Synthesis and electroluminescence properties of novel deep blue emitting 6,12-dihydro-diindeno[1,2-b;1′,2′-e]pyrazine derivatives†

Young-Il Park,[a] Ji-Hee Son,[a] Ji-Soung Kang,[a] Soo-Kang Kim,[a] Ji-Hoon Lee[b] and Jong-Wook Park*[a]

Received (in Cambridge, UK) 6th December 2007, Accepted 7th February 2008
First published as an Advance Article on the web 3rd March 2008
DOI: 10.1039/b718873k

Deep blue emitting materials with a new core structure containing indenopyrazine have been synthesized; a non-doped device using one of these materials as a blue emitter was found to exhibit high external quantumn efficiency of 4.6% and excellent color purity of (0.154, 0.078) as well as narrow emission band of 47 nm FWHM.

In recent, the range of applications of functional organic materials has rapidly expanded, with especially innovative uses discovered in the field of optoelectronics.[1] Researchers have begun to report how the properties of functional organic materials can be modified by varying their core and side groups.[2] A key research area is thus the development of new core and side groups and the study of how they combine in functional organic materials. In this study, we designed and synthesized a new core system, which we tested in organic light-emitting diodes (OLEDs).

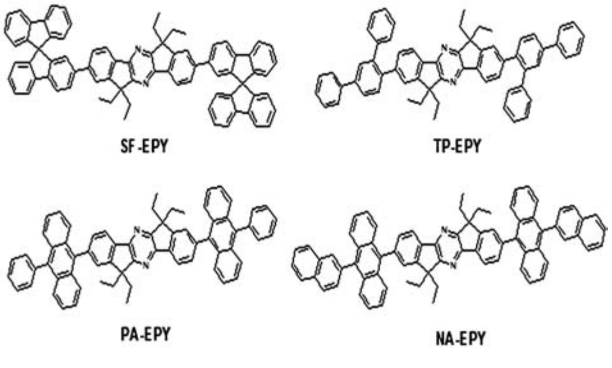
OLEDs are currently the subject of extensive research because of their potential applications in full-color large displays.[1] Most reported conjugated organic molecules exhibit red to green and blue electroluminescence (EL).[2c,3] High performance red, green, and blue materials with high EL efficiencies, good thermal properties, long lifetimes, and pure color coordinates (Commission Internationale de l'Eclairage (CIE)) are required for the fabrication of full-color OLED displays. Red emitting materials with CIE coordinates (0.67, 0.23) and long lifetimes of more than 100 000 h at 11 cd/A and green emitting materials with CIE coordinates (0.29, 0.64) and lifetimes of 100 000 h at 21 cd/A have recently been developed, but the best blue emitting materials have lifetimes of only 12 000 h at 7 cd/A and CIE coordinates (0.14, 0.16).[4]

It is not easy to produce highly efficient deep blue emitting materials with long device lifetimes; all materials synthesized thus far have disadvantages such as low efficiency and poor color purity and lifetime. The efficiency can be improved by adding layers or doping,[5,6] but the thermal properties and color purity of organic materials are intrinsic properties that are directly related to device lifetime and color performance, so new organic materials with high performance are urgently required.

In this study, an indenopyrazine (IPY) derivative with good color purity and superior thermal properties (IPY: T_m 280 °C and T_d 341 °C) was synthesized for the first time and used as the core component of new blue OLED materials, and their optical, thermal, and electroluminescence properties were examined. Even though the synthesis of the basic indenopyrazine heterocyclic ring structure was first reported by Ebel in 1956, no derivatives or applications of interest have yet been presented.[7] In preliminary experiments, we found that IPY solutions have a high fluorescence efficiency and a maximum emission wavelength at 399 nm. This luminescence in the violet region means that films of this material are likely to be blue emitting because of bathochromic shift (see Fig. S1†). However, films can also have disadvantages in their photoluminescence (PL) spectra, such as the broadening effect, and decreases in fluorescence efficiency due to π–π* stacking.

In the case of IPY, these problems can easily be overcome by the substitution of alkyl groups at the 6 and 12 carbons of the IPY ring and of various aromatic side groups at the 2 and 8 carbons. In particular, the latter substitutions with four kinds of side groups were found in this study to result in positive effects on the fluorescence yield and color purity of these materials.

The superior chromophores spirofluorene, *m*-terphenyl, and anthracene derivatives were added as side groups to synthesize blue emitting materials that are appropriate for OLEDs. The synthesized blue emitting materials are 6,6,12,12-tetraethyl-2,8-bis(9′,9″-spirobifluorene-2-yl)-6,12-dihydrodiindeno[1,2-b:1,2-e]-pyrazine (SF-EPY), 6,6,12,12-tetraethyl-2,8-bis-[1,1′;3′,1″]-terphenyl-4′-yl-6,12-dihydro-diindeno[1,2-b;1′,2′-e]pyrazine (TP-EPY), 6,6,12,12-tetraethyl-2,8-(10-phenyl-9-anthracyl)-



Scheme 1 Chemical structures of the synthesized materials.

---

[a] Department of Chemistry/Display Research Center, The Catholic University of Korea, Bucheon, Kyeonggi, 420-743, Korea. E-mail: hahapark@catholic.ac.kr; Fax: +82-2-2164-4764; Tel: +82-2164-4821
[b] Department of Polymer Science and Engineering, Chungju National University, Chungju, Chungbuk, 380-702, Korea

† Electronic supplementary information (ESI) available: Synthesis and characterization of synthesized materials and OLED fabrications. See DOI: 10.1039/b718873k

Table 1 Optical and electrical properties of the synthesized compounds

Compounds	Solution (THF) UV$_{max}$ [nm]	Solution (THF) PL$_{max}$ [nm]	Film on glass UV$_{max}$ [nm]	Film on glass PL$_{max}$ [nm]	FWHM	HOMO (eV)
SF-EPY	416	447, 468	401, 414	452, 473	52	5.90
TP-EPY	398	450	400	450	54	6.04
PA-EPY	385, 400	450	385, 400	458	56	5.69
NA-EPY	385, 401	455	385, 405	468	87	5.60

6,12-dihydrodiindeno(1,2-b;1,2-e)pyrazine (PA-EPY), and 6,6,12,12-tetraethyl-2,8-bis-(10-naphthalen-2-yl-anthracen-9-yl)-6,12-dihydro-diindeno[1,2-b;1′,2′-e]pyrazine (NA-EPY) (see Scheme 1). The UV-visible maximum absorption wavelengths of the four synthesized materials, SF-EPY, TP-EPY, PA-EPY, and NA-EPY in solution are in the range 400–420 nm and the maximum wavelengths of the PL spectra are in the blue region near 450 nm (see Table 1). In addition, the PL spectra of films of these materials were found to be around 10 nm red-shifted with respect to those of their solutions. 10 nm is a relatively small red shift, which could be due to the suppression of the intermolecular π–π* stacking of IPY by the introduction of bulky side groups. Further, in the case of TP-EPY, the PL maximum wavelength is 450 nm for both solution and film, as shown in Fig. 1. The FWHM (full width at half maximum) values are 47 nm for the solution state and 54 nm for the solid state; these widths are narrower than those of other blue emitting materials.

The HOMO energy levels of the synthesized materials were obtained with cyclic voltammetry (CV) and these results are summarized in Table 1. The HOMO levels of SF-EPY and TP-EPY were found to be 5.90 and 6.04 eV, respectively, which are similar to that of the core 6,6,12,12-tetraethyl-6,12-dihydro-diindeno[1,2-b;1′,2′-e]pyrazine (EIPY), 5.94 eV. In contrast, the HOMO energy levels of PA-EPY and NA-EPY, which have anthracene substituents, were found to be 5.69 eV and 5.60 eV, respectively, an increase of about 0.3 eV. This increase could be due to the introduction of the anthracene substituents, which accelerate the oxidation of the materials and increase their HOMO energy levels. It has been reported that the HOMO energy levels of 9,10-*di*(2-naphthyl)anthracene (ADN) and 2-methyl-9,10-*di*(2-napthyl)anthracene (MADN) as well as of many other compounds containing an anthracene group are also near 5.5–5.6 eV. Thus our results for the HOMO energy levels of our compounds with anthracene substituents are consistent with previous results.[2c]

Several differential scanning calorimetry (DSC) scans were carried out to obtain T_g for these materials. The T_m of TP-EPY and NA-EPY were found to be 340 °C and 295 °C, respectively, and the T_g and T_d of PA-EPY were found to be 112 °C and 383 °C, respectively; all of the synthesized materials exhibit better thermal stability than a commercial material used in blue OLEDs, 4,4′-bis(2,2-diphenylvinyl)-1,1′-biphenyl (DPVBi). We believe that the thermal properties of the films used in OLEDs are strongly associated with device lifetimes because of Joule heating during device operation. Therefore, the changes in the morphology of DPVBi and the synthesized materials that result from heating and storage were determined by depositing them onto glass in vacuum and monitoring the surfaces of the films with atomic force microscopy (AFM). The results are shown in Fig. 2.

As shown in Fig. 2, the surface of the DPVBi film became rough after one day of storage from the time of deposition at 25 °C. In contrast, the condition of the TP-EPY film surface was found to be maintained even when heated, and this is typical of the synthesized materials. The average surface roughnesses (Ra) of the films of the synthesized materials were found immediately after deposition to be in the range 0.4–0.8 nm, *i.e.* the quality of these films is better than that of DPVBi (Ra = 1.3 nm). After DPVBi was stored at 25 °C and 65 °C for 24 hours, Ra was found to be 44.1 and 43.0 nm, respectively, *i.e.*, the film surface

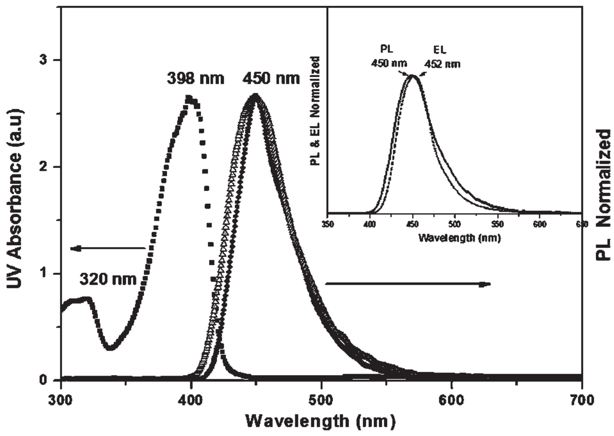


Fig. 1 UV-visible (■) and PL spectra (solution: ●, film: △) of TP-EPY (UV: 6.06 × 10^{-5} M, PL: 4.85 × 10^{-4} M in THF). The inset shows the EL (dash) and PL film (line) spectra.

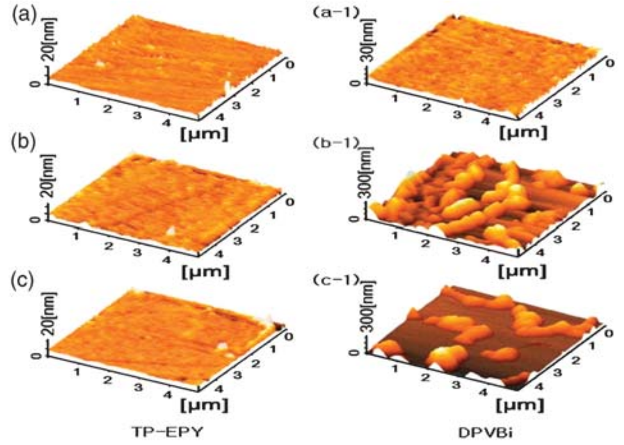


Fig. 2 AFM images of TP-EPY (left column) and DPVBi (right column): (a, a-1) just after evaporation, (b, b-1) after treatment at 25 °C for 24 h in a nitrogen atmosphere, (c, c-1) after treatment at 65 °C for 24 h in a nitrogen atmosphere.

Table 2 EL performance of the synthesized compounds: ITO/2-TNATA (60 nm)/NPB (15 nm)/synthesized materials or DPVBi (30 or 40 nm)/Alq_3 (30 or 20 nm)/LiF (1 nm)/Al (200 nm) at 10 mA/cm^2

Compounds	EL_{max} (nm)	Voltage (V)	Luminance efficiency (cd/A)	Power efficiency (lm/W)	C.I.E. (x,y)
SF-EPY[a]	458, 469	8.5	2.62	0.96	(0.152, 0.142)
TP-EPY[a]	452	7.5	2.01	0.92	(0.154, 0.078)
PA-EPY[a]	466	7.8	4.11	1.66	(0.194, 0.247)
NA-EPY[a]	474, 505	7.9	4.25	1.69	(0.273, 0.417)
NA-EPY[b]	469, 499	9.6	3.95	1.29	(0.229, 0.329)
DPVBi[a]	467	8.6	3.59	1.31	(0.153, 0.167)

[a] Emitting material (30 nm)/Alq_3 (30 nm). [b] Emitting material (40 nm)/Alq_3 (20 nm).

became very rough. However, in the case of the TP-EPY film, Ra was found to be 0.7 and 0.9 nm after the same heating processes, with little change in its surface properties.

The same experiments were performed on the other materials (SF-EPY, PA-EPY, NA-EPY), and even though the differences of Ra values after 24 hours were ranged from 0.6 to 2.3 nm, their surface properties were found to be much better than those of DPVBi. Based on the TGA/DSC and AFM results, these synthesized materials have excellent thermal properties that should improve the lifetimes when used in OLED devices. The synthesized materials and DPVBi were used as the emitting layers (EMLs) in OLEDs with the following structure: ITO/2-TNATA (60 nm)/NPB (15 nm)/synthesized materials or DPVBi (30 or 40 nm)/Alq_3 (30 or 20 nm)/LiF (1 nm)/Al (200 nm). The OLED properties were then measured and the results are summarized in Table 2. The EL spectra of the devices with SF-EPY, TP-EPY, and PA-EPY as emitting layers were found to be almost identical to the PL spectra. In the case of the NA-EPY device, electroluminescence at both 505 nm and 474 nm was observed, and it was thought that this luminescence was due to the NA-EPY and Alq_3 interface. In order to confirm this, a new device was fabricated with a NA-EPY (40 nm)/Alq_3 (20 nm) structure. In this device, electrons pass relatively quickly through the thin electron transporting layer (ETL), which generates additional recombination centers in the emitting layer. As a result, the EL intensity at 499 nm was found to be significantly weakened, and thus the emission at 505 nm in the original device is due to the Alq_3 interface, and arises because hole movement in NA-EPY is faster than in the other synthesized materials. Even though the PA-EPY and NA-EPY non-doped devices exhibit a high efficiency of about 4 cd/A, their CIE coordinates were found to be (0.194, 0.247) and (0.229, 0.329), respectively, *i.e.*, in the sky-blue region, because the EL spectra of these two materials are broad. The SF-EPY and TP-EPY non-doped devices were found to exhibit luminescence efficiencies of 2.62 and 2.01, cd/A, respectively. Interestingly, the absolute PL quantum efficiency of the film in TP-EPY is only 58.7% of that of DPVBi, but its EL external quantum efficiency (E.Q.E.) is 114% (at 10 mA/cm^2) and 93% (at 100 mA/cm^2) higher than that of the DPVBi device. Further, the EL maximum wavelengths of the SF-EPY and TP-EPY devices are 458 and 452 nm, respectively, *i.e.*, in the deep blue region, with CIE coordinates (0.152, 0.142) and (0.150, 0.078), respectively, which is a purer blue than obtained with DPVBi (0.153, 0.167). C. F. Shu's, C. T. Chen's and S. K. Kwon's groups reported OLED performance of CIE(0.14, 0.12) with E.Q.E. 5.3%, CIE(0.15, 0.25) with E.Q.E. 7.9% and CIE(0.15, 0.09) with FWHM 53 nm, respectively.[8] Compared to these results, non-doped device of TP-EPY showed 4.6% of E.Q.E. and CIE(0.15, 0.078) with 47 nm FWHM. As shown in Fig. 1, TP-EPY in particular has an EL maximum wavelength that is almost the same as its PL maximum wavelength at 452 nm in the deep blue region; thus this material produces a very pure deep blue. In summary, we have for the first time synthesized and utilized an indenopyrazine derivative as a core moiety in different functional organic materials. Non-doped devices using these materials as blue emitters were found to exhibit high luminance efficiencies of up to 2.01–4.3 cd/A at a current density of 10 mA/cm^2. The CIE coordinates of TP-EPY were found to be excellent with a Y-axis value less than 0.08, (0.150, 0.078), which are almost the same as the standard blue CIE coordinates of the National Television Standards Committee (NTSC). Furthermore, these synthesized materials exhibit excellent thermal properties that should improve the lifetimes of OLED devices. In particular, TP-EPY exhibits properties that are superior to those of the commercialized emitting material DPVBi, particularly with regards to its morphological stability and CIE coordinates.

This study was supported by the Research Fund, 2007 The Catholic University of Korea and a grant from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Commerce, Industry and Energy, Republic of Korea.

Notes and references

1 (*a*) M. A. Baldo, M.E. Thompson and S. R. Forrest, *Nature*, 2000, **403**, 750; (*b*) J. J. M. Halls, C. A. Walsh, N. C. Greenham, E. A. Marseglia, R. H. Friend, S. C. Moratti and A. B. Holmes, *Nature*, 1995, **376**, 498.

2 (*a*) K. T. Wong, Z. J. Wang, Y. Y. Chien and C. L. Wang, *Org. Lett.*, 2001, **3**, 2285; (*b*) T. H. Huang and J. T. Lin, *Chem. Mater.*, 2004, **16**, 5387; (*c*) S. K. Kim, Y. I. Park, I. N. Kang and J. W. Park, *J. Mater. Chem.*, 2007, **17**, 4670.

3 (*a*) B. J. Jung, J. I. Lee, H. Y. Chu, L. M. Do, J. M. Lee and H. K. Shim, *J. Mater. Chem.*, 2005, **15**, 2470; (*b*) J. Ding, J. Gao, Y. Cheng, Z. Xie, L. Wang, D. Ma, X. Jing and F. Wang, *Adv. Funct. Mater.*, 2006, **16**, 575.

4 T. Arakane, M. Funahashi, H. Kuma, K. Fukuoka, K. Ikeda, H. Yamamoto, F. Moriwaki and C. Hosokawa, *SID Dig.*, 2006, 37.

5 M. Pfeiffer, S. R. Forrest, K. Leo and M.E. Thompson, *Adv. Mater.*, 2002, **14**, 1633.

6 M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson and S. R. Forrest, *Appl. Phys. Lett.*, 1999, **75**, 5.

7 F. Ebel and W. Deuschel, *Chem. Ber.*, 1956, **89**, 2794.

8 (*a*) P. I. Shih, C. Y. Chuang, C. H. Chien, E. W.-G. Diau and C. F. Shu, *Adv. Funct. Mater.*, 2007, **17**, 3141; (*b*) Y. Wei and C. T. Chen, *J. Am. Chem. Soc.*, 2007, **129**, 7478; (*c*) Y. H. Kim, H. C. Jeong, S. H. Kim, K. Yang and S. K. Kwon, *Adv. Funct. Mater.*, 2005, **15**, 1799.