

Blue light-emitting and hole-transporting amorphous molecular materials based on diarylamino-biphenyl-functionalized bimesitylenes†

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Received (in Cambridge, UK) 27th November 2007, Accepted 5th February 2008

First published as an Advance Article on the web 5th March 2008

DOI: 10.1039/b718250c

The diarylamino-biphenyl-functionalized bimesityls **1 and **2** exhibit amorphous nature, high thermal stability and excellent blue emission in the solid state. They serve as both hole-transporting and emissive materials in OLEDs for blue emission with high external quantum efficiencies.**

The exciting prospects of organic compounds for lighting have fueled active research on organic light emitting diodes (OLEDs) in recent times.¹ The quest for newer materials with improved properties (endurance, high performance efficiency and low driving voltage) for application in OLEDs continues unabated.² The importance of small molecular weight organic compounds arises from several factors that include structural diversity, ready synthetic accessibility, facile purification, ease of casting as well as homogeneity in device fabrications, *etc.* Insofar as small molecule-based triarylaminos as hole-transporting materials (HTMs) are concerned, *N,N'*-di(1-naphthyl)-*N,N'*-diphenyl-[1,1'-biphenyl]-4,4'-diamine (NPB) and *N,N'*-bis(3-methylphenyl)-*N,N'*-diphenyl-[1,1'-biphenyl]-4,4'-diamine (TPD) constitute excellent HTMs that are extensively employed in OLEDs. Incidentally, it is the HTM that is associated with lowest thermal stability in most of the OLED device structures, *e.g.*, $T_g(\text{TPD}) = 65\text{ }^\circ\text{C}$ and $T_g(\text{NPB}) = 95\text{ }^\circ\text{C}$.³ As the low thermal stability is highly detrimental to the lifetimes of devices, organic amorphous HTMs that exhibit high T_g s are much sought after. In general, rigid molecules that possess high symmetry lead to amorphous nature and high thermal stabilities, while amines with such features are expected to display hole-transporting properties.^{2a,b} A variety of dendritic-type starburst molecules have been investigated for their amorphous nature and hole-transporting properties.²

We derived inspiration from our recent work on tetra-arylbimesityls⁴ and tetramesityl pyrenes⁵ to target the development of amine-based HTMs that exhibit amorphous properties and high glass transition temperatures; we have found that attachment of aryl rings to the bimesityl scaffold *via* facile Pd(0)-catalyzed coupling protocols leads to rigid noncoplanar aryl-substituted bimesityls, which exhibit amorphous properties due to packing difficulties.⁴ In the course of our investigations toward the synthesis of amorphous amines that display

high thermal stability, we discovered that the 2-fold functionalized bimesityls linked by diarylamino-substituted biphenyls **1** and **2** (Chart 1) show excellent blue emission. Incidentally, there are only a few instances of amines that function both as emitting as well as hole-transporting materials.^{6–9} Herein, we have examined the potential of novel bimesitylene-based triarylaminos **1** and **2** to serve as emitting as well as hole-transporting materials. In addition to the respectable thermal properties observed for the amines **1** and **2**, excellent bright blue electroluminescence (EL) with CIE (Commission Internationale de l'Éclairage) coordinates nearest to the NTSC (National Television Systems Committee) standard blue is observed for the devices of the two amines; the blue emission from a non-doped two-layer device structure constructed for **2** reaches a maximum external quantum efficiency of 2.73%, which is comparable to those reported for the other commonly used blue emitting HTMs, *vide infra*.

The disubstituted bimesityl-based triarylaminos **1** and **2** were readily synthesized by a convergent approach involving Pd(0)-catalyzed cross-coupling between diarylamine-substituted arylboronic acids and 3,3'-diiodobimesityl, *cf.* ESI.† The UV-vis absorption spectra for both triarylaminos **1** and **2** are shown in Fig. 1. While the absorption maxima for the two amines are comparable, the amine **2** shows a significant absorption in the region between 350–400 nm as compared to that of **1**. In fact, a closer inspection of the spectra reveals that each compound exhibits two low and high energy bands. While the latter appears to be strong for amine **2**, the low energy band corresponds to the absorption maximum for **1**.

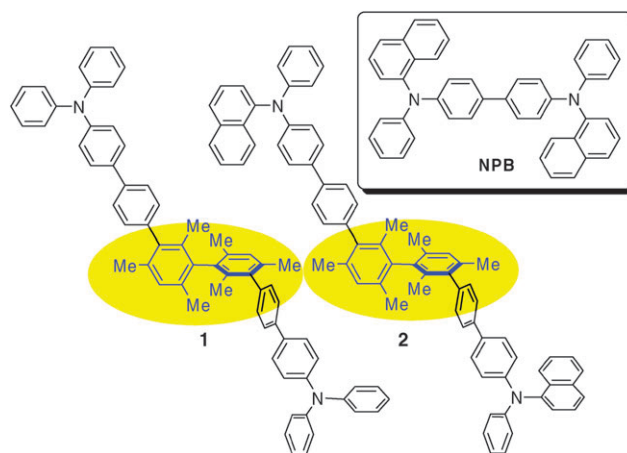


Chart 1 Bimesitylene-based HTMs **1** and **2**, and NPB.

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† Electronic supplementary information (ESI) available: Details of synthesis and characterization data of the bimesitylene-based amines **1** and **2**. See DOI: 10.1039/b718250c

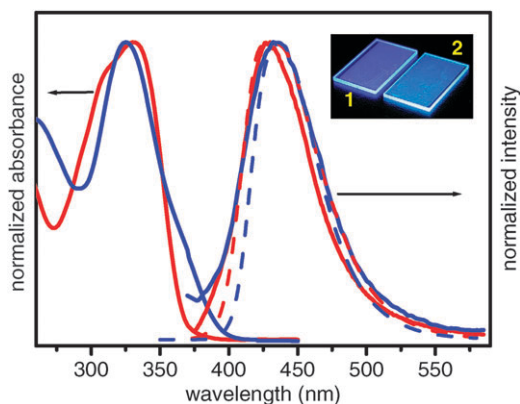


Fig. 1 UV-vis absorption (left) and photoluminescence (right) spectra of **1** (red line) and **2** (blue line) in chloroform (*ca.* 10^{-6} M) and in vacuum deposited films (dotted lines). Inset shows the photographs of blue emission from vacuum-sublimed films of **1** and **2** upon excitation with a hand-held UV lamp.

The two-band feature observed for **1** and **2** is consistent with the pattern reported for the absorption of analogous diaryl-amino-substituted biphenyls.^{10,11} The dilute solutions (*ca.* 1×10^{-6} M) of both **1** and **2** in chloroform were found to exhibit excellent blue emission with their maximum at 430–432 nm (Table 1). As is evident from Fig. 1, the emissions for the two compounds are similar despite differences in their absorption spectra. The emission in the film was found to parallel that observed for the solutions in chloroform. The absence of any long wavelength emission attests to ‘no-aggregation’ behavior. The fluorescence quantum efficiencies of **1** and **2** for their solutions in dichloromethane and vacuum-deposited films were estimated by the integrating sphere method, *cf.* ESI.† While the values were found to be similar in both media (Table 1), one observes a striking reduction in the quantum efficiency for the naphthyl analog **2** as compared to that for **1**. The fluorescence lifetimes for **1** and **2** in dichloromethane were found to be 1.27 and 3.24 ns, respectively. Clearly, the replacement of a phenyl by naphthyl ring has a dramatic bearing on the quantum yields as well as fluorescence lifetimes.

Insofar as the amorphous properties and thermal stabilities are concerned, the amine **1** shows a broad endotherm corresponding to T_g at *ca.* 122 °C with a melting transition around 164 °C, while **2** exhibits a much higher T_g at *ca.* 152 °C without any melting transition; the T_g for the latter was found to be stable when subjected to repeated heating and cooling cycles. The decomposition temperatures for **1** and **2** are as high as 438 and 460 °C, respectively (Table 1). It should be noted that the

thermal properties for the amines **1** and **2** based on a bimesitylene scaffold are significantly better than NPB, a most commonly employed HTM. Electrochemically, both **1** and **2** show a reversible one-electron oxidation behavior. The energies of HOMOs (Table 1) derived from the oxidation potentials (E_{ox}), as determined by cyclic voltammetry, were found to be comparable to the ionization potentials determined by UV photoelectron spectroscopy. The LUMO values for **1** and **2** were calculated from their respective onset potentials (band gap energy) obtained from the tail-end of their absorptions and HOMO values.

The functional behavior of **1** and **2** was investigated by constructing multilayer devices for capturing EL. The configurations of the multilayer devices were: (A) ITO/NPB (400 Å)/**1** (100 Å)/TPBI (400 Å)/LiF (10 Å)/Al (1500 Å); (B) ITO/NPB (400 Å)/**2** (100 Å)/TPBI (400 Å)/LiF (10 Å)/Al (1500 Å), where ITO (indium tin oxide) was the anode, NPB served as a hole-transporting layer, **1/2** was employed as an emitting layer, TPBI (2,2',2''-(1,3,5-benzenetriyl)-tris(1-phenyl-1-*H*-benzimidazole) as an electron transporting layer, and LiF:Al as the composite cathode. The performance characteristics, *viz.*, turn-on voltage, power efficiency, luminance efficiency, external quantum efficiency and CIE coordinates, of these devices are summarized in Table 2. As can be seen, these non-doped devices exhibit a low turn-on voltage, bright luminance and high external quantum efficiency. The EL spectra recorded for **1** and **2** shown in Fig. 2 reveal a pure-blue emission (λ_{max} *ca.* 440 nm) according to the CIE chromaticity diagram with (*x*, *y*) coordinates nearest to the standard NTSC blue. The luminance efficiencies and external quantum efficiencies for the devices of **1** and **2** were 3.04 cd/A and 4.09%, and 2.88 cd/A and 3.89%, respectively, at a current density of 20 mA/cm². The maximum external quantum efficiencies achieved for **1** and **2** were 4.09% (4.5 V @ 25.68 mA/cm²) and 4.23% (8.5 V @ 8.65 mA/cm²), respectively.

The dual role of the amines **1** and **2** to function as both emitting as well as hole-transporting materials was specifically examined for the naphthyl-substituted amine **2**. Thus, the device C was constructed by omitting NPB with the following simplified configuration: ITO/**2** (600 Å)/TPBI (400 Å)/LiF (10 Å)/Al (1500 Å). This device showed both hole-transporting as well as emitting behavior with the emission of blue light of a very high color purity as observed for device B. The maximum luminance and external quantum efficiencies achieved for the device C were 1.94 cd/A and 2.73%, respectively, at a current density of 6.32 mA/cm² (6.5 V). The turn-on voltages for all cases were as low as 2.9–4.0 V.

Table 1 Optical absorption, photoluminescence (PL), quantum yield and electrochemical data, and thermal properties of **1**, **2** and NPB

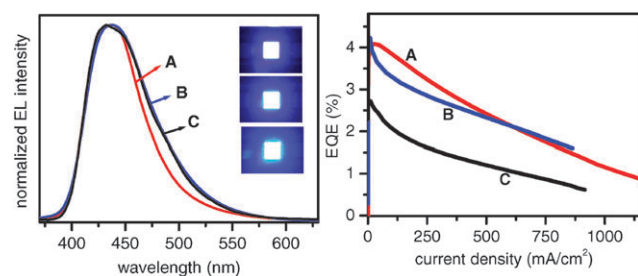
HTM	λ_{max}^a /nm	Band gap ^b	$\lambda_{max}^{a,c}$ sol/film nm	Φ^d sol/film	HOMO/LUMO ^e	T_d^f /°C	T_g^g /°C
1	330	3.23	430/431	0.51/0.52	5.53/2.30	438	122
2	325	3.08	432/435	0.17/0.17	5.54/2.46	460	152
NPB	340	— ^h	450	— ^h	5.40/2.30	— ^h	95

^a In chloroform (*ca.* 10^{-6} M). ^b From absorption onset values. ^c $\lambda_{ex}^{sol} = 330$ nm and $\lambda_{ex}^{film} = 325$ nm. ^d For dichloromethane solutions and vacuum-deposited films (1000 Å) by using the integrating sphere method. ^e HOMO values were calculated from oxidation potentials, while LUMO values were calculated by subtracting band gap values from their HOMO values. ^f By TGA. ^g By DSC; melting temperature of **1** is 164 °C. ^h Not available.

Table 2 EL data for the amines **1** and **2**

Device	V_{on}^a	η_{ex}^b/V	η_{p}^c	η_{l}^d/V	λ_{max}	L_{max}^e/V_d^f	CIE (x, y)
A	2.9	4.09/4.5	2.23	3.06/4.5	438	9849/11.0	0.15, 0.09
B	4.0	4.23/8.5	0.99	3.13/8.5	438	10 243/15.5	0.15, 0.09
C	3.5	2.73/6.5	1.03	1.94/6.5	436	5780/14.5	0.15, 0.10

^a Turn-on voltage. ^b External quantum efficiency (%). ^c Power efficiency (lm/W) @ 20 mA/cm². ^d Luminance efficiency (cd/A). ^e Maximum luminance achieved (cd/m²). ^f Driving voltage (V_d).

**Fig. 2** The EL spectrum (left) and the external quantum efficiency (right) of the non-doped devices of structure A, B and C. The inset photographs show the blue light emission captured from the EL devices A, B and C (top → bottom), respectively.

In general, amines are not ideal as emitting materials due to self-quenching problems. However, a few amino-substituted fluorophores such as anthracenes,⁶ phenanthrenes,^{6a} fluorenes,⁷ coumarins,⁸ pyrenes,⁹ etc. have been shown to exhibit high emission. Recently, rigid spiro bifluorene-based triaryl-amines have been shown to emit blue to blue-green light under non-doped device conditions.¹² For example, the diphenyl-amino end-capped bifluorene, *i.e.*, 2,2'-bis(diphenylamino)-bis[9,9-bis(*n*-butyl)fluorene] ($T_g = 91^\circ\text{C}$),¹³ shows deep-blue emission with CIEs close to the NTSC standard blue under a non-doped device configuration, but with an efficiency of only 0.8 cd/A.¹⁴ There is a particular emphasis on blue-emitting materials with high color purity at the current time in view of their low power consumption for full-color display applications¹⁵ and utility as effective host materials for generation of other primary colors *via* energy transfer.¹⁶ With this in mind, it is important to note that the devices for **1** and **2** display a low turn-on voltage behavior (2.9–4.0 V) and exhibit maximum luminances of 9849 cd/m² @ 11.0 V (for **1**) and 10243 cd/m² @ 14.0 V (for **2**). Moreover, they function both as HTL and emitting materials with a good color purity as shown for the amine **2** (device C); such materials are most desirable from the point of view of technological applications, as they simplify device constructions. It is compelling to probe the utility of these amines as dopants in phosphorescent OLEDs.

In summary, we have shown that diarylamino-substituted biphenyls linked to a unique 3-dimensional core, *viz.*, bimesitylene, exhibit amorphous property with glass transition temperatures higher than that of NPB, a most common HTM. Intriguingly, the amines **1** and **2** are found to exhibit bright blue emission in the solid state. By employing both **1** and **2** as emissive materials in OLED devices, we have captured *pure blue* electroluminescence under non-doped conditions with

high brightness and external quantum efficiency. That the amines **1** and **2** can simultaneously function as hole-transporting as well as emissive materials is demonstrated *via* device C constructed for the amine **2**. It is remarkable that EQEs of 4.1–4.2% observed for the non-doped pure blue light-emitting devices of **1** and **2** are comparable to those of the best doped blue-emitting devices reported for diphenylamine end-capped oligofluorene (4.1%)^{7b} and distyrylamine (5.1%).¹⁷

JNM is thankful to DST, India for generous financial support.

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