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

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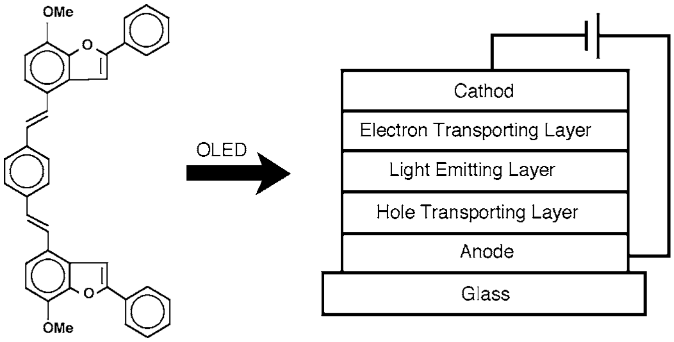
ABSTRACT



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═CPh$_2$, 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/m^2 (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 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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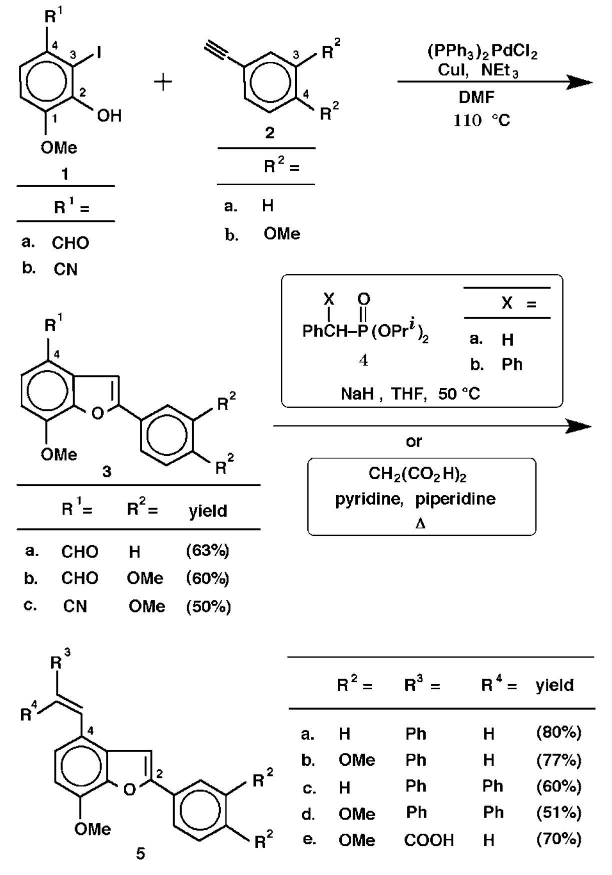
improvement. Herein we report our recent development of functionalized benzo[*b*]furans,[13] especially bis-benzo[*b*]furan derivatives, as competent new materials for OLEDs.

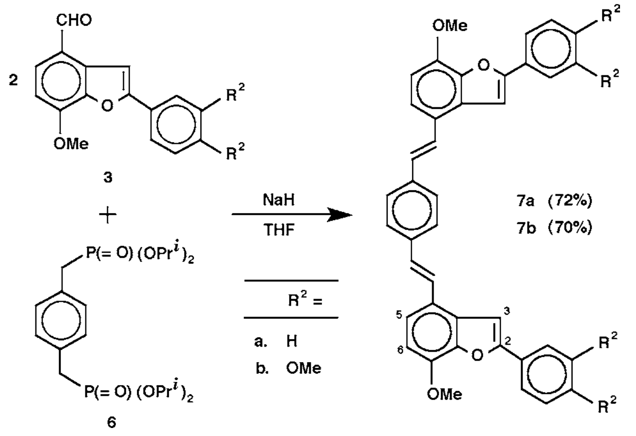
For the synthesis of functionalized benzo[*b*]furans **3**, we first treated 4-formyl-2-hydroxy-3-iodoanisole[14] (**1a**) with a phenylacetylene[15] (**2**, 2.0 equiv) in the presence of (PPh$_3$)$_2$PdCl$_2$ (0.060 equiv), CuI (0.060 equiv), and triethylamine (3.0 equiv) in DMF at 110 °C (Scheme 1).[16] 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]

Scheme 1



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).

Scheme 2



Structures of the new compounds **3b**,**c**, **5b**–**e**, and **7a**,**b** were fully characterized by ^{1}H NMR, ^{13}C 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 ^{1}H 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 ^{13}C 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*]-

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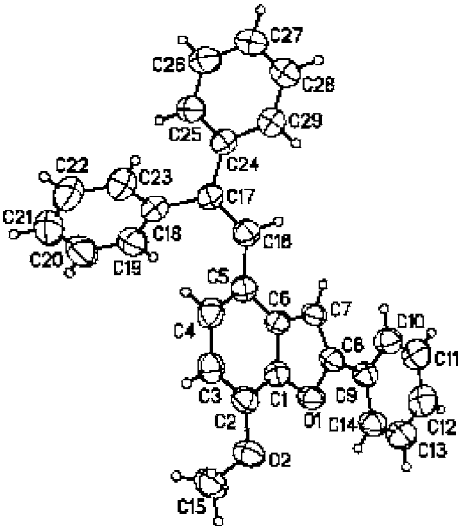

Figure 1. ORTEP diagram of diphenylvinylbenzo[*b*]furan **5c** obtained by X-ray analysis.

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

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

[a] The photoluminescence quantum yields in CH_2Cl_2 were measured in comparison with anthracene in ethanol (0.27).[19] The excitation wavelength was fixed at 340 nm.

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, $\alpha = 103.796(3)°$, $\beta = 98.545(3)°$, and $\gamma = 90.565(3)°$. The dihedral angle was 12° between the benzofuran 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**, cyano-containing 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 bis-benzo[*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 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 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).

Table 2. Electrochemical Data of Mono- and Bis-benzo[*b*]furan Derivatives

entry	benzo[*b*]-furan	substituent	E_{ox}(V) vs Ag/AgCl	HOMO (eV)	LUMO (eV)	energy gap (eV)
1	**3b**	CHO	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**	$C_6H_4CH=CH$	0.98	5.26	2.48	2.78
5	**7b**	$C_6H_4CH=CH$	0.89	5.06	2.32	2.74

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

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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)/Alq_3 (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, Alq_3, 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 Alq_3 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/m^2 at 1.0 mA and 6.0 V as well as 1298 cd/m^2 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/m^2 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/cm^2, 22418 cd/m^2). 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═CPh_2, and CH═CHCOOH groups at the C4-position. 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/Alq_3/Mg−Ag/Ag structure, which emitted light in the blue region with high maximum external quantum efficiency and great brightness. Accordingly, bis-benzo[*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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