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Communication

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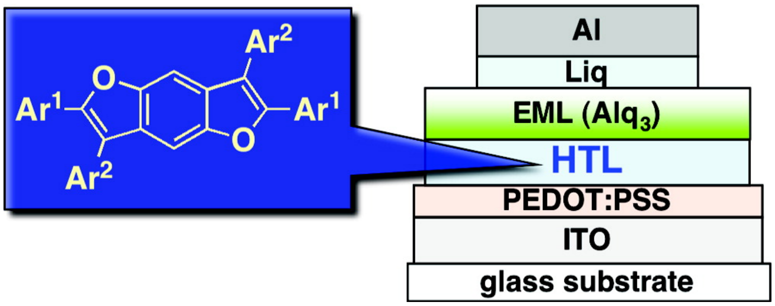

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Synthesis and Properties of 2,3,6,7-Tetraarylbenzo[1,2-*b*:4,5-*b*′]difurans as Hole-Transporting Material

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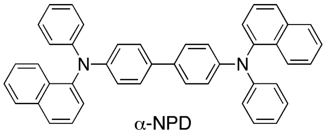
Arylamine derivatives have been used as the hole-transporting material (HTM) in multilayer organic light-emitting diodes (OLEDs) for 20 years.[1,2] α-NPD,[3] which is a diarylamino-substituted biphenyl, is the current standard,[4] giving us the impression that the arylamino group is indispensable for high-performance HTMs. Indeed, there have been scarcely any attempts to find new HTMs that do not contain any arylamino groups.[5] We describe herein a new method for the synthesis of a series of 2,3,6,7-tetraarylbenzo[1,2-*b*:4,5-*b*′]difurans (BDFs), and report that they function as HTMs in layered OLEDs. The BDF skeleton by itself serves as an excellent HTM, and improvement of the physical properties can be achieved by suitable functionalization.

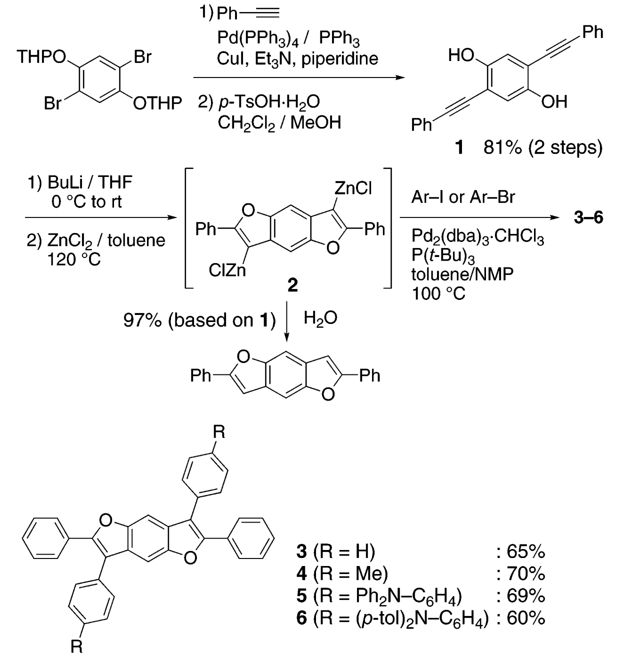


α-NPD

The synthesis of BDFs has been known for a century, but none of these compounds has found any practical use perhaps because of very limited synthetic availability: limited scope and low yield.[6,7] The key chemical finding that we report herein is a new synthetic route shown in Scheme 1.

It is based on a recently reported zinc-mediated annulation strategy that allows modular construction of the benzofuran moiety and hence shows considerable flexibility toward the substituents and functionality.[8] The synthesis starts with the 100% regioisomerically pure 2,5-dibromohydroquinone protected by tetrahydropyran (THP). The Sonogashira-coupling reaction[9] with phenylacetylene followed by deprotection afforded **1**. Double cyclization[8b] of the substrate **1** afforded the desired 3,7-dizinciobenzodifuran **2** as a thermally stable intermediate in quantitative yield (determined by protonation of **2**). This intermediate permits introduction of the substituents into 3,7-positions. The Negishi cross-coupling reaction[10] of the dizincio intermediate **2** with an aryl halide was achieved in the presence of a catalytic amount of palladium(0) and tri-*tert*-butylphosphine[11] to obtain analytically pure 2,3,6,7-tetraarylbenzo[1,2-*b*:4,5-*b*′]difurans **3**−**6** in good yields. The use of a toluene/*N*-methylpyrrolidinone (NMP) mixture as solvent was found to be beneficial to improve the yields.[12] The two BDFs **3** and **4** lack any functional groups other than the BDF core, while **5** and **6** contain arylamino groups. The products were purified by chromatography and repeated sublimation for the use in the physical measurements.

Scheme 1 [a]



[a] Yields for **3**−**6** are based on the analytically pure products obtained by sublimation.

To evaluate the device properties, we employed the standard OLED configuration, that is, ITO (indium tin oxide) (145 nm)/PEDOT:PSS (poly(ethylenedioxy)thiophene:polystyrene sulfonate)[13] (70 nm)/hole-transport layer (HTL) (45 nm)/Alq$_3$ (tris(8-hydroxyquinolinato)aluminum) (60 nm)/Liq (8-hydroxyquinolinato lithium) (1 nm)/Al (80 nm), where HTL is either one of the BDF derivatives **3**−**6** or α-NPD deposited under vacuum. The performance of six devices was evaluated for three standard criteria, driving voltage (V_{1000}), luminance efficiency (η_{1000}), and current efficiency (L/J_{1000}) as summarized in Table 1. The device **F** at the bottom is a reference standard that lacks the HTL, and expectedly exhibited the lowest performance by every criterion. Most interestingly, the OLED devices **A** and **B** containing the non-arylamino BDFs **3** and **4**, respectively, displayed excellent device performance. Thus, the device **A** generated electroluminescence of 1000 cd/m^2 at the driving voltage V_{1000} (5.1 V), which is slightly lower than the one required in the α-NPD-based device **E** (5.2 V). Moreover, the luminance efficiency η_{1000} and current efficiency L/J_{1000} of **A** (2.6 lm/W and 4.1 cd/A) at a luminance of 1000 cd/m^2 were significantly higher than those of **E** (2.0 lm/W and 3.6 cd/A). For the device **B**, the current efficiency L/J_{1000} was noticeably improved (4.9 cd/A).

The results obtained for the devices **C** and **D** based on the arylamino BDFs **5** and **6**, respectively, indicated that the introduction of proper substituents can improve the overall performance of the BDF, demonstrating that the synergetic effect of the BDF core

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Table 1. Performance of OLED Composed of either BDF **3**−**6** or α-NPD as the Hole-Transport Layer (HTL)[a]

device	HTL	V_{1000}[b] [V]	η_{1000}[c] [lm/W]	L/J_{1000}[d] [cd/A]
A	**3**	5.1	2.6	4.1
B	**4**	6.3	2.6	4.9
C	**5**	5.3	2.2	4.3
D	**6**	5.0	2.7	4.4
E	α-NPD	5.2	2.0	3.6
F	none[e]	5.8	1.6	3.1

[a] All performance data were collected at a luminance of 1000 cd/m^2. [b] Driving voltage. [c] Luminance efficiency. [d] Current efficiency. [e] No HTL. The thicknesses of other layers are the same as the other devices.

Table 2. Properties of the BDFs **3**−**6** and α-NPD in the Solid State

compound	IP[a] [eV]	μ[b] [cm^2/Vs]	T_g[c] [°C]
3	5.75	6.4×10^{-4}	92
4	5.56	8.0×10^{-5}	90
5	5.53	2.8×10^{-3}	124
6	5.47	5.6×10^{-4}	135
α-NPD	5.43	3.6×10^{-4}	96

[a] Ionization potential measured by PYS for vacuum-deposited thin films. [b] Hole mobility measured by the TOF method using vacuum-deposited films at room temperature at an electric field of 2.5×10^5 V/cm. [c] Glass transition temperature measured by DSC.

and the substituents which effectively extend the π-conjugated system. Thus, the device **D** displayed the highest overall performance.

By taking the device **F**, which lacks HTL, as a reference standard, we can evaluate the relative performance of the HTMs. Thus, α-NPD increased $\Delta\eta_{1000}$ and $\Delta L/J_{1000}$ values[14] by 0.4 lm/W and 0.5 cd/A, respectively, while the increases caused by the use of BDFs were twice to three times as much, that is, 0.6−1.1 lm/W and 1.2−1.8 cd/A, respectively. These data highlight the much higher improvement of the OLED performance of the BDF-based device compared with α-NPD.

To gain insight into the high performance of the BDF-based devices, basic physical properties of the BDFs **3**−**6** and α-NPD were measured in the solid state (Table 2). The ionization potentials (IPs) of thin films[15] of **3**−**6** were evaluated by photoemission yield spectroscopy (PYS).[16,17] The IP value of **3** shown in the first column is particularly high (5.75 eV) among the BDFs examined (5.47−5.56 eV), and it is much higher than that of α-NPD (5.43 eV). The high IP value of **3** must still be within the operating range of the device (because the device showed high performance), and suggests a potential advantage of BDFs over the low IP of arylamine-based HTMs that may be more prone to oxidative degradation.[18]

Carrier-transporting properties of these compounds were measured by the time-of-flight (TOF) technique using films (thickness: 4.6−8.3 μm) at room temperature at an electric field of 2.5×10^5 V/cm. The hole drift mobility of the BDFs **5** was 2.8×10^{-3} cm^2/Vs, 1 order of magnitude higher than that of α-NPD (3.6×10^{-4} cm^2/Vs). The BDFs **3** and **6** displayed higher and **4** displayed lower mobilities than α-NPD.

The glass-transition temperature (T_g) obtained by differential scanning calorimetry (DSC, Table 2) suggested that the arylamino groups contribute to raise the T_g of the BDF compounds. Thus, the T_g values of the arylamino BDFs **5** and **6** (124 and 135 °C, respectively) are much higher than those of **3** and **4**, which in turn are comparable to that of α-NPD (96 °C).

In conclusion, we have developed an efficient and versatile synthesis of BDF compounds and demonstrated that BDFs function as efficient HTMs. The high performance of the compounds is primarily due to the BDF core itself, which is in sharp contrast to the fact that the biphenyl scaffold in α-NPD alone does not function as a HTM. We also found that there is a synergetic effect of the BDF core and the substituents as demonstrated by the arylamine-substitued BDFs. We can therefore expect that the BDF molecule will serve as a useful new molecular scaffold on which multiple functional groups can be attached to obtain new properties.

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Supporting Information Available: Detailed experimental procedures and properties of the compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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