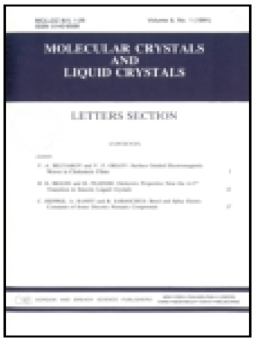

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New Amino Methyl Coumarin Derivative for OLED Blue Emitter

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A new blue emitting material including coumarin moiety, 7-phenylamino-bis(4-methyl-coumarin) (P-DMC), was synthesized by Ullman reaction.[1] Optical and electronic properties were examined by UV-Vis. absorption spectrum, PL spectrum, and cyclic voltammetry. The UV-Vis. spectra of P-DMC in solution and film states showed maximum absorption wavelengths of 396 nm and 403 nm, respectively. The PL spectra of P-DMC showed maximum emission wavelengths of 449 nm and 488 nm in solution and film states. A non-doped OLED was fabricated using the synthesized material as an emitting material. The P-DMC compound exhibited efficient luminescence property. The EL spectrum of P-DMC had a maximum value of 482 nm.

Keywords Organic light-emitting diode; blue emitting materials; coumarin derivatives

Introduction

Intensive studies have been conducted on organic light emitting diodes (OLEDs) as they have a great potential to be applied to large full-color displays and mobile displays.[1] Most of the conjugated organic molecules have been reported as red, green, and blue electroluminescence (EL).[2] These red, green and blue emitters are required to show high EL efficiency, good thermal properties, long lifetime, and pure color coordinates (Commission Internationale de l'Eclairage (CIE)) in order to be applied to large full-color displays.

Red emitters with CIE coordinates of (0.67, 0.33), long lifetime of more than 100,000 hours, and luminance efficiency of 11 cd/A have been produced, and green emitters with CIE coordinates of (0.29, 0.64), lifetime of 100,000 hours, and luminance efficiency of 21 cd/A have also been developed.[3] Blue emitters, however, have CIE coordinates of (0.14, 0.16), efficiency of 7 cd/A, and lifetime of only 12,000 hours despite the use of doping.[3] Since blue emitters have exhibited relatively lower efficiency and shorter lifetime compared to red and green emitters, new blue emitters are in much need for development. However, electronic levels of blue materials with a wide band gap are generally mismatched

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with the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels of other OLED layers, such as the hole transporting layer (HTL) and the electron transporting layer (ETL). These differences between the electronic levels result in a mismatched carrier balance of electrons and holes and low EL efficiency.[4]

We reported several kinds of new blue emitters in our previous studies.[5–10] In this study, we propose a new blue emitter based on coumarin derivative. A coumarin group includes an ester group, which shows the electron withdrawing effect.[11] In order to increase hole and electron transporting properties of emitters, blue host materials were designed based on the bipolar chemical structure.[12–14] The new blue emitter combines a coumarin group with an aromatic amine group to provide an electron push-pull effect for ambipolar property. The proposed compound is Phenylamino-di-4-methyl-coumarin (P-DMC).

Experimental

General Method

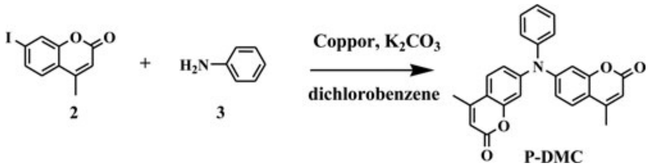
^{1}H-NMR spectra were recorded on Brucker, Advance 500 and Fast atom bombardment (FAB) mass spectra were recorded by JEOL, JMS-AX505WA, HP5890 series II. Optical absorption spectra were obtained by HP 8453 UV-VIS-NIR spectrometer. Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube) was used for photo-luminescence (PL) spectroscopy. Redox potential of the synthesized materials was measured at a scanning rate of 100 mV/s by WBCS 3000 system, and a cyclic voltammeter (CV).Acetonitrile (AN) containing 0.1 M tetrabutylammonium perchlorate was used as an electrolyte during measurement. Indium tin oxide (ITO) was used as a working electrode and saturated Ag/$AgNO_3$ as a reference electrode. Ferrocene was a reference compound for potential calibration. EL devices were fabricated with the following structure: ITO /2-TNATA (60 nm) /NPB (15 nm)/synthesized materials or ADN (30 nm)/Alq3 (30 nm)/LiF (1 nm)/Al (200 nm), where 4,4′,4′-tris(N-(2-naphthyl)-N-phenyl-amino)-triphenylamine (2-TNATA) was used as a hole injection layer, N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)benzidine (NPB) as a hole transporting layer, the synthesized material (P-DMC) as an emitting layer, 8-hydroxyquinoline aluminum (Alq3) as an electron transporting layer, lithium fluoride (LiF) as an electron injection layer, ITO as anode, and Al as cathode. The organic layer was vacuum deposited by using thermal evaporation at a vacuum base pressure of 10^{-6} torr and the rate of deposition of 1 Å/s to give an emitting area of 4 mm^2, and the Al layer was continuously deposited under the same vacuum condition. Current–voltage-luminance (I-V-L) characteristics of the fabricated EL devices were obtained by Keithley 2400 electrometer and light intensity was obtained by Minolta CS-1000A.

Synthesis of N,N-Bis(4-methylcoumarin-7-yl)Aniline (P-DMC)

To the mixture of compound 1 (2.400 g, 8.390 mmol), coppor powder (0.426 g, 6.712 mmol), potassium carbonate (1.855 g, 13.423 mmol), and 18-crown-6 (0.089 g, 0.336 mmol) in 1,2-dichlorobenzene (40 ml) were added with aniline 2 (0.306 ml, 3.356 mmol). The mixture was refluxed for 4 days, cooled to room temperature, and then filtered to remove remaining catalyst and unreacted materials. The filtrate was evaporated to dryness under reduced pressure. The crude product was dissolved in dichloromethane (10 ml), diluted with hexane (50 ml), and then filtered off. The filtrate was evaporated to dryness once more. The product, thus obtained, was recrystallized by hexane and chromatographed on silica gel with dichloromethane/methanol (49:1) to yield P-DMC (0.156 g, 11.7%) as a yellow solid. Mp 248°C. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 2.39$ (s, 6H), 6.15 (s, 2H), 6.94 (s, 2H), 7.01 (d, 2H), 7.15 (d, 2H), 7.24 (t, 1H), 7.38 (t, 2H), 7.44 (d, 2H). FT-IR (KBr): v = 3054, 2987, 2306, 1720, 1600, 1421, 1265, 1122, 896, 738 cm^{-1}. MS (MALDI-TOF) for $C_{26}H_{19}NO_4$ (M = 409.42): m/z = 410.10 (M^+). Anal. Calcd: C, 76.27%; H, 4.68%; N, 3.42%. Found: C, 76.19%; H, 4.76%; N, 3.36%.

Results and Discussion

The preparation of the compound, P-DMC, was performed by following the steps depicted in Scheme 1. Reaction of 7-iodo-4-methyl coumarin (1) with diphenylamine was carried out under a typical Ullmann reaction condition to give P-DMC (yield: 29.7%).[15–17]



Scheme 1. Synthetic routes of the newly synthesized compound

The compound of P-DMC is soluble in aromatic solvents (i.e., toluene, o-dichlorobenzene and benzonitrile) and other common organic solvents such as acetone, CH_2Cl_2, $CHCl_3$ and THF. Structure and purity of the newly synthesized compound was confirmed mainly by ^{1}H NMR and elemental analysis. ^{1}H NMR spectra of P-DMC are consistent with the proposed structure, showing the expected features with the correct integration ratios. MALDI-TOF mass spectra provided a direct evidence for the structure of P-DMC showing singly charged molecular ion peaks at *m/z* = 410.10 for P-DMC, respectively.

UV–visible absorption (UV-Vis.) and PL spectra of the synthesized material in solution and film states are described and summarized in Fig. 1 and Table 1. As shown in Fig. 1 and Table 1, P-DMC exhibited UV-Vis. Maximum value of 396 nm in solution state and 403 nm in film state, respectively. PL maximum value of P-DMC was 449nm in solution state and 488 nm in film state, respectively. It means that this material shows quite different PL maximum value in solid state compared to solution state. This can be explained as special molecular packing and interaction in film state. Also, PL of film state showed red shift result compared to that of solution state. It is due to the intramolecular charge transfer

Table 1. Optical, electrical properties of the synthesized material

	Solution		Film on glass				
Compounds	UV_{max} (nm)	PL_{max} (nm)	UV_{max} (nm)	PL_{max} (nm)	HOMO (eV)	LUMO (eV)	E_g[a] (eV)
P-DMC	396	449	403	488	−5.49	−2.49	3.00

[a] E_g (band gap) calculated from the optical absorption edge.

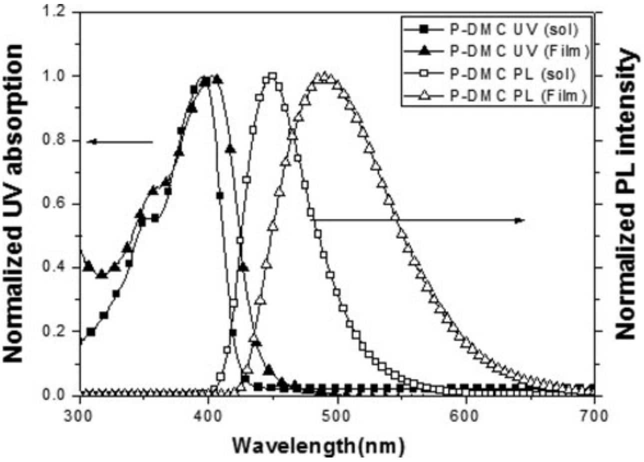


Figure 1. UV–visible absorption and PL spectra of P-DMC in solution and film states.

(ICT) property from bipolar compound including donor-acceptor moiety. This result can be regarded by disadvantage but it has another advantage of low operating voltage and increased efficiency. It can be explained by that bipolar compound assist to smoothly inject and transport hole and electron carriers.[18–19] P-DMC can also show relatively higher EL efficiency than that of ADN based on this explanation.

Based on UV-Vis. and cyclic voltammetry (CV) result, highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels were calculated as shown in Table 1, and Fig. 5. The band gap energy of P-DMC was estimated to be 3.0 eV from the analysis of the absorption edge with a plot of (hν) vs. $(\alpha h\nu)^2$, where α, h, and ν are the absorbance, Plank's constant, and the frequency of light, respectively. From CV data, the oxidation onset was 0.73V. HOMO is equal to -(E^{ox} + 4.76 eV), where 4.76 eV is calibrated ferrocene reference value. From the CV measurements, the HOMO energy level of P-DMC was calculated to be 5.49 eV. Thus LUMO level was 2.49eV.[20]

Non-doped OLED devices were fabricated by using the synthesized material and ADN as emitting layers. Device configuration is ITO/2-TNATA (60 nm)/NPB (15 nm)/synthesized materials or ADN (30 nm)/Alq3 (30 nm)/LiF (1 nm)/Al (200 nm). I-V-L characteristics and Luminance efficiency results of the two devices are shown in Fig. 2, Fig. 3 and Table 2. All two devices showed typical rectifying characteristics. Also, turn-on

Table 2. EL performances of multilayered devices with the synthesized compound at 10 mA/cm^2

Emitting material	Operating voltage (V)	EL$_{max}$^{a} (nm)	L. E.^{b} (cd/A)	CIE^c (x,y)
P-DMC	6.41	482	2.9	0.199, 0.317
ADN	7.42	460	2.54	0.188, 0.209

^{a}EL maximum spectrum, ^{b}power efficiency, ^{c}commission internationale de L'Eclairage x,y coordinates.

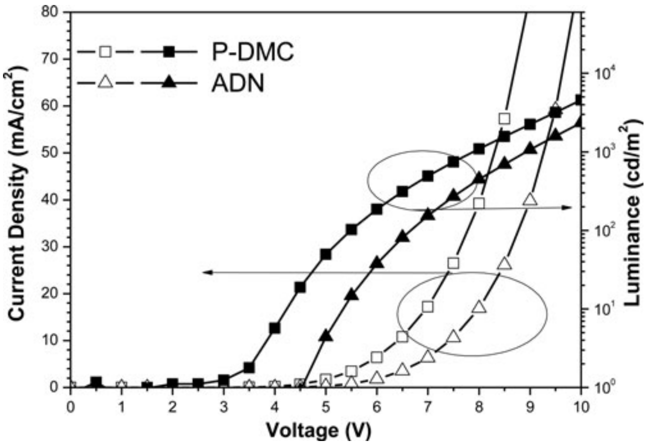


Figure 2. I-V-L graphs of P-DMC and ADN OLED devices. (Device: ITO/2-TNATA (60nm)/NPB (15 nm)/synthesized materials or ADN (30 nm)/Alq3 (30 nm)/LiF (1 nm)/Al (200 nm)).

voltage and operating voltage were shown in the order of P-DMC < ADN. According to the previous explanation, higher HOMO level of P-DMC made easier hole injection from hole transporting layer (HTL) to emitting layer (EML), as well as lowering of operating voltage. As shown in Fig. 3, P-DMC exhibited slightly higher luminance efficiency than ADN.

In Fig. 4, EL spectra were described with PL spectra in film state in order to compare the maximum values. The EL maximum values of the fabricated devices follow the same trend as the PL maximum values. It means that the EL maximum wavelength may be interpreted by a suitable recombination zone inside EML. Related EL performance of the two devices is summarized in Table 2. Luminance efficiency of P-DMC and ADN are 2.90 cd/A and 2.54 cd/A, respectively. P-DMC shows the highest values of luminance

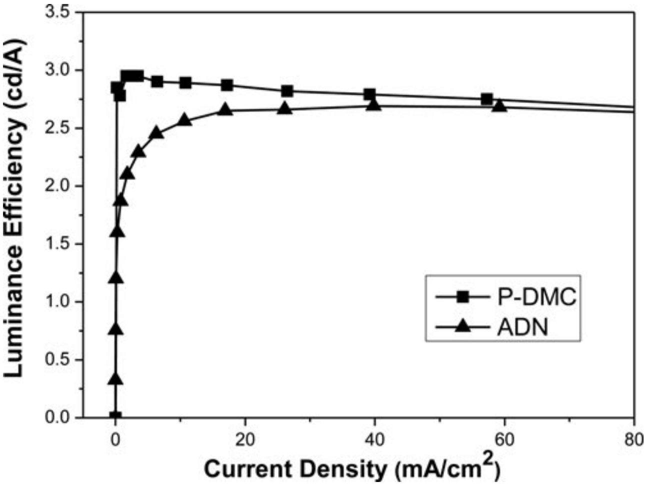


Figure 3. Luminance efficiency results of P-DMC and ADN devices. (Device: ITO/2-TNATA (60nm)/NPB (15 nm)/synthesized materials or ADN (30 nm)/Alq3 (30 nm)/LiF (1 nm)/Al (200 nm)).

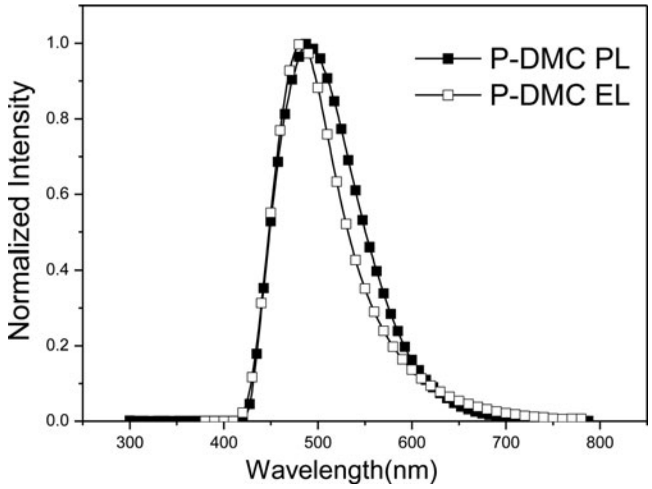


Figure 4. PL spectra of the synthesized compound in film state and EL spectra of the P-DMC (Device: ITO/2-TNATA (60 nm)/NPB (15 nm)/synthesized materials (30 nm)/Alq3 (30 nm)/LiF (1 nm)/Al (200 nm)).

efficiency in this study. Also, the P-DMC compound shows lowest operating voltage, and it may provide high efficiency results since it exhibited relatively high luminance efficiency. P-DMC especially has superior properties to ADN, which was commercialized in the past. It shows 16% higher luminance efficiency than ADN, which may be caused by lowered operating voltage. The efficiency difference between P-DMC and ADN may be explained by the energy diagram of Fig. 5. HOMO level value of P-DMC is −5.49 eV and is matched with −5.3 eV of NPB HTL material, but ADN has a value of −5.9 eV and constraints for injecting hole into emitter. This may cause the difference in efficiency. Also, P-DMC includes two coumarin groups which have electron withdrawing effects and N-type characteristics. It also has a diphenylamine group which has electron donating effect and

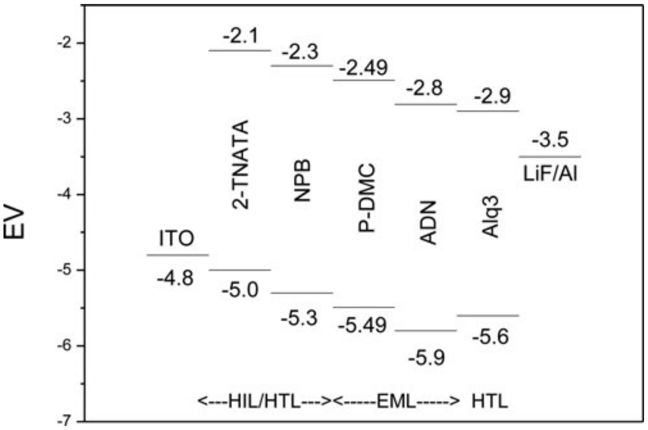


Figure 5. Energy level diagram of the material used.

P-type characteristics. Therefore, P-DMC has a symmetrical dipole state. These factors may have been caused by higher efficiency.

Conclusions

A new blue emitting material including coumarin moiety, P-DMC, was synthesized by Ullman reaction. P-DMC combines a coumarin group with an aromatic amine group in order to provide electron push-pull effects for ambipolar properties. UV-visible absorption maximum values of P-DMC in solution and film states were 396 nm and 403 nm. PL maximum values of P-DMC in solution and film states were 449 nm and 488 nm. With application of the synthesized material and a commercialized material (ADN) as emitters in a non-doped OLED, EL maximum values of the P-DMC device was 482 nm. As for the luminance efficiency results, P-DMC especially has superior property to ADN. Luminance efficiency was increased by more than 16% in P-DMC (2.90 cd/A) compared to the commercialized material, ADN (2.54 cd/A).

Acknowledgment

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