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New Benzo[b]furans as Electroluminescent Materials for Emitting Blue Light

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ABSTRACT



New functionalized mono- and bis-benzo[*b*]furan derivatives were synthesized and developed as blue-light emitting materials. They possessed a CN, CHO, CH=CHPh, CH=CPh₂, or CH=CHCOOH group at the C4-position. Two benzo[*b*]furan nuclei in bis-benzo[*b*]furan derivatives were connected by a divinylbenzene bridge. With good volatility and thermal stability, bis-benzo[*b*]furan 7a was fabricated as a device. It emitted blue light with brightness 53430 cd/m² (at 15.5 V) and high maximum external quantum efficiency 3.75% (at 11 V).

New organic light-emitting devices (OLEDs) are in great demand by modern electronic industries.¹ They can be used for the manufacture of flat panel display and portable electronic products.² By modification of the molecular structure, organic materials can emit the desired color with low-drive voltage.^{3,4} In contrast, difficulties often arise in the fabrication of inorganic materials as efficient light-emitting devices.⁵

Nowadays, compounds with blue luminescence are highly desirable because of their wide applicability.⁶ The existing organic materials with blue light-emitting capability include

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styrylarylenes,⁷ polyphenyls,⁸ perylenes,⁹ benzofurans,¹⁰ indoles,¹¹ oxadiazoles,¹² thiophenes, etc.¹³ Due to critical requirements on physical and optical properties for fabrication, most of the existing devices leave much room for

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 ⁽¹⁾ For recent reports, see: (a) Ziemelis, K. *Nature* **1999**, *399*, 408–409. (b) Hung, L. S.; Chen, C. H. *Mater. Sci. Eng.* **2002**, *R39*, 143–222. (c) Kolosov, D.; Adamovich, V.; Djurovich, P.; Thompson, M. E.; Adachi, C. J. Am. Chem. Soc. **2002**, *124*, 9945–9954.

⁽²⁾ Shinar, J. Organic Light-Emitting Devices A Survey; Springer: New York, 2002.

⁽³⁾ For recent development, see: (a) Müllen, K.; Wegner, G. *Electronic Materials: The Oligomer Approach*; Wiley-VCH: Weinheim, Germany, 1998. (b) Hanack, M.; Behnisch, B.; Häckl, H.; Martinez-Ruiz, P.; Schweikart, K. H. *Thin Solid Films* **2002**, *417*, 26–31. (c) Li, C. L.; Shien, S. J.; Lin, S. C.; Liu, R. S. *Org. Lett.* **2003**, *5*, 1131–1134. (d) Kan, Y.; Wang, L.; Duan, L.; Hu, Y.; Wu, G.; Qiu, Y. *Appl. Phys. Lett.* **2004**, *84*, 1513–1515.

⁽⁴⁾ Kido, J.; Kimura, M.; Nagai, K. Science 1995, 267, 1332–1334.
(5) Sheats, J. R.; Antoniadis, H.; Hueschen, M.; Leonard, W.; Miller,

J.; Moon, R.; Roitman, D.; Stocking, A. Science 1996, 273, 884–888.
 (6) Shen, Z.; Burrows, P. E.; Bulovic, V.; Forrest, S. R.; Thompson, M.

⁽d) Shen, 2., Burrows, 1. E., Burrows, V., Portest, S. K., Thompson, W. E. Science **1997**, 276, 2009–2011.

⁽⁷⁾ Hosokawa, C.; Higashi, H.; Nakamura, H.; Kusumoto, T. Appl. Phys. Lett. **1995**, 67, 3853–3855.

⁽⁸⁾ Zheng, S.; Shi, J. Chem. Mater. 2001, 13, 4405-4407.

⁽⁹⁾ Jacob, J.; Sax, S.; Piok, T.; List, E. J. W.; Grimsdale, A. C.; Müllen, K. J. Am. Chem. Soc. **2004**, *126*, 6987–6995.

^{(10) (}a) Anderson, S.; Taylor, P. N.; Verschoor, G. L. B. *Chem. Eur. J.* **2004**, *10*, 518–527. (b) Conley, S. R. U.S. Patent 0 081 853, 2004.

improvement. Herein we report our recent development of functionalized benzo[*b*]furans,¹³ especially bis-benzo[*b*]furan derivatives, as competent new materials for OLEDs.

For the synthesis of functionalized benzo[*b*]furans **3**, we first treated 4-formyl-2-hydroxy-3-iodoanisole¹⁴ (**1a**) with a phenylacetylene¹⁵ (**2**, 2.0 equiv) in the presence of (PPh₃)₂-PdCl₂ (0.060 equiv), CuI (0.060 equiv), and triethylamine (3.0 equiv) in DMF at 110 °C (Scheme 1).¹⁶ The desired



4-formylbenzo[*b*]furans **3a,b** were generated as solids in 60– 63% yield. Second, we obtained 4-cyanobenzo[*b*]furan **3c** in 50% yield from 4-cyano-2-hydroxy-3-iodoanisole (**1b**) and (3,4-dimethoxyphenyl)acetylene (**2b**).¹⁵

(11) Lin, T. S. U.S. Patent 0 001 967, 2004.

(12) Jin, S. H.; Kim, M. Y.; Kim, J. Y.; Lee, K.; Gal, Y. S. J. Am. Chem. Soc. 2004, 126, 2474–2480.

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The formyl group in benzo[*b*]furans **3a,b** provided a chance to elongate their π -system by addition of another functionality, including a styryl, β , β -diphenylvinyl, and carboxyvinyl group. Attachment of these auxochromes at the C4-position would enable us to tune the emitting light with bathochromic and hypsochromic shifts. Therefore, we condensed aldehydes **3a,b** with a benzylphosphonate (i.e., **4a** or **4b**)¹⁷ in the presence of NaH in THF to give vinylbenzo-[*b*]furans **5a**-**d** in 51–80% yields (Scheme 1). Moreover, the Knoevenagel reaction was applied to aldehyde **3b** and manolic acid (1.0 equiv) in the presence of pyridine and piperidine to produce **5e** in 70% yield. Finally, reaction of aldehydes **3a,b** with bisphosphonate **6** produced the desired bis-benzo[*b*]furan derivatives **7a,b** in 70–72% yields (see Scheme 2).



Structures of the new compounds **3b,c**, **5b**–e, and **7a,b** were fully characterized by ¹H NMR, ¹³C NMR, IR, UV, photoluminescence (PL), and mass spectroscopic methods. For example, bis-benzo[*b*]furan **7a** exhibited one characteristic singlet at 6.85 ppm in its ¹H NMR spectrum for the C3-protons. Two doublets with J = 8.4 Hz appeared at 7.40 and 7.91 ppm for the C5- and C6-protons; another two doublets with J = 16.2 Hz appeared at 7.18 and 7.42 ppm for the vinylic protons. In its ¹³C NMR spectrum, the resonance occurred at 157.09 and 125.70 ppm for the C2- and C3-carbons, respectively, at 128.34 and 122.26 ppm for the two vinylic carbons. In its IR spectrum, one medium absorption band appeared at 1514 cm⁻¹ for the OC=C stretching vibration in the furan moiety.

We unambiguously confirmed the molecular framework of a benzo[*b*]furan by using single-crystal X-ray diffraction analysis (see Figure 1). Among our synthesized benzo[*b*]-

⁽¹³⁾ For the pioneering works and recent reports, see: (a) Tang, C. W.;
VanSlyke, S. A. Appl. Phys. Lett. **1987**, 51, 913–915. (b) Tang, C. W.;
VanSlyke, S. A.; Chen, C. H. J. Appl. Phys. **1989**, 65, 3610–3616. (c)
Burroughes, J. H.; Bradley, D. D. C.; Brown, A. R.; Marks, R. N.; Mackay,
K.; Friend, R. H.; Burns, P. L.; Holmes, A. B. Nature **1990**, 347, 539–
541. (d) Kim, Y. H.; Shin, D. C.; Kim, S. H.; Ko, C. H.; Yu, H. S.; Chae,
Y. S.; Kwon, S. K. Adv. Mater. **2001**, 13, 1690–1693. (e) Shi, J.; Tang, C.
W. Appl. Phys. Lett. **2002**, 80, 3201–3203. (f) Zhang, X.; Matzger, A. J.
J. Org. Chem. **2003**, 68, 9813–9815. (g) Itami, K.; Ushiogi, Y.; Nokami,
T.; Ohashi, Y.; Yoshida, J. Org. Lett. **2004**, 6, 3695–3698. (h) Wu, C. C.;
Lin, Y. T.; Wong, K. T.; Chen, R. T.; Chien, Y. Y. Adv. Mater. **2004**, 16, 61–65. (i) Kuwahara, A.; Nakano, K.; Nozaki, K. J. Org. Chem. **2005**, 70, 413–419. (j) Wu, Y.; Li, Y.; Gardner, S.; Ong, B. S. J. Am. Chem. Soc. **2005**, 127, 614–618.

⁽¹⁴⁾ Markovich, K. M.; Tantishaiyakul, V.; Hamada, A.; Miller, D. D.; Romstedt, K. J.; Shams, G.; Shin, Y.; Fraundorfer, P. F.; Doyle, K.; Feller, D. R. *J. Med. Chem.* **1992**, *35*, 466–479.

⁽¹⁵⁾ Pelter, A.; Ward, R. S.; Little, G. J. Chem. Soc., Perkin Trans. 1 1990, 10, 2775–2790.

⁽¹⁶⁾ For the conditions, see: (a) McGarry, D. G.; Regan, J. R.; Volz, F. A.; Hulme, C.; Moriarty, K. J.; Djuric S. W.; Souness, J. E.; Miller, B. E.; Travis, J. J.; Sweeney, D. M. *Bioorg. Med. Chem.* **1999**, *7*, 1131–1139. (b) Flynn, B. L.; Hamel, E.; Jung, M. K. J. Med. Chem. **2002**, *45*, 2670–2673.

⁽¹⁷⁾ Salomon, C. J.; Breuer, E. Tetrahedron Lett. 1995, 36, 6759-6760.



Figure 1. ORTEP diagram of diphenylvinylbenzo[*b*]furan **5c** obtained by X-ray analysis.

furans, **5c** was the only compound that can be obtained in single-crystal form. Its triclinic crystals possessed space group *P*1 with a = 11.0613(2) Å, b = 11.2060(2) Å, c = 18.367(3) Å, $\alpha = 103.796(3)^\circ$, $\beta = 98.545(3)^\circ$, and $\gamma = 90.565(3)^\circ$. The dihedral angle was 12° between the benzo-furan nucleus and the C2-benzene moiety. Compounds with a nonplanar structure generally have less tendency to pack into crystal lattice and, hence, favor amorphous morphology.¹⁸ Our X-ray data indicate that the aryl moiety attached at the C2-position was not coplanar with the benzofuran nucleus. This would lead to amorphism, which facilitates device fabrication by use of various 2′-substituted benzo[*b*]-furans.

Among monobenzo[*b*]furans **3a**–**c** and **5a**–**e**, cyanocontaining derivative **3c** exhibited hypsochromic shift and appealing photoluminescence (PL) quantum yield (Φ_{PL} , entry 3 in Table 1). It is due to conjugation of the aromatic π -system therein to an electron-withdrawing cyano group.³ Thus the cyano group can be used to tune the electronic and the optical properties of benzo[*b*]furans. On the other hand, bis-benzo[*b*]furans **7a**,**b** showed significant bathochromic shift (entries 9 and 10) with high Φ_{PL} values (0.43–0.46).

Thermal properties of benzo[*b*]furans were analyzed by differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) methods. Our results indicate that the bis-benzo[*b*]furans were more stable than mono-benzo[*b*]-furans. The glass transition temperature (T_g), melting temperature, and onset decomposition temperature of bisbenzo[*b*]furan **7a** were 83, 282–283, and 320 °C, individually. Generally morphological instabilities of organic layers do not seem to be a dominant factor in intrinsic degradation of OLEDs, especially for operating conditions at room temperature.²⁰ The T_g value of **7a** (83 °C) is higher than the general organic materials used for OLEDs (≥ 60 °C). While

Table 1	. UV and Photoluminescent Properties	s of
Benzo[b	furans 3, 5, and 7	

		,			
entry	benzo[b]- furan	substituent	UV λ_{\max} , nm (ϵ)	$\operatorname{PL}_{nm}^{\lambda_{\max}},$	${\operatorname{PL}} \Phi_{\operatorname{PL}}{}^a$
1	3a	СНО	332 (13800)	406	0.03
			263(17310)		
2	3b	CHO	352(19640)	457	0.36
			282(19310)		
3	3c	CN	330~(25530)	393	0.45
			272(10020)		
4	5a	CH=CHPh	314~(26200)	426	0.12
			282(23200)		
5	5b	CH=CHPh	342(29880)	425	0.23
			310(25240)		
6	5c	$CH=CPh_2$	336 (38360)	450	0.01
			294(35120)		
7	5d	$CH=CPh_2$	338 (36320)	462	0.01
			300(12600)		
8	5e	CH=CHCOOH	342(8970)	483	0.21
			276(15630)		
9	7a	$C_6H_4CH=CH$	398 (63030)	463	0.43
		~ ~ ~ ~ ~ ~ ~ ~ ~	296 (41220)		
10	7b	$C_6H_4CH=CH$	400 (62020)	470	0.46
			320(42610)		

 a The photoluminescence quantum yields in CH₂Cl₂ were measured in comparison with anthracene in ethanol (0.27).¹⁹ The excitation wavelength was fixed at 340 nm.

being made as a device, compound 7a was found stable at 3.6, 7.0, 11, and 15.5 V. Nevertheless, degradation in this OLED appeared in the form of a decrease in device photoluminescence after the voltage reached 17.0 V.

We measured the HOMO energy of the materials with high Φ_{PL} by cyclic voltammetry (CV) with ferrocene (4.8 eV) as the reference. The LUMO energy was calculated from the HOMO and the lowest energy absorption edge of the UV/ Vis absorption spectra.²¹ Their first oxidation potential (E_{ox}), HOMO energy, LUMO energy, and band gaps are shown in Table 2. The conjugation degrees of the aromatic π -system

Table 2. Electrochemical Data of Mono- andBis-benzo[b]furan Derivatives

entry	benzo[b]- furan	substituent	<i>E</i> _{ox} (V) vs Ag/AgCl	HOMO (eV)	LUMO (eV)	energy gap (eV)
1	3b	СНО	1.50	5.90	2.76	3.14
2	3c	CN	1.56	5.72	2.37	3.35
3	5b	CH=CHPh	1.17	5.37	2.36	3.01
4	7a	C ₆ H ₄ CH=CH	0.98	5.26	2.48	2.78
5	7b	$C_6H_4CH=CH$	0.89	5.06	2.32	2.74

can influence the energy gap. Our results indicate that the energy gaps between HOMO and LUMO were significantly lower for bis-benzofurans (entries 4 and 5 of Table 2) than the mono-benzofurans (entries 1-3).

Among our synthesized benzo[b]furans, we selected **7a** for the device fabrication because of its higher PL quantum

⁽¹⁸⁾ Shirota, Y. J. Mater. Chem. 2000, 10, 1-25.

⁽¹⁹⁾ Scaiano, J. C. CRC Handbook of Organic Photochemistry; CRC: Boca Raton, 1989.

⁽²⁰⁾ Aziz, H.; Popovic, Z. D. Chem. Mater. 2004, 16, 4522-4532.

⁽²¹⁾ Anderson, J. D.; McDonald, E. M.; Lee, P. A.; Anderson, M. L.; Ritchie, E. L.; Hall, H. K.; Hopkins, T.; Mash, E. A.; Wang, J.; Padias, A.; Thayumanavan, S.; Barlow, S.; Marder, S. R.; Jabbour, G. E.; Shaheen, S.; Kippelen, B.; Peyghambarian, N.; Wightman, R. M.; Armstrong, N. R. J. *Am. Chem. Soc.* **1998**, *120*, 9646–9655.

yield, better thermal stability, and sublimation capability. Moreover, the HOMO energy measured for 7a was 5.26 eV; thus, hole injection from the NPB (5.40 eV) anode to 7a should be feasible. The HOMO energy for TPBI is 6.2 eV; its application as a hole-blocking layer would not favor holes to enter the TPBI layer. As a result, recombination and emission can take place in the layer of 7a. On the basis of this design, we made our device by ITO/NPB (40 nm)/7a (4.0%) in ADN (30 nm)/TPBI (10 nm)/Alq₃ (30 nm)/Mg-Ag (50 nm)/Ag (10 nm). The ADN functioned as a host material layer and the TPBI as the hole blocking material. The ITO, NPB, ADN, TPBI, Alq₃, Mg-Ag represent indium tin oxide, 4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl, 9,10-di(2-naphthyl)anthracene, 1,3,5-tris(N-phenylbenzimidizol-2-yl)benzene, tris(8-hydroxyquinoline)aluminum, and magnesium-silver alloy (~10:1) individually. The NPB and Alq₃ were used as the hole and electron-transporting material, respectively.

The device of **7a** had turn-on voltage of 3.6 V; its brightness reached 303 cd/m² at 1.0 mA and 6.0 V as well as 1298 cd/m² at 2.48 mA and 7.0 V. The initial color of our device was blue-green (x = 0.15 and y = 0.25) in the Commission Internationale de L'Eclairage (CIE) chromaticity coordinates. The observed maximum brightness was 53430 cd/m² at 85.5 mA and 15.5 V. The external maximum quantum and power efficiency for the **7a** device were 3.75% and 2.03 lm/W, which were achieved at 11 V (314 mA/cm², 22418 cd/m²). To the best of our knowledge, the device of **7a** showed the greatest brightness and the maximum power efficiency in comparison with all reported compounds in the family of benzofurans.¹⁰

In conclusion, a series of new mono- and bis-benzo[b]furan derivatives were synthesized successfully, which possessed various substituents including CHO, CN, CH= CHPh, CH=CPh₂, and CH=CHCOOH groups at the C4position. Several compounds exhibited appealing photoluminescence quantum yields and thermal stability. A device containing bis-benzo[b]furan (i.e., ITO/NPB/7a) was fabricated in the ADN/TPBI/Alq₃/Mg-Ag/Ag structure, which emitted light in the blue region with high maximum external quantum efficiency and great brightness. Accordingly, bisbenzo[b]furans possess great potential as highly efficient blue OLED materials. The key factors to our success include the following: (1) Choosing benzo[b] furan as the nucleus with an aryl group attached at the C2-position. This design leads to nonplanarity of the molecules, which provides amorphous morphology. (2) Elongating the π -system therein while holding geometric symmetry for the target molecules (i.e., bis-benzo[b]furans). Subsequently, the light of the desired wavelength is emitted brightly. (3) Controlling molecular size and weight of the benzo[b]furan in its dimeric form. Thus, the thermal stability and volatility of the target molecules allow them to be easily fabricated as an OLED device.

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Supporting Information Available: Experimental procedures, spectral data, and physical properties for new benzo-[*b*]furans **3b,c**, **5b–e**, and **7a,b** as well as fabrication of OLEDs and their measurement. This material is available free of charge via the Internet at http://pubs.acs.org.

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