-blue region for compound **1** with CIE coordinates ($x = 0.164$, $y = 0.232$), **4** (0.204, 0.195), **5** (0.219, 0.240) and in the deep blue region for **2** (0.167, 0.072) and **3** (0.157, 0.082). The EL spectra of compounds **1**, **3**, and **5** from the fabricated devices exhibited maxima close to those observed in their PL (solid) spectra. The peak intensity of the EL spectrum for **3** was at 440 nm, and the full width at half-maximum was about 52 nm. The color is pure blue ($x = 0.157$, $y = 0.082$) in CIE chromaticity

Table 2. EL Performance of the Synthesized Compounds **1**−**5**

Compd	$EL_{\max}$ (nm)	Brightness (cd/m^2)	Efficiency (cd/A)	CIE (x, y)
1	464	678	0.42	(0.163, 0.198)
2	420	796	0.41	(0.167, 0.072)
3	440	4100	1.34	(0.157, 0.082)
4	448	75	0.096	(0.204, 0.195)
5	448	21	0.062	(0.219, 0.240)

coordinates, which is quite close to the standard blue value of the National Television Standards Committee (NTSC) (0.14, 0.08). Figure 3 shows the EL spectra for **3** measured at different applied currents. No obvious spectrum shifts were observed. These high color purities of blue emissions confirm that the noncoplanar molecular structures of the 1-fold functionalized derivatives can effectively hinder intermolecular aggregation.

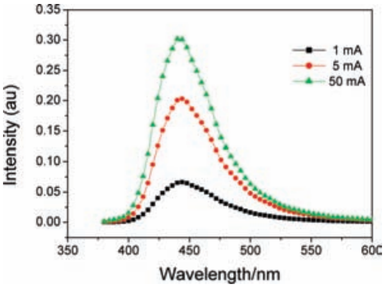


Figure 3. EL spectra for **3** at different applied currents.

The device made from compound **1** exhibited a maximum luminance of 678 cd/m^2 at 18 V and a maximum efficiency of 0.42 cd/A at 7.0 V with a turn-on voltage of 7.4 V. The device of **2** had a lower turn-on voltage of about 5.2 V, with a maximum brightness of 796 cd/m^2 at a driving voltage of 16 V and a maximum efficiency of 0.41 cd/A at 9.0 V. To our surprise, the device of **3** exhibited a much higher luminance of 4100 cd/m^2 at a lower voltage of 12 V with a lower turn-on voltage of 4.3 V. The maximum efficiency reached up to 1.36 cd/A. Figure 4 shows the current density (I)−voltage (V)−luminance characteristics of the device of **3**, and the insert is its $L-I$ (luminance efficiency vs current density) characteristics. It is worthwhile to note that the overall performances for the **3** based device are among the best ever reported for high-efficiency, nondoped deep-blue OLEDs with a CIE coordinate of $y < 0.1$, although they are still in the minority in the literature.[10] These unexpected results reveal that the modification at the C-9 position of fluorene-functionalized anthracene not only strengthens the rigidity of the molecules but also significantly improves the electroluminance.

However, the devices fabricated from 2-fold substituted derivatives **4** and **5** yielded a much poorer blue brightness. The performance characteristics of devices fabricated for 1-fold substituted derivatives **1**, **2**, and **3** were far more superior to those of 2-fold derivatives **4** and **5**.

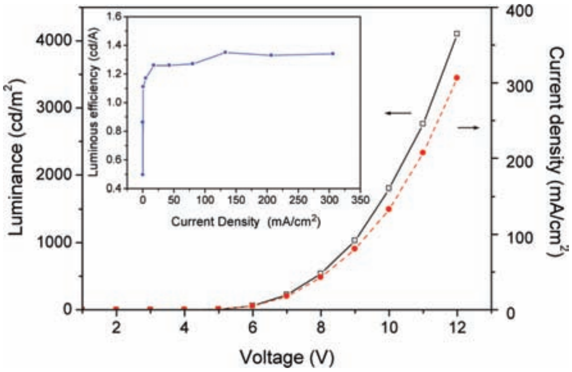


Figure 4. Current density (I)−voltage (V)−luminance characteristics of the device of **3**. Insert shows its $L-I$ (luminance efficiency vs current density) characteristics.

In conclusion, we have described here the first preparation of 1- and 2-fold fluorene-functionalized anthracene derivatives, in which a novel rigid linkage of a tetrahedral sp^3-hybridized carbon atom between fluorene and anthracene moieties (at the C-9 position of the fluorene) is presented. The tetrahedral nature of the C-9 carbon atom is found to preserve the electrical and optical properties of the fluorene and anthracene units. Our initial results from the unoptimized devices indicate that the 1-fold functionalized anthracenes **1**, **2**, and **3** are novel blue light emitters. Especially, the introduction of a methyl group into the C-9 position of the fluorene moiety has been demonstrated to strongly enhance the 1-fold based OLED properties. This work, which appears as the first report of a nondoped OLED based on the C-9 fluorenyl substituted anthracenes, may pave the way to the development of this novel class of materials.

Acknowledgment. This work was financially supported by the National Natural Science Foundation of China (No. 20772079), Science and Technology of Shanghai Municipal Committee (07ZR14040, 07JC14020, 08JC1409900), and Shanghai Municipal Education Commission.

Supporting Information Available: Experimental procedures, spectroscopic characterizations of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

OL101553A

---

[10] (a) Cocherel, N.; Poriel, C.; Vignau, L.; Bergamini, J.; Rault-Berthelot, J. *Org. Lett.* **2010**, *12*, 452–455. (b) Zhengt, C. J.; Zhao, W. M.; Wang, Zh. Q.; Huang, D.; Ye, J.; Ou, X. M.; Zhang, X. H.; Lee, Ch. S.; Lee, Sh. T. *J. Mater. Chem.* **2010**, *20*, 1560–1566. (c) Park, Y.; Son, J. H.; Kang, J. S.; Kim, S. K.; Lee, J. H.; Park, J. W. *Chem. Commun.* **2008**, 2143–2145.