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[a] Display and Nano Devices Laboratory, DGIST, Daegu, Korea

[b] Department of Polymer Science, Kyungpook National University, Daegu, Korea

[c] Department of Chemical Engineering, Daegu University, Gyeongsan, Gyeongbuk, Korea

[d] Department of Chemical Engineering, Keimyung University, Daegu, Korea

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[1]Display and Nano Devices Laboratory, DGIST, Daegu, Korea
[2]Department of Polymer Science, Kyungpook National University, Daegu, Korea
[3]Department of Chemical Engineering, Daegu University, Gyeongsan, Gyeongbuk, Korea
[4]Department of Chemical Engineering, Keimyung University, Daegu, Korea

Three different cyclic amine dyes, 9-(2-chlorophenyl)-9H-carbazole (CPCz; $C_{18}H_{12}ClN$), 10-(2-chlorophenyl)-10H-phenoxazine (CPPo; $C_{18}H_{12}ClNO$), and 10-(2-chlorophenyl)-10H-phenothiazine (CPPt; $C_{18}H_{12}ClNS$), were synthesized to systematically investigate their optical properties and electronic band structures with molecular microstructure. By the insertion of oxygen or sulfur atom into carbazole moiety, the absorption and photoluminescence (PL) spectra showed bathochromic shift, and the Stoke's shift was increased. Ionization potential of CPCz was measured as 5.75 eV, on the other hand, CPPo and CPPt showed their ionization potentials of 5.37 and 5.39 eV, respectively. The minute difference in chemical structure such as insertion of oxygen or sulfur atom caused huge change of optical property and electronic band structure.

Keywords: carbazole; cyclic amine compound; electronic band structure; phenothiazine; phenoxazine

INTRODUCTION

Organic light emitting diode (OLED) has attracted much attention due to its self-emitting property, high luminous efficiency, high contrast

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Address correspondence to Byeong-Dae Choi, Display and Nano Devices Laboratory, Daegu Gyeongbuk Institute of Science Technology, 711, Hosan-dong, Dalseo-gu, Daegu 704-230, Korea. E-mail: bdchoi1@dgist.ac.kr

ratio, fast response time, and wide color gamut. Due to these potential strong points, OLED has been widely studied for application to full color display, back light unit, illuminators and light source of projection displays. Especially, active matrix (AM) OLED has been considered to become the strong candidate for next generation TV [1,2]. In order to realize AMOLED TV, many scientists and engineers are endeavoring to solve three major problems such as TFT backplane, RGB patterning technology for large screen size and display performance. Among these problems, display performances such as life time, efficiency and color gamut are strongly related in emitting materials. Numerous organic emitting materials have been reported for the application of OLED [3–6]. Current emitting materials are suitable for mobile phone application in terms of life time and luminance(or efficiency), but they are not applicable for the AMOLED TV.

Many emitting materials containing carbazole [7–12], phenoxazine [13–16] or phenothiazine [17–20] moiety have been reported, and have shown different emission color and charge mobility which are originated from variation of electronic band structure. Evaluation of electronic band structure with minute structural change of emitting materials is able to contribute to develop new materials with high performances.

In this work, we synthesized and characterized three different dyes containing cyclic amine group, and their optical properties such as absorption and PL emission band, Stoke's shift with molecular microstructure were investigated. The electronic band structures constituted with band gap energy, ionization potential and electron affinity were also discussed.

EXPERIMENTAL

Materials

TLC analyses were carried out on a precoated 0.2 mm HPTLC silica gel 60 plate (E. Merck, Darmstadt). Flash column chromatography was performed with silica gel Merck silica gel 60 (70–230 mesh). 9,10-dibromoanthracene, K_2CO_3, 9*H*-carbazole, copper powder, *N*,*N*-dimethylacetamide, 10*H*-phenoxazine and 10*H*-phenothiazine were purchased from Aldrich Chemical, and used without further purification.

Synthesis of Cyclic Amine Dyes

The synthetic scheme of the cyclic amine dyes studied in this work is illustrated in Figure 1.

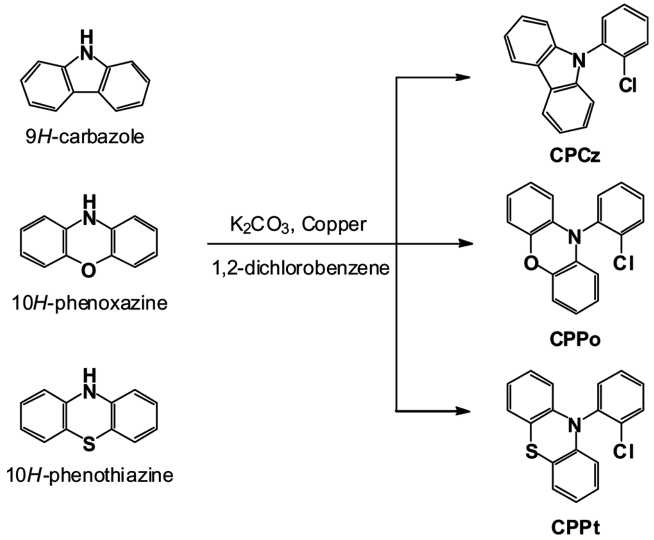


FIGURE 1 Synthetic scheme of the cyclic amine type dyes.

9-(2-Chlorophenyl)-9H-carbazole (CPCz)

To a solution of 9*H*-carbazole (2.0 g, 11.9 mmol) in 1,2-dichlorobenzene (20 mL), copper powder (150 mg, 2.38 mmol) and K_2CO_3 (3.3 g, 23.8 mmol) were added. The mixture was stirred at 180℃ for 12 hr and then extracted with ethyl acetate. The combined organic extractors were dried over Na_2SO_4 and concentrated under vacuum to leave a residue which purified by silica gel chromatography eluting with EtOAc/hexane (1:9). The collected compound was sublimed at 10^{-5} torr of high vacuum to give CPCz as a high purity of white solid. R_f 0.62 (EtOAc-hexane 1:9). ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm) 8.13 (s, 2H), 8.11 (s, 2H), 7.62 (m, 2H), 7.41–7.34 (m, 8H), 7.26 (m, 4H), 7.07 (s, 2H), 7.05 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ(ppm) 143.5, 133.3, 131.9, 131.4, 129.1, 128.1, 127.5, 127.0, 124.8, 123.4, 120.2, 116.4; FAB+: 277 (M+); Anal. Calcd for $C_{18}H_{12}ClN$: C, 77.84; H, 4.35; N, 5.04. Found: C, 77.61; H, 4.34; N, 4.99.

10-(2-Chlorophenyl)-10H-phenoxazine (CPPo)

With using phenoxazine as reactant, a synthetic procedure similar to that of **CPCz** was used to synthesize **CPPo**. ^{1}H NMR ($CDCl_3$, 400 MHz) δ(ppm) 8.66 (d, $J = 9.0$ Hz, 1H), 8.30 (d, $J = 8.6$ Hz, 1H), 7.66–7.62 (m, 2H), 7.54–7.50 (m, 2H), 6.79 (dd, $J = 7.7$, 1.5 Hz, 2H), 6.63 (m, 2H), 6,38 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ(ppm) 144.3, 134.2, 132.2, 131.1, 129.2, 128.1, 124.8, 124.3, 124.0, 122.1, 116.0, 113.8; FAB+: 294.1 (MH+); Anal. Calcd for $C_{18}H_{12}ClNO$: C, 73.60; H, 4.12; N, 4.77. Found: C, 73.61; H, 4.24; N, 4.51.

10-(2-Chlorophenyl)-10H-phenothiazine (CPPt)

With using phenothiazine as reactant, a synthetic procedure similar to that of **CPCz** was used to synthesize **CPPt**. ^1H NMR ($CDCl_3$, 400 MHz) δ(ppm) 8.67 (d, $J = 9.0$ Hz, 1H), 8.32 (d, $J = 8.5$ Hz, 1H), 7.66–7.62 (m, 2H), 7.54–7.50 (m, 2H), 7.04 (dd, $J = 7.5$, 1.5 Hz, 2H), 6.77–6.72 (m, 2H), 6,58 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ(ppm) 140.8, 135.0, 133.7, 130.9, 130.8, 129.7, 128.0, 125.9, 123.3, 120.3, 119.9, 109.9; FAB+: 310 (MH+); Anal. Calcd for $C_{18}H_{12}ClNS$: C, 69.78; H, 3.90; N, 4.52; S, 10.35. Found: C, 70.01; H, 4.04; N, 4.69; S, 10.83.

Measurements

^1H NMR and ^{13}C NMR spectra were recorded either on a Bruker AM-400 (400 MHz) or a Varian unity plus 300 (300 MHz) spectrometers in $CDCl_3$. Elemental analyses were performed on a Carlo Erba 1106 analyzer. Infrared spectra were taken in KBr pellets using a Nicolet Magna-IR 550°C Spectrometer. UV-visible absorption spectra of the dyes were obtained by Varian Easy 50 Conc. The photoluminescence spectra excited by 150 watts of Xe lamp were monitored by Jasco FP-6500. The ionization potential (Ip) was measured by a photoelectron spectroscopy (Riken Keiki, AC-2).

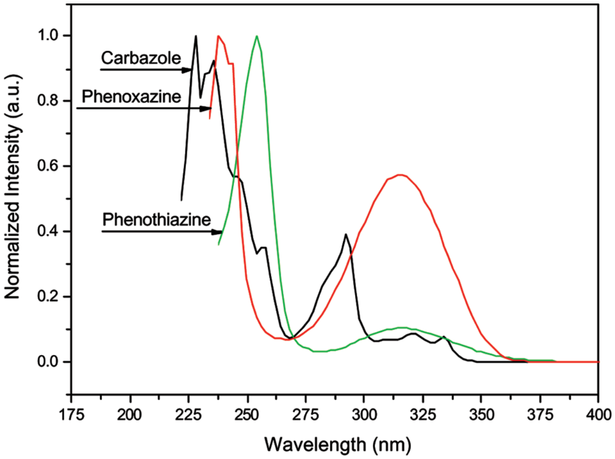
RESULTS AND DISCUSSION

Synthesis and Characterization

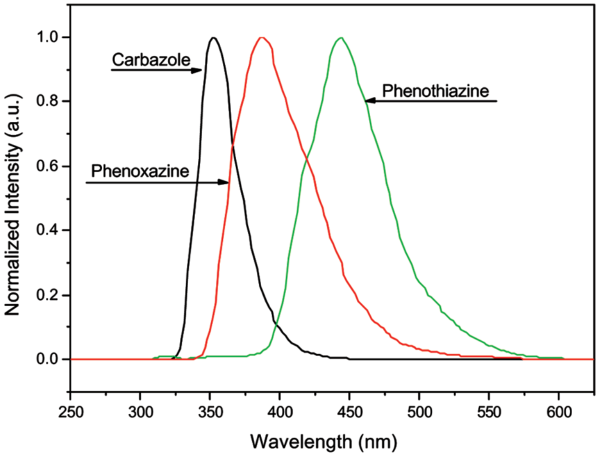
Three types of cyclic amine dyes were synthesized to compare their optical properties and electronic band structures from the viewpoint of microstructure. All synthesized dyes were characterized with ^1H-NMR, ^{13}C-NMR and elemental analysis, and their resulting spectral data were listed in experimental section. The proton peaks from hydrogens of aromatic rings in DPCz were found at 8.13–7.05 ppm, but the proton peak from H-N < in carbazole (10.2 ppm) was not appeared.

Optical Properties of Cyclic Amine Compounds

As earlier mentioned, many organic emitting materials containing cyclic amine compounds such as carbazole, phenoxazine and phenothiazine have been reported for OLED application. This means that the cyclic amine compounds play important role of designing new emitting materials with high luminous efficiency, high color purity and long life time. We firstly investigated the optical properties of substrate materials, carbazole, phenoxazine and phenothiazine. Figure 2 shows absorption and PL spectra detected from 0.5 mM solution of the substrate materials. The absorption maximum ($\lambda_{\max,\mathrm{UV}}$) of carbazole corresponding to maximum π-π^* transition was measured to be 228 nm with several shoulders. Phenoxazine and phenothiazine, however,



(a)



(b)

FIGURE 2 Absorption (a) and PL (b) spectra of carbazole, phenoxazine and phenothiazine.

TABLE 1 Optical Properties of Substrate Materials

Compounds	$\lambda_{\max,\mathrm{UV}}$ (nm/eV)	$\lambda_{\max,\mathrm{PL}}$ (nm/eV)	FWHM (nm)	Eg (eV)	Stoke's shift (nm)
Carbazole	228/5.44 292[a]/4.35	354/3.50	35	3.62	126
Phenoxazine	238/5.21 314[a]/3.95	386/3.21	66	3.43	148
Phenothiazine	254/4.88 316[a]/3.92	444/2.79	64	3.26	190

[a] Wavelength of shoulder peaks in absorption spectra.

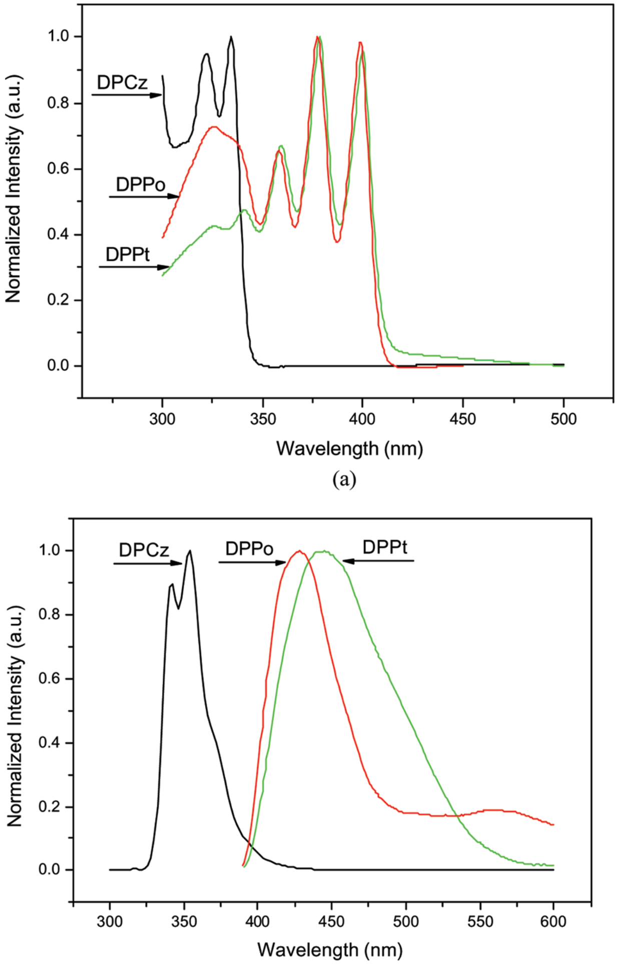
showed $\lambda_{\max,\mathrm{UV}}$ at 238 and 254 nm with a new broad peak at 314 and 316 nm, respectively. PL maximum ($\lambda_{\max,\mathrm{PL}}$) values of carbazole, phenoxazine and phenothiazine were observed at 354, 386 and 444 nm, when excited at their own wavelength of absorption peak, respectively.

The optical properties of the substrate materials are listed in Table 1. The insertion of oxygen or sulfur atom into carbazole molecule derived bathochromic shift in both absorption and PL spectra, and also showed larger Stoke's shift [21,22]. The HOMO (the highest occupied molecular orbital)-LUMO (the lowest unoccupied molecular orbital) band gap energies (Eg) calculated from the onset points of absorption spectra [23] were increased in the order of carbazole > phenoxazine > phenothiazine. The smaller band gap energy of phenoxazine or phenothiazine than that of carbazole might have been due to the extension of conjugation (hyperconjugation) length through the oxygen or sulfur atom containing nonbonding electron pairs. The PL from carbazole showed smaller FWHM (full width at half maximum) compared to that from phenoxazine or phenothiazine.

Optical Properties of the Synthesized Dyes

In many cases, the protons bonded with nitrogen in cyclic amine compounds were replaced with fused aromatic ring to increase chemical stability, or long alkyl group to enhance solubility. As shown in Figure 1, we synthesized three cyclic amine dyes in which protons bonded with nitrogen atoms were replaced with phenyl groups, and their optical properties with molecular microstructure were investigated. And also, we believed that comparing the synthesized dyes and their substrate materials will help chemists design new emitting materials for OLED application.

The optical absorption and PL spectra of the synthesized dyes were compared in Figure 3. The absorption peaks of DPCz were showed at 334 and 322 nm, and PL maximum ($\lambda_{\max,\mathrm{PL}}$) value was observed at 354 nm with a additional peak at 342 nm when excited at 334 nm. The Stoke's shift and band gap energy (Eg) of DPCz were calculated as 20 nm and 3.56 eV, respectively. Unlike DPCz, DPPo and DPPt showed similar aspect in their absorption behaviors, namely, the



(a)

(b)

FIGURE 3 Absorption (a) and PL (b) spectra of the synthesized dyes.

TABLE 2 Optical Properties of the Synthesized Dyes

Synthesized dyes	$\lambda_{\max,\mathrm{UV}}$ (nm/eV)	$\lambda_{\max,\mathrm{PL}}$ (nm/eV)	FWHM (nm)	Eg (eV)	Stoke's shift (nm)
DPCz	334/3.71 322[a]/3.85	354/3.50 342[a]/3.63	10	3.56	20
DPPo	377/3.29 399[a]/3.11 358[a]/3.46 325[a]/3.82	428/2.90	57	3.00	51
DPPt	378/3.28 400[a]/3.10 359[a]/3.45 341[a]/3.64 326[a]/3.80	445/2.79	89	2.93	67

[a] Wavelength of additional peaks in absorption or PL spectra.

absorption spectra of DPPo and DPPt indicated five peaks, and they were almost overlapped. Similarly with the case of substrate materials, the absorption pattern was greatly changed, and the PL spectra were also red-shifted by the insertion of oxygen or sulfur atom into carbazole unit. The change of band gap energy, FWHM and Stoke's shift showed a similar tendency with those of substrate materials.

The optical properties of the synthesized dyes are summarized in Table 2. From the comparison of Tables 1 and 2, we could find that all the absorption peaks of the synthesized dyes were red-shifted from those of their substrate materials. The PL spectra of carbazole and DPCz were recorded at a similar wavelength range, and the phenothiazine and DPPt also showed their emission at a similar wavelength range. Both band gap energies and Stoke's shifts of the synthesized dyes were significantly decreased by introduction of chlorophenyl group.

Electronic Band Structure of the Synthesized Dyes

Electronic band structure of emitting materials in OLED is important factor to deciding emission color and electron (and/or hole) mobility. Ionization potential of the synthesized dyes was measured by photoelectron spectroscopic analysis, and electron affinities were calculated from band gap energies and ionization potentials. The electronic band diagram of the synthesized dyes is outlined in Figure 4. DPCz showed the largest ionization potential of 5.75 eV. By the insertion of oxygen or sulfur atom into carbazole moiety, the electron affinity was increased, on the other hand, ionization potential was decreased.

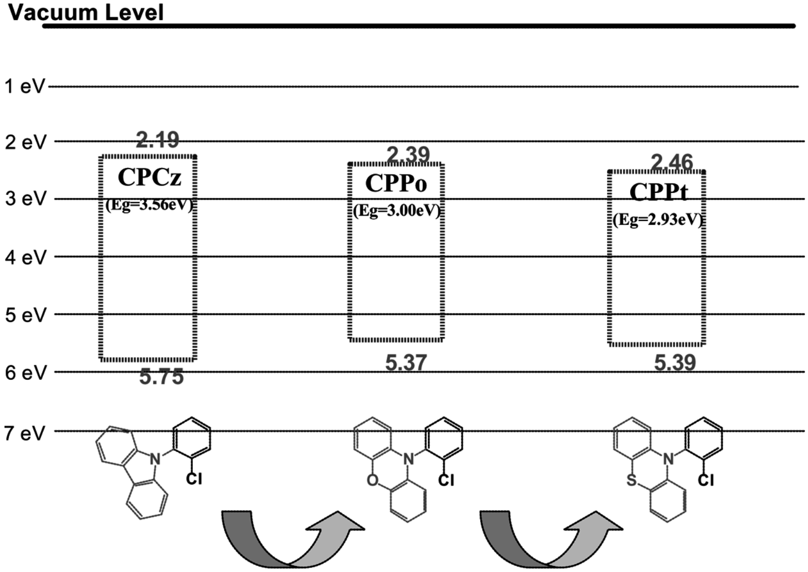


FIGURE 4 Electronic band structure of the synthesized dyes.

The minute difference in chemical structure caused great change in electronic band structure.

CONCLUSIONS

In summary, we synthesized three different dyes, DPCz, DPPo and DPPt, containing cyclic amine moiety, and investigated optical properties such as absorption, photoluminescence and electronic band structure with molecular microstructure. Even though these cyclic amine dyes have a minute difference in chemical structure, their UV-visible absorption and PL spectra were dramatically changed, and electronic band structure organized with band gap energy, HOMO(Ip) and LUMO(Ea) level was also greatly different.

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