Mol. Cryst. Liq. Cryst., Vol. 550: pp. 149–155, 2011

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2011.599700

Highly Induced Photoluminescense Indenopyrazine Derivatives

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We designed and synthesized new blue deep-blue photoluminescense materials base on indenopyrazine core. The synthesized materials are meta-positioned phenyl ring substituted by methyl (DMP-EIP), trifluoromethyl (TFDMP-EIP) and phenyl groups (DPP-EIP). These compounds also showed deep-blue PL_{max} values, 440 ∼ 447 nm, in film state. But PL intensity in film state with same thickness was over about 8 ∼ 10 times higher in TFDMP-EIP than DMP-EIP and DPP-EIP. TFDMP-EIP also showed about stronger PL intensity than DMP-EIP and DPP-EIP in PL spectrum and absolute quantum efficiency data.

Keywords Indenopyrazine; photoluminescence; blue emitting material; core-side group; OLED; absolute quantum efficiency

1. Introduction

Many types of blue-light emitters for organic light-emitting diodes (OLED) have been intensively investigated and attempts have been made to improve their electroluminescence (EL) properties [1, 2]. However, it is not easy to produce highly efficient deep blue emitting materials and many researchers continue to strive to develop a new high-efficiency deep blue-light emitter.

In our preliminary experiments, we found that 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) material including an indenopyrazine core moiety showed excellent property [3]. In a recent study, the impact of molecular aggregation such as H, J-aggregation on the PL efficiency was worked out by Park group [4].

In this study, we investigated that change of PL efficiency by various side group based on new indenopyrazine core. We not only designed and synthesized new indenopyrazine (IP) derivatives 2,8-Bis-(3,5-dimethyl-phenyl)-6,6,12,12-tetraethyl-6,12-dihydro-diindeno[1,2-b;1′,2′-e]pyrazine (DMP-EIP), 2,8-Bis-(3,5-bis-trifluoromethyl-phenyl)-6,6,12,12-tetraethyl-6,12-dihydro-diindeno[1,2-b;1′,2′-e]pyrazine (TFDMP-EIP), and 6,6,12,12-Tetraethyl-2,8-bis-[1,1′;3′,1″]terphenyl-5′-yl-6,12-dihydro-diindeno[1,2-b;1′,2′-e]pyrazine (DPP-EIP) (see Scheme 1), but also compared electrical and luminescent properties of the synthesized compounds. In this investigation, we introduced CF_3 group

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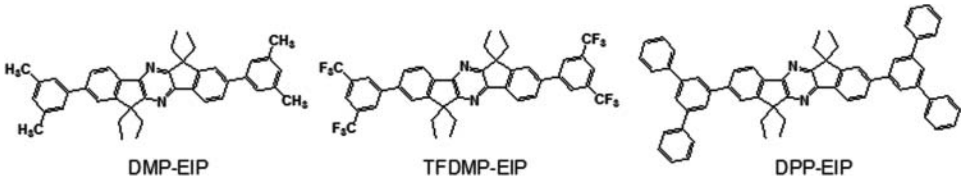


Scheme 1. Synthesized materials of indenopyrazine derivatives.

as well as similar group of methyl (CH_3) group and phenyl group into an indenopyrazine core group.

2. Experimental

2.1. General Method and General Syntheses of New Emitters [3]

These emitters were synthesized by Suzuki aryl-aryl coupling reaction using Pd catalyst. A typical synthetic procedure was as follows : To 2,8-dibromo-6,6,12,12-tetraethyl-6,12-dihydro-diindeno[1,2-b;1′,2′-e]pyrazine (1g, 1.9 mmol) and 4,4,5,5-Tetramethyl-2-[1,1′;3′,1″]terphenyl-5′-yl-[1,3,2]dioxaborolane (1.49g, 4.19 mmol) in a 500mL round-bottomed flask under a nitrogen atmosphere were added $Pd(OAC)_2$ (0.042g, 0.19 mmol), tri-cyclohexyl-phosphine (0.053g, 0.19 mmol) and toluene. The temperature was increased to 50°C, and tetraethylammonium hydroxide (13.5mL, 19.0 mmol, 20 wt% in water) was added. Stirring was continued at this temperature and the reaction was monitored by TLC. When the reaction was complete, extraction of the product was performed with water and toluene. The organic extract was dried with $MgSO_4$ added, and then filtered the solvent removed in vacuo. The resulting crude mixture was passed through a short-column of silica with THF as the eluent and then recrystallized from THF to obtain DPP-EPY as a white solid.

2.2. 2,8-Bis-(3,5-dimethyl-phenyl)-6,6,12,12-tetraethyl-6,12-dihydro-diindeno[1,2-b;1′,2′-e]pyrazine (DMP-EIP)

The yield was 72%.^{1}H-NMR (500 MHz, $CDCl_3$) : δ (ppm) 0.40–0.43 (t, 12H), 2.11–2.17 (m, 4H), 2.36–2.40 (m, 4H), 2.43 (s, 12 H), 7.04 (s, 2H), 7.31 (s, 4H), 7.63 (s, 2H), 7.66–7.68 (d, 2H), 8.12–8.13 (d, 2H) ^{13}C-NMR (500 MHz, $CDCl_3$) : 163.1, 152.2, 150.3, 142.6, 141.5, 138.6, 138.5, 129.3, 126.7, 125.4, 121.9, 121.4, 54.2, 31.5, 29.9, 21.6, 8.9, Fab$^+$-MS *m/e* : 577.

2.3. 2,8-Bis-(3,5-bis-trifluoromethyl-phenyl)-6,6,12,12-tetraethyl-6,12-dihydro-diindeno[1,2-b;1′,2′-e]pyrazine (TFDMP-EIP)

The yield was 80%. ^{1}H-NMR (500 MHz, $CDCl_3$) : δ (ppm) 0.38–0.41 (t, 12H), 2.22–2.26 (m, 4H), 2.40–2.45 (m, 4H), 7.93–7.94 (d, 2H), 7.98 (s, 2H), 8.04 (s, 2H), 8.19–8.21 (d, 2H), 8.36 (s, 4H) ^{13}C-NMR (500 MHz, $CDCl_3$) : 164.3, 153.2, 151.8, 144.6, 141.0, 140.3, 134.3, 133.2, 132.8, 128.1, 126.6, 123.2, 123.0, 122.7, 122.0, 55.4, 32.0, 30.7, 14.5, 9.1, Fab$^+$-MS *m/e* : 793.

Table 1. Optical and electronic property of synthesized materials

	Solution ($CHCl_3$)		Film on glass (on glass)					
Sample	UV_{max}	PL_{max}	UV_{max}	PL_{max}	Quantum Yield (%)[a]	HOMO	LUMO	Band gap
DMP-EIP	403	432	408	444	10	6.03	2.97	3.06
TFDMP-EIP	399	423	411	440	36	6.06	2.99	3.07
DPP-EIP	403	432	408	447	16	6.05	2.99	3.06

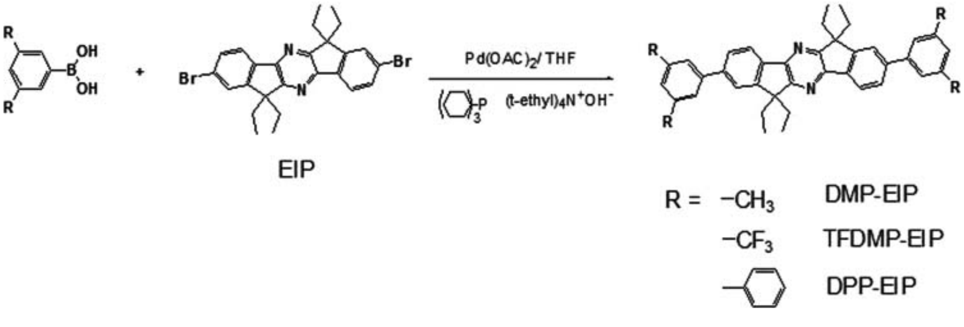
a : quantum yield was measured by using a calibrated integrating sphere system.

2.4. Synthesis of 2,8-bis(3,5-diphenylphenyl)-6,6,12,12-tetraethyl-6,12-dihydrodiindeno [1,2-b:1′,2′-e]pyrazine (DPP-EPY)

The final yield was 90%. ^1H NMR (500 MHz, $CDCl_3$) : δ (ppm) : 8.21 (d, 2H). 7.88 (s, 4H), 7.81 (m, 4H), 7.75 (m, 10H), 7.42 (t, 4H), 2.41 (m, 4H), 2.17 (m, 4H), 0.43 (t, 12H), ^{13}C NMR (300 MHz, $CDCl_3$) : 163.2, 152.2, 150.5, 142.8, 142.6, 142.3, 141.4, 138.9, 129.1, 127.8, 127.6, 127.0, 125.5, 122.0, 121.7, 54.3, 31.5, 9.0, Fab^+-MS m/e : 825.

3. Results and Discussion

New indenopyrazine derivatives were substituted various side group such as methyl, trifluoromethyl and phenyl groups (see Scheme 1). New indenopyrazine derivatives were synthesized for this reason that change of molecular staking by various side groups and it makes change of PL efficiency. All compounds were purified with the silica column method and recrystallization, producing very pure powders that we characterized with ^1H-NMR, ^{13}C-NMR and FAB-MS analysis. The synthesis routes to the three compounds are shown in Scheme 2. Boration and Suzuki aryl–aryl coupling reactions were used in all the syntheses. The side groups are meta-positioned phenyl ring substituted by methyl, trifluoromethyl and phenyl groups, so it was easy to couple them with core indenopyrazine moiety by using the metal-catalyzed aryl–aryl coupling reaction.



Scheme 2. Synthetic routs of indenopyrazine derivatives.

The UV-visible (UV) and PL spectra of the synthesized compounds in the $CHCl_3$ solution state and the thin-film state were measured as shown in Table 1 and Fig. 1. In the $1.0 * 10^{-6}$ M $CHCl_3$ solution state, the three materials all exhibit UV_{max} value of around 400 nm and PL_{max} values in the range of $423 \sim 432$ nm. These compounds also showed

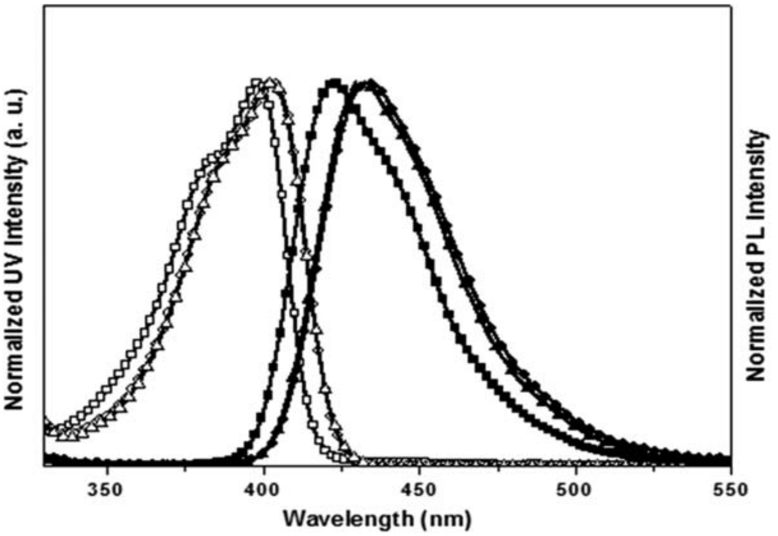


Figure 1. UV and PL spectrum of indenopyrazine derivatives in 10^{-6} M $CHCl_3$ solution (● : DMP-EIP, ■ : TFDMP-EIP, ▲: DPP-EIP).

deep-blue PL_{max} values, 440 ∼ 447 nm, in film state. All PL_{max} values are in the range of deep-blue color and it is not easy to get this kind of deep-blue and narrow PL spectrum based on the new chemical structure. In addition, the PL spectra of all these materials in the solid-film state were red-shifted by about 12 ∼ 17 nm with respect to those of the solution state.

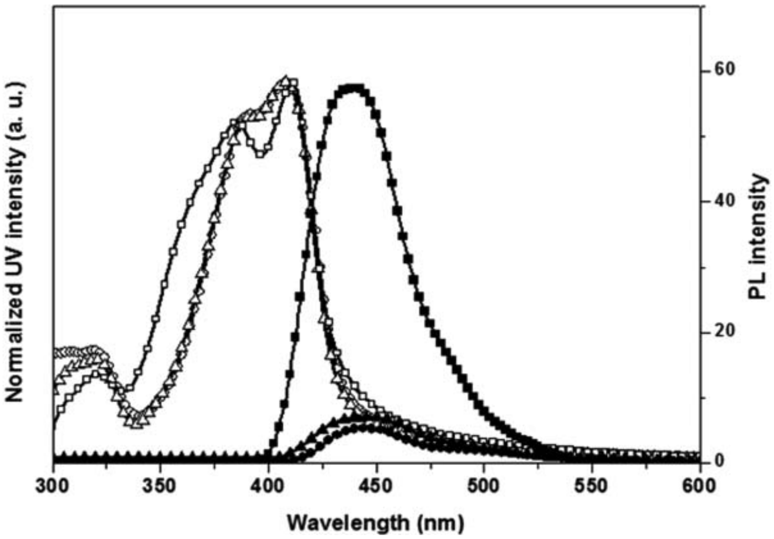


Figure 2. UV and PL spectrum of indenopyrazine derivatives in film on the glass (● : DMP-EIP, ■ : TFDMP-EIP, ▲: DPP-EIP).

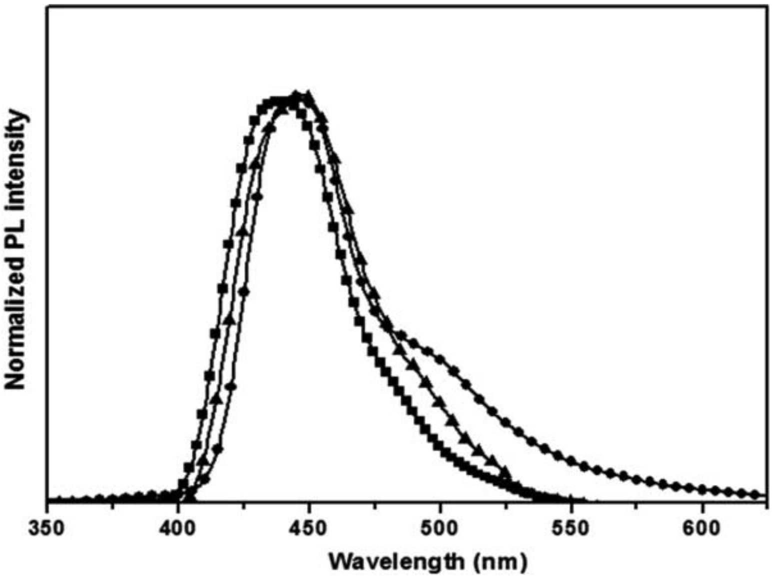


Figure 3. Normalized PL spectrum of indenopyrazine derivatives in film on the glass (● : DMP-EIP, ■ : TFDMP-EIP, ▲: DPP-EIP).

Also the UV and PL spectra in film state were summarized in Table 1 and Fig. 2. Most importantly, PL intensity in film state with same thickness was over about 8 ∼ 10 times higher in TFDMP-EIP than DMP-EIP and DPP-EIP (See Fig. 2).

Such tendency of luminance efficiency had no trend as in solution state, and film state showed larger difference in luminescence than solution state. These results could be due to the capability of molecular repulsion, TFDMP-EIP includes fluorine atom at side group and it makes dilution effect as well as repulsion between molecules.[4a] Therefore, there is special increase of the PL_{max} value 440 nm peak which might be caused by the repulsion interaction between molecules. In order to check and measure the accurate PL enforced effect, absolute PL quantum efficiency (Q.E.) was measured by using an integrating sphere [5]. As shown in Table 1, PL quantum efficiency was 10, 36, and 16% for DMP-EIP, TFDMP-EIP, and DPP-EIP, respectively. TFDMP-EIP exhibited two or three times higher efficiency than other two compounds. We believe that it would be applied to OLED device. Further studies on OLED device including doping effect are underway. Figure 3 shows the Normalized PL spectra of three compounds in film state. DMP-EIP and DPP-EIP are broadened at 480 ∼ 550 nm region in comparison to TFDMP-EIP. Such phenomenon can be interpreted as more efficient blocking of molecular $\pi - \pi^*$ stacking interaction in TFDMP-EIP than DMP-EIP and DPP-EIP. More excellent luminescence property and sharper PL spectrum are shown in TFDMP-EIP film state.

We also observed PL intensity variation as a function of solute concentration (see Fig. 4). Under the dilution concentration of less than 10^{-4} M, PL intensities of three compounds were similar, but as compound concentration increased, PL peak intensity was different between 10^{-3} M and thin film state. Concentration could not be increased more than 5×10^{-3} M due to the limitation of solubility.

The energy band gaps and the highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) level of DMP-EIP, TFDMP-EIP, and DPP-EIP are

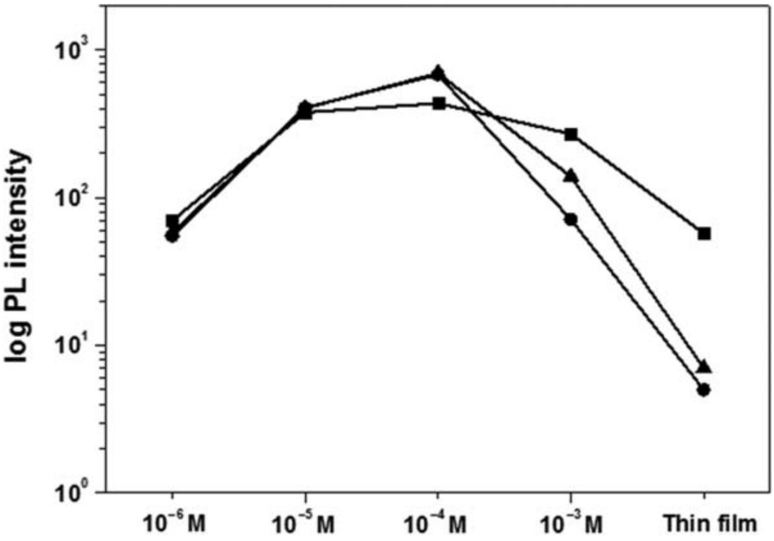


Figure 4. PL intensity at different concentration from 10^{-6} M to Thin film (● : DMP-EIP, ■ : TFDMP-EIP, ▲: DPP-EIP).

also summarized in Table 1. Those were estimated by CV and the analysis of absorption edge with a plot of (*hv*) *vs*. (*ahv*) [2] where *a*, *h*, and *v* are absorbance, Plank's constant, and the frequency of light.[1a] The band gaps of three compounds were found to be about 3.0 eV and HOMO and LUMO levels were 6.0 and 3.0 eV, respectively.

4. Conclusions

New deep-blue photoluminescence materials using indenopyrazine core moiety were synthesized. In particular, TFDMP-EIP showed about stronger PL intensity than DMP-EIP and DPP-EIP in PL spectrum and absolute quantum efficiency data. It might be due to the repulsion effect of CF_3 side group between molecules. Also π-π^* stacking interaction band of DMP-EIP and DPP-EIP was observed in the range of 480 ~ 550 nm and TFDMP-EIP exhibited narrower PL spectrum compared to others.

Acknowledgment

This research was supported by a grant (Catholic Univ.) from the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy (MKE), Republic of Korea. This work was supported by Mid-career Researcher Program through NRF grant funded by the MEST (No. 20100000422).

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