

# Journal of Materials Chemistry C

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## COMMUNICATION

# Blue Fluorescent Dihydro-indenoindene Derivatives with Unusual Low Oxidation Potentials as Multifunctional OLED Materials

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

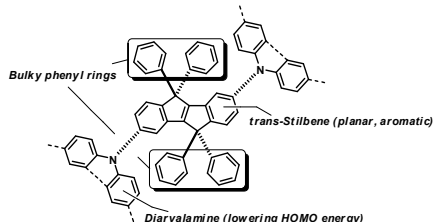
DOI: 10.1039/x0xx00000x

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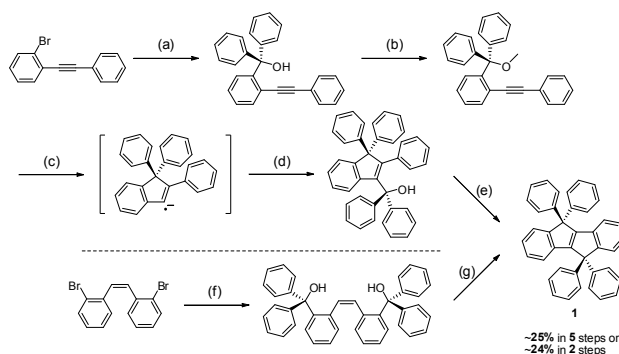
Several stable, blue fluorescent bis(diarylamino)dihydro-indenoindene derivatives have been synthesized and applied to OLED. The obtained HOMO energies are up to 4.79 eV. Under the applied voltage of 11 V, the current density generated from the hole only device is 1161 mA/cm<sup>2</sup>, showing their excellent hole mobility.

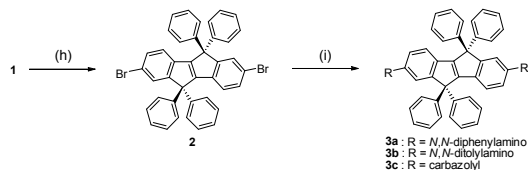
In the past decades, the aromatic compounds have been wide investigated for their potential to non-linear optics,<sup>1</sup> optical switches,<sup>2</sup> data storage,<sup>3</sup> chemical and biological sensing,<sup>4</sup> flat-panel displays,<sup>5</sup> and sustainable energy.<sup>6</sup> Some of these discoveries eventually become commercial and enhance our everyday lives. Organic light-emitting diodes (OLED), which is one of the most innovative technology for high-resolution display and lighting,<sup>7</sup> are basically composed of electrodes, charge transporting layers, and high emissive R–Y–G–B layers. Notably, molecule architecture plays a dominant role in designing these materials. While regarding the candidates, bis(diarylamino)dihydro-indenoindene derivatives (Scheme 1) that integrate two diarylamino units at the 2- and 7-positions of the 5,5',10,10'-tetraphenyl-5,10-dihydro-[2,1,a]-indenoindene (**1**)<sup>8</sup> catch my eye because of their unique structures. The dihydro-indenoindene has 14  $\pi$  electrons (aromatic). Because they are more delocalized than the anti-aromatic  $\pi$  electrons in dibenzopentalene (16 electrons), the additional electrons or holes generated at the opposite diarylamino substituents in this framework can communicate more easily. From another point of view, bis(diarylamino)stilbenes are well-known high fluorescent molecules. **1** can be taken as a constrained *trans*-stilbene. This rigid structure prohibits the photo-isomerization process, therefore, allows us to utilize this high emissive chromophore in OLED. The unfavorable non-radiative decay is also reduced because direct substitutions at the methylene carbons consolidate the molecule.



Scheme 1 Concepts of Designing Fluorescent Dihydro-indenoindene Derivatives.

As illustrated in Scheme 2, the precursor **1** has been reported through multi-step synthesis.<sup>8b,c</sup> Unfortunately, the promising yield is not reproducible in our hand due to lack of some essential apparatuses. When we carried out those reactions reported in the literature, the condition became more complicated owing to the incomplete air- and moisture- isolation in a simple schlenk line. The large amount of byproducts caused the difficulty in purification and resulted in the low yield in each step. We hence established a new synthetic route deriving from the addition of *cis*-stilbene moiety to benzophenone through halogen-metal exchange reaction. The resulting tertiary alcohol was then dehydrated intramolecularly. According to our approach, it can be synthesized in 2 steps without crucial purifications,<sup>9</sup> and the overall yield is competitive to the original method (24% and 25%, respectively). Moreover, direct bromination of **1** successfully yields the other precursor **2**, on which the Buchwald-Hartwig coupling reactions were performed to obtain the target molecules **3a–c** in good yields. Based on the orientation in three dimensions, these molecules are highly symmetric and nonpolar. However, we suppose the rigid structures inhibit the effective  $\pi$ – $\pi$  stacking to any other aromatic compound. It makes them barely soluble in general organic solvents such as pyridine, benzene, and toluene. The fraction works were done by sublimation under reduced pressure. All the molecular structures were identified by NMR spectroscopy properly.





Scheme 2 Synthetic Strategy for **1–3**. Reagents and conditions: (a) *n*-BuLi and benzophenone, Ether, 0 °C, 1 h. (b) CAN, MeOH, reflux, 16 h. (c) Li and naphthalene, THF, r. t., 30 min. (d) benzophenone, THF, r. t., 30 min. (e) BF<sub>3</sub>·OEt<sub>2</sub>, CH<sub>2</sub>Cl<sub>2</sub>, r. t., 1 h. (f) *n*-BuLi and benzophenone, Ether, 0 °C, 2 h. (g) cat. HCl, acetic acid, reflux, 4 h. (h) CuBr<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub>, CCl<sub>4</sub>, reflux, 30 h. (i) Pd<sub>2</sub>(dba)<sub>3</sub>, P(*t*-Bu)<sub>3</sub>, NaOt-Bu, and the corresponding amine, toluene, reflux, 4 h.

The steady-state photophysical properties of **3a–c** in CH<sub>2</sub>Cl<sub>2</sub> were identified at ambient temperature. As summarized in Table 1, the maximum absorption peaks (Abs. λ<sub>max</sub>) obtained are in the order of **3b** (427 nm) > **3a** (422 nm) > **3c** (385 nm), which are consistent with the DFT calculation results.<sup>9</sup> The calculated values for **3a–c** are 439, 446 and 410 nm, respectively. We conclude this trend is attributed to the extent of electron donating nature of different diarylamino substituents, and **3b** has a slight bathochromic shift in absorption to the others. On the other hand, all the longest absorptions for these molecules result in the S<sub>0</sub> → S<sub>1</sub> electronic transitions. Their molecular orbital surfaces show the π electrons in the HOMOs are delocalized in the whole molecules except the perpendicular phenyl rings. However, they are mainly localized in the central *trans*-stilbene fragment in the LUMOs (Fig. 2).

Table 1 Morphological, Photophysical, and Electrochemical Data for **3a–c**.

	Abs. λ <sub>max</sub> <sup>a,b</sup> (nm)	Abs. λ <sub>max</sub> <sup>c,d</sup> (nm)	Em. λ <sub>max</sub> <sup>a,e</sup> (nm)	Φ <sub>f</sub> (%)	T <sub>g</sub> /T <sub>d</sub> (°C)	E <sub>ox</sub> <sup>a</sup> (V)
<b>3a</b>	310 (20.4),	439	452	49	163/492	+0.21,
	404 (38.0),	(0.909)	(51)			+0.33
	422 (35.5)					
<b>3b</b>	310 (19.7),	446	459	47	165/514	-0.01,
	410 (34.2),	(0.959)	(47)			+0.21
	427 (33.1)					
<b>3c</b>	294 (26.9),	410	434	80	204/546	+0.69
	370 (37.7),	(0.674)	(59)			
	385 (31.6)					

<sup>a</sup> Measured in CH<sub>2</sub>Cl<sub>2</sub>. <sup>b</sup> The data in parentheses correspond to ε × 10<sup>-3</sup>. <sup>c</sup> Simulated by DFT/TD-DFT model. <sup>d</sup> The data in parentheses are *f* (relevant to absorption intensities). <sup>e</sup> The data in parentheses correspond to fwhm.

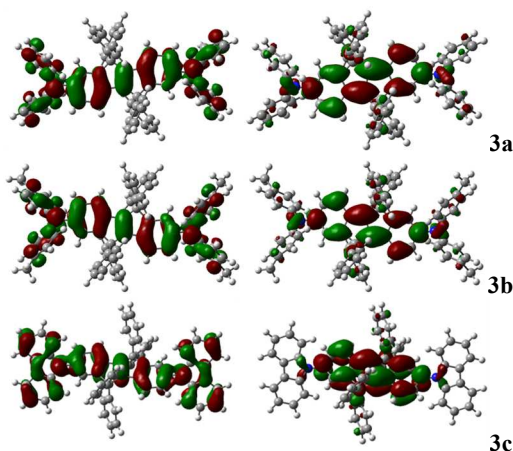


Fig. 2 Diagram of HOMO (left) and LUMO (right) surfaces for **3a–c**.

Upon excitation, **3a–c** emit sky blue fluorescence. The maximum emission peaks (Em. λ<sub>max</sub>) are observed at 452, 459, and 434 nm, respectively, with individual full width at half maximum (fwhm) of 53 ± 6 nm. The narrow emission profiles, as well as the high external quantum yields (Φ<sub>e</sub>) up to 80%, indicate these molecules may be utilized as good emitting materials.

They also exhibit excellent thermal stability because of their rigid structures. The T<sub>d</sub> were recorded in the range of 492–546 °C, and the phenyl rings hanging at the 5- and 10- positions of the central dihydro-indenoindene framework may contribute to the high T<sub>g</sub> (163–204 °C). In addition, the redox behaviours were evaluated by CV experiments using ferrocene as an internal reference.<sup>10</sup> The first oxidation potentials (E<sub>ox</sub>) of **3a–c** which can be correlated to their HOMO energy levels were observed reversibly at +0.21, -0.01 and +0.69 V, respectively. Notably, owing to the pendent electron donating diarylamino units, **3a,b** have extremely high HOMO energies rather than **3c** (with carbazolyl units instead) and other organic compounds (Fig. 3). The difference value (ΔE = 0.22 V) between **3a,b** is attributed to the methyl substitution at the *para*-position of the anilyl group. Similar tendency can be observed in the raise of their LUMO energy levels as well. This unusual phenomenon may facilitate the hole injection from cathode, and thus enhance the corresponding optoelectronic performances. We did a preliminary study of **3a**.<sup>9</sup> Under the same applied voltage of 11 V, the current density measured for the hole only device (ITO/NPB<sup>11</sup>/**3a**/NPB/LiF/Al) is 1161 mA/cm<sup>2</sup>, which is ~480 times higher than the value (2.4 mA/cm<sup>2</sup>) obtained from the electron only device (ITO/BCP/**3a**/TPBI<sup>12</sup>/LiF/Al). The dramatically difference suggests that these molecules may be adequate for hole transports. As other supports, it is higher than the data reported for several known hole transporting (HT) materials (TCTA, etc.).<sup>13</sup>

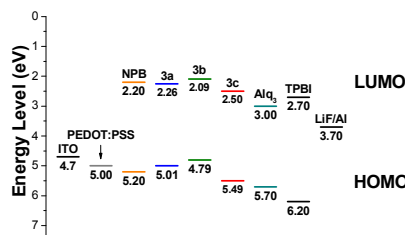


Fig. 3 Illustration of Relative Energy Levels.

In order to examine our assumptions, two types of OLED devices were made for advanced inspections. **3a–c** were utilized as both HT and emitting materials in combination with commercial electron transporting (ET) material TPBI in the bi-layer devices (configuration A). On the other hand, trilayer devices (configuration B) where **3a–c** only work as emitting materials can be fabricated by depositing a layer of NPB on the top of the cathode (indium tin oxide, ITO) due to its excellent hole mobility.<sup>11</sup> The EL data are summarized in Table 2. All these devices exhibit high efficient sky-blue fluorescence. The emission profiles reveal vibronic feature, showing two λ<sub>max</sub> in the range of 474 ± 18 and 442 ± 10 nm for **3a,b** and **3c**, respectively. In device-A, the low turn-on voltages (V<sub>on</sub>) for **3a,b** imply that the hole injection from ITO proceeds smoothly, and which is identical to our prediction. Moreover, the luminance and power efficiencies (η<sub>e</sub>/η<sub>p</sub>) measured at 20 mA/cm<sup>2</sup> are 2.8/1.9, 2.8/1.9, and 1.8/1.2 cdA<sup>-1</sup>/lmW<sup>-1</sup>, respectively, for **3a–c**. The performances are slightly ahead to how the corresponding trilayer devices display, furthermore, the enhancement (110–130%) is proportional to the relative operational brightness (L<sub>20</sub>) obtained at 20 mA/cm<sup>2</sup> (347–563 to 324–476 cd/m<sup>2</sup>, ~115% in average). A more

imbalanced ratio between the holes and electrons may result from the existence of additional HT material, and causes the inefficient charge recombination. Based on the preliminary results, we further utilize **3a** (configuration C) and NPB (configuration E) as simple HT materials where Alq<sub>3</sub> was chosen as ET and emitting material based on its HOMO and LUMO energy levels. In comparison, similar emission profiles obtained from both devices show that the holes are properly transported and injected into the emitting layer, and the  $\eta_c$  (3.0 cd/A) and  $L_{20}$  (590 cd/m<sup>2</sup>) show 10–15% enhancements in device-C. According to these observations, we now confirm that **3a–c** work well as HT and host materials. An attempt to optimize the EL efficiency of **3b** was carried out by fabricating a tetralayer device (configuration D) where 30 nm of PEDOS:PSS<sup>14</sup> was spin-coated. Interestingly, a significant enhancement up to 50% was observed when this individual hole injection layer further fixed the interface between ITO and **3b**. The resultant  $\eta_c$  and  $\eta_p$  are 3.6 and 2.2, respectively, with the  $L_{20}$  of 712 cd/m<sup>2</sup>.

Table 2 Summary of the EL Results in OLED Devices for **3a–c**.

Device Config. <sup>a</sup>	Em. $\lambda_{\max}^b$ (nm)	$V_{\text{on}}^c$ (nm)	$\eta_c/\eta_p^c$ (cdA <sup>-1</sup> /lmW <sup>-1</sup> )	$L_{20}^c$ (cd/m <sup>2</sup> )
<b>3a/A</b>	460, 484 (88)	2.5 (4.6)	2.8/1.9	551
<b>3a/B</b>	456, 484 (88)	2.5 (5.0)	2.4/1.5	476
<b>3a/C</b>	532 (107)	3.1 (7.9)	3.0/1.2	590
<b>3b/A</b>	468, 492 (82)	2.5 (4.8)	2.8/1.9	563
<b>3b/B</b>	464, 484 (70)	2.5 (4.5)	2.4/1.6	471
<b>3b/D</b>	468, 492 (83)	2.5 (5.2)	3.6/2.2	712
<b>3c/A</b>	432, 452 (76)	3.0 (4.7)	1.8/1.2	347
<b>3c/B</b>	432, 448 (76)	3.1 (5.6)	1.6/0.9	324
<b>NPB/E</b>	532 (100)	2.5 (4.1)	2.6/2.0	530

<sup>a</sup> Device configuration: **A**: ITO/**3a–c** (40 nm)/TPBI (40 nm)/LiF (1 nm)/Al; **B**: ITO/NPB (40 nm)/**3a–c** (40 nm)/TPBI (40 nm)/LiF (1 nm)/Al; **C**: ITO/**3a** (20 nm)/Alq<sub>3</sub> (40 nm)/LiF (1 nm)/Al; **D**: ITO/PEDOT:PSS (30 nm)/**3b** (40 nm)/TPBI (40 nm)/LiF (1 nm)/Al; **E**: ITO/NPB (40 nm)/Alq<sub>3</sub> (40 nm)/LiF (1 nm)/Al. <sup>b</sup> The data in parentheses correspond to fwhm. <sup>c</sup>  $\eta_c$ ,  $\eta_p$ ,  $L_{20}$ , and the data in parentheses of  $V_{\text{on}}$  were measured at 20 mA/cm<sup>2</sup>.

## Conclusions

Conclusively, we have developed a new strategy for the synthesis and purification of stable bis(diarylamino)dihydroindenoindene derivatives. Their HOMO energies are close to the work function of ITO, which causes facile hole injection and high hole mobility. In OLED, these molecules show high sky blue fluorescence and serve as good HT and host materials. The bifunctional feature exhibited by the device study is useful to simplify the complex fabrication progress.

## Acknowledgements

We thank Prof. Chien-Tien Chen for the generous support of laboratory apparatuses.

## Notes and references

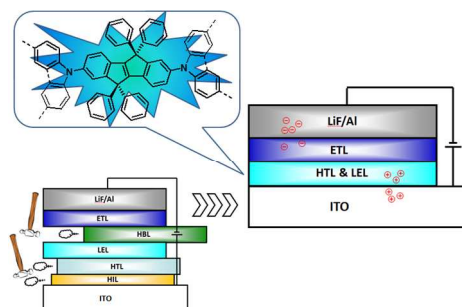
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† Electronic Supplementary Information (ESI) available: Experimental, spectra, CV, device, and DFT calculation details for **1–3**. See DOI: 10.1039/c000000x/

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- See Supporting Information for the complete syntheses of **1–3**, computational data for **3a–c**, and device details for **3a–c**, and NPB.
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## COMMUNICATION



The blue fluorescent bis(diarylamino)dihydro-indenoindene derivatives are the candidates of Multifunctional OLED Materials