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Excimer Formation Promoted by Steric Hindrance in Dual Core Chromophore for Organic Light-Emitting Diodes Emitters

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A new dual core derivative of 1-(3,5-dipyrid-3-yl-phenyl)-6-(10-(3,5-dipyrid-3-yl-phenyl)-anthracen-9-yl)-pyrene (3P-AP-3P) was synthesized by introducing pyridine groups. 1-[1,1';3',1'']Terphenyl-5'-yl-6-(10-[1,1';3',1'']terphenyl-5'-yl-anthracen-9-yl)-pyrene (TP-AP-TP) was used to compare with 3P-AP-3P. Unlike TP-AP-TP, 3P-AP-3P exhibited an excimer emission at 602 nm by introducing pyridine groups despite its highly twisted core. Two materials were used as emitting layer (EML) in OLED devices: ITO/2-TNATA (60 nm)/NPB (15 nm)/the synthesized materials (35 nm)/Alq₃ (20 nm)/LiF (1 nm)/Al (200 nm). The 3P-AP-3P device exhibited EL maximum values at 463 nm and 601 nm.

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1. INTRODUCTION

 π -Conjugated compounds are useful in a variety of applications, including organic light-emitting diodes (OLEDs),^{1,2} organic thin film transistors (OTFTs),³ and organic photovoltaic cells (OPVCs).⁴ The key factors that determine their performance in such applications are the molecular structure and the interactions between molecules.⁵ Thus, the study of the intermolecular interactions of π -conjugated compounds is very important and has received significant attention.

In the recent, molecular orientation effects were first implemented in a highly twisted core group to produce white emission from a single molecule.⁶ White emission with two sharp intense emissions at 455 and 591 nm was obtained from a single molecule through the orientation effect, which controlled excimer formation as a result of linear molecular shape.

We recently reported synthesis of new dual core chromophore materials containing anthracene and pyrene that exhibit high photoluminescence (PL) efficiencies.⁷ There is a dihedral angle of approximately 90° between the two chromophores in a dual core, which consists of anthracene and pyrene. Dual core derivatives have advantages such as the prevention of excimer formation. In this work, we synthesized 1-(3,5-dipyrid-3-yl-phenyl)-6-(10-(3,5-dipyrid-3-ylphenyl)-anthracen-9-yl)-pyrene (3P-AP-3P) using pyridine groups as a new dual core derivative, as shown in Scheme 1. 1-[1,1';3',1"]Terphenyl-5'-yl-6-(10-[1,1';3',1"] terphenyl-5'-yl-anthracen-9-yl)-pyrene (TP-AP-TP) was used to compare with 3P-AP-3P. Unlike TP-AP-TP, 3P-AP-3P exhibited an excimer emission at 602 nm by introducing pyridine groups despite its highly twisted core chromophore. Electroluminescence (EL) devices were fabricated with these materials as non-doped emitting layers.

2. EXPERIMENTAL DETAILS

2.1. Synthesis

The method of synthesis for TP-AP-TP in Scheme 1 was introduced elsewhere.⁷ 3P-AP-3P was synthesized by Suzuki aryl–aryl coupling reaction using Pd catalyst. A typical synthetic procedure is as follows (see Scheme 2).

2.1.1. Synthesis of Compound (4)

Compound (3) (3.0 g, 9.64 mmol) and bis(pinacolato) diboron (3.18 g, 12.5 mmol) were added to $Pd_2(dba)_3$

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Scheme 1. Chemical structures of the synthesized materials.

(0.0894 g, 0.0964 mmol), 2-dicyclohexylphosphino-2',4',6'-triisopropyl biphenyl (0.0919 g, 0.193 mmol), KOAc (2.84 g), and dioxane (150 ml) in a 250 mL roundbottomed flask under nitrogen. The mixture was refluxed for 6 hours under nitrogen. When the reaction was completed, the product was extracted with MC and water. The organic extract was dried with MgSO₄ and then filtered. The solvent was removed under vacuum. The product was re-crystallized from hexane to obtain pure solid material in white color (1.73 g, 50.2%). ¹H-NMR (300 MHz, CDCl₃) δ (ppm): 8.94–8.93 (*d*, 2H), 8.64–8.62 (*d*, 2H), 8.07–8.06 (*d*, 2H), 7.99–7.95 (*m*, 2H), 7.87–7.86 (*t*, 1H), 7.42–7.37 (*m*, 2H), 1.39 (*s*, 12H). Fab⁺-MS 358 m/z.

2.1.2. Synthesis of 1-(3,5-dipyrid-3-yl-phenyl)-6-(10-(3,5-dipyrid-3-yl-phenyl)-anthracen-9-yl)pyrene (3P-AP-3P)

In a 250 mL round-bottomed flask, compound (9) spectrometer LS (0.7 g, 1.31 mmol), compound (4) (1.03 g, 2.87 mmol), the PL spectra, and Pd(PPh₃)₄ (0.151 g, 0.131 mmol) were added to The EL devic 60 mL/5 mL anhydrous toluene/ethanol solution under 2-yl)-N-phenyl-

nitrogen. 2 M K₂CO₂ solution (20 mL) dissolved in H₂O was added to the reaction mixture at 50 °C. The mixture was refluxed for 12 hours under nitrogen. When the reaction was completed, the product was extracted with chloroform and water. The organic extract was dried with MgSO₄ and then filtered. The solvent was removed under vacuum. The mixture was columned in THF:chloroform (1:2) mixed solvent. The product was concentrated under reduced pressure and re-precipitated with chloroform and methanol to obtain pure solid material in light yellow color (0.157 g, 14.3%). ¹H-NMR (300 MHz, CDCl₃) $\delta(\text{ppm})$: 9.09–9.06 (m, 4H), 8.71–8.69 (m, 4H), 8.46–8.43 (d, 1H), 8.41-8.38 (d, 1H), 8.28-8.24 (m, 2H), 8.15-8.04 (m, 7H), 7.96–7.88 (*m*, 8H), 7.51–7.39 (*m*, 9H), 7.28–7.26 (*m*, 2H). Fab+-MS 838 m/z. Anal. Calculated for C₆₂H₃₈N₄: C, 88.76; H, 4.57; N, 6.68 Found: C, 88.81; H, 4.51; N, 6.59.

2.2. General Experiment

¹H-NMR spectra were recorded by Bruker, Advance 300, while Fast atom bombardment (FAB) mass spectra were recorded by JEOL, JMS-AX505WA, HP5890 series II. The elementary analysis (EA) was checked using EA1110 and EA1112 of CE Instruments. The optical absorption spectra were obtained using a Lambda 1050 UV/Vis/NIR spectrometer (PerkinElmer). A Perkin-Elmer luminescence spectrometer LS50 (Xenon flash tube) was used to collect the PL spectra.

The EL devices were prepared using tris(N-(naphthalen-2-yl)-N-phenyl-mino)triphenylamine (2-TNATA) as the



Scheme 2. Synthetic routes of 3P-AP-3P.

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hole injection layer (HIL) and N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl) benzidine (NPB) as the hole transporting layer (HTL). The synthesized materials were used as the EML, 8-hydroxyquinoline aluminum (Alq₃) as the electron transporting layer (ETL), lithium fluoride (LiF) as the electron injection layer (EIL), and ITO as the anode, and Al as the cathode. All organic layers were deposited under 10^{-6} Torr, at a rate of deposition of 1 Å s⁻¹, to give an emitting area of 4 mm². The LiF and aluminum layers were continuously deposited under the same vacuum conditions. The luminance efficiency data of the fabricated EL devices were obtained using a Keithley 2400 electrometer.

under encapsulation in a glove box.

3. RESULTS AND DISCUSSION

Light intensities were obtained using a Minolta CS-1000A.

The operational stabilities of the devices were measured

The optical properties of the synthesized materials are summarized in Table I. Figure 1 exhibits UV-Visible (UV-Vis.) absorption and PL spectra of TP-AP-TP and 3P-AP-3P in THF solution and film state. UV-Vis. absorption of the two materials in solution and film state shows the typical anthracene absorption band in the range of 350~400 nm. Major absorption peaks of TP-AP-TP and 3P-AP-3P in THF solution state were exhibited at 360, 379, 400 nm and 360, 378, 399 nm, respectively (see Fig. 1(a)). Compared to solution state, UV-Vis. absorption in film state was slightly red shifted, which indicated an increase in conjugation length in solid state. The increase in conjugation length might be due to the more planar conformation of π -stacked compounds in solid state.⁸ The PL maximum wavelengths of TP-AP-TP and 3P-AP-3P were also measured at 446 nm and 444 nm in solution state. As shown by PL spectra in Figure 1(b), unlike TP-AP-TP, 3P-AP-3P exhibited an excimer emission at 602 nm by introducing pyridine groups despite its highly twisted core chromophore. Pyridine group is known to increase molecular orientation in evaporated film because of intermolecular hydrogen bond between C-H and N.⁹ Therefore, molecular orientation of 3P-AP-3P would be more increased in comparison to TP-AP-TP, which can promote molecular orientation suitable for excimer formation in film state.6

OLED devices were fabricated by using the synthesized materials as the EML layer, and the EL characteristics were examined with device configuration of

Table I. Optical properties of the synthesized materials.

| | Solution ^{<i>a</i>} | | Film ^b | |
|----------------------|--------------------------------|------------------------|--------------------------------|------------------------|
| | UV _{max} (nm) | PL _{max} (nm) | UV _{max} (nm) | PL _{max} (nm) |
| TP-AP-TP 3P-AP-TP | 360, 379, 400 360, 378, 399 | 446 444 | 361, 382, 403 365, 383, 404 | 458 463, 602 |

Notes: ^aTHF solution $(1 \times 10^{-5} \text{ M})$, ^bevaporated film



Figure 1. UV-Vis. absorption (solid line) and PL spectra (open line) of TP-AP-TP (square) and 3P-AP-TP (triangle): (a) solution in THF $(1.0 \times 10^{-5} \text{ M})$, (b) evaporated film.

ITO/2-TNATA (60 nm)/NPB (15 nm)/the synthesized materials (35 nm)/Alq₃ (20 nm)/LiF (1 nm)/Al (200 nm). The results are summarized in Table II.

As shown in Figure 2(a), the EL maximum value of TP-AP-TP was 455 nm. 3P-AP-3P showed blue emission at 463 nm, and excimer emission was observed at 601 nm similar to PL measurement in film state. Figure 2(b) shows the luminance (cd/A) and power (lm/W) efficiencies versus current density of 3P-AP-3P. OLED devices based on TP-AP-TP and 3P-AP-3P showed luminance efficiencies of 5.34 cd/A and 3.45 cd/A at 10 mA/cm², respectively. Power efficiencies (lm/W) were 2.58 lm/W and

Table II. EL performance of the devices: ITO/2-TNATA (60 nm)/NPB (15 nm)/the synthesized materials (35 nm)/Alq₃ (20 nm)/LiF (1 nm)/Al (200 nm) at 10 mA/cm².

| | L. E. ^{<i>a</i>} (cd/A) | P. E. ^b (lm/W) | $CIE(x, y)^c$ | EL _{max} (nm) |
|----------|----------------------------------|---------------------------|----------------|------------------------|
| TP-AP-TP | 5.34 | 2.58 | (0.150, 0.130) | 455 |
| 3P-AP-TP | 3.45 | 1.67 | (0.192, 0.203) | 463, 601 |

Notes: ^aL. E.: luminance efficiency, ^bP. E.: power efficiency, ^cCIE: Commission Internationale de l'Eclairage.

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Figure 2. (a) EL spectra of the devices and (b) luminance and power efficiencies of the 3P-AP-3P device. ered by ingenta to: State Uni IP: 5.101.220.147 On: W

1.67 lm/W. Reduced efficiency of 3P-AP-3P device compared to TP-AP-TP was due to fluorescence quenching of excimer. In case of CIE values, TP-AP-TP and 3P-AP-3P also exhibited (0.150, 0.130) and (0.192, 0.203).

4. CONCLUSION

Pyridine groups were introduced into a highly twisted dual core chromophore to promote anisotropic intermolecular alignment (orientation effects). Excimer emission at 602 nm was obtained from the orientation effects, which controlled excimer formation as a result of intermolecular C–H/N hydrogen bonds. 3P-AP-3P was used as the emitting layer in an OLED device that exhibited CIE values of (0.192, 0.203).

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