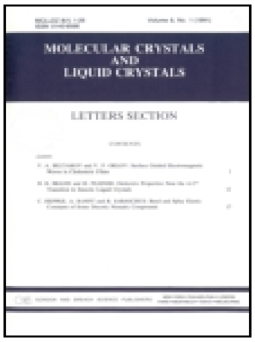

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New Emitting Materials Based on HTL Moiety with High Hole Mobility for OLEDs

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New green emitting compounds based on tris(N-methylindolo)benzene (NMT), anthracene and pyrene were synthesized. NMT-An and NMT-Py were used as an emitting layer in OLED device to examine emitting property. OLED device containing NMT-An emitting layer and conventional hole transporting layer (HTL) of NPB was found to exhibit better characteristics compared to NMT-Py. And that device showed maximum EL emission at 502 nm and 550 nm, CIE coordinates (0.38, 0.48), and a luminance efficiency of 2.06 cd/A. Also when NMT and NMT-An were used as a HTL instead of NPB, the device including NMT-An emitter showed 2.67 cd/A and 2.29 cd/A in luminance efficiency.

Keywords Emitting material layer; Hole transporting later; Anthracene; Pyrene; OLED

Introduction

Many studies on organic light emitting diode (OLED) have been extensively investigated because of various applications such as mobile display, flexible display, and lightings.[1-3] Many researchers are engaged in ongoing efforts to systematically elucidate the correlation between their molecular structures and properties, with the aim of developing materials with good performance and stability for particular optoelectronic applications. Most conventional studies of emitters use molecules with excellent fluorescence characteristics such as anthracene, pyrene and fluorene as core or side moieties.[4] In order to fabricate full color OLED displays, we need high performance red-, green-, and blue-light emitters with high electroluminescence (EL) efficiencies, good thermal properties, long device lifetimes, and pure color coordinates.[5] Furthermore, balanced carrier injection and carrier transportation between device layers are required for high device efficiency. Unbalanced hole and electron current form a narrow combination zone, which leads to low efficiency with high roll-off and shorter lifetime.[6] In general, multi-layer structure is fabricated in OLED devices using vacuum deposition method for efficient carrier injection and carrier transportation. Reducing the number of layers can result in simplification of the fabrication process and shortening of preparation time.

In this study, new anthracene derivative and pyrene derivative were synthesized as materials in which hole transporting layer and emitting material layer can be used

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together. Several studies have reported 5,10,15-trimethyl-10,15-dihydro-5H-5,10,15-triaza-diindeno[1,2-a;1′,2′-c]fluorine (NMT) as a good hole transport material.[6,7] Anthracene and pyrene derivatives including NMT as a core were prepared as HTL and EML in OLED devices.

Experimental

Measurements

^{1}H-NMR spectra were recorded on Bruker Avance 300 spectrometers. The 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. Thermal degradation temperature (T_d) of the compounds was measured by thermo-gravimetric analysis (TGA) using SDP-TGA2960 (TA instrument). The HOMO energy levels were determined with ultraviolet photoelectron yield spectroscopy (Riken Keiki AC-2). The LUMO energy levels were derived from the HOMO energy levels and the band gaps. All DFT calculations (B3LYP/6-31G(d)) were performed with the Gaussian 09 program.

Fabrication of OLED

EL devices were fabricated as the following structure : ITO/ 2-TNATA 60 nm/ NPB or NMT 15 nm/ emitting layer(EML) 35 or 50 nm/ Alq3 20 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 (HIL), N,N′-bis(naphthalene-1-ly)-N,N′-bis(phenyl)benzidine (NPB) as a hole transporting layer (HTL), the synthesized materials as emitting layer (EML), Tris-(8-hydroxyquinoline)aluminum (Alq3) as an electron transporting layer (ETL) and hole blocking layer (HBL), lithium fluoride (LiF) as an electron injection layer (EIL), 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 being 1 Å/S to give an emitting area of 4 mm and the Al layer was continuously deposited under the same vacuum condition. The 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

Synthesis of N-methyloxindole (1). N-methylaniline (20 mL, 186 mmol) was dissolved in toluene (250 mL), and chloroacetyl chloride (15.8 mL, 198 mmol) was added slowly. Then the mixture was refluxed for 2h. Water (50 mL) was added after the mixture was cooled to room temperature and the mixture was stirred for 3h to decompose the chloroacetyl chloride. Toluene layer was washed first with 10% K_2CO_3 in water solution. And it was continuously added with HCl (2M) before drying overnight with sodium sulfate. After toluene was evaporated, $AlCl_3$ (82 g) was added, and the mixture was stirred for 10 min at 70°. Then the above mixture was stirred at 210° for 90 min. The reaction mixture was slowly poured into ice water, and then concentrated HCl (50 mL) was added. The mixture was extracted with chloroform and chloroform layer was dried over sodium sulfate. After evaporating chloroform, the solid was recrystallized with hexane. N-methyloxindole (16 g) was prepared in total yield 66.6% of the two step.

^{1}H-NMR (300MHz, $CDCl_3$) δ(ppm) : 7.29–7.20 (m, 2H), 7.05–7.00 (t, 1H), 6.81–6.78 (d, 1H), 3.47 (s, 2H), 3.18 (s, 3H).

Synthesis of 5-bromo-N-methyloxindole (2). N-methyloxindole (0.5 g, 3.4 mmol) in acetonitrile (5 mL) was stirred at 0°C, and then NBS (0.62 g) in 10 mL acetonitrile was added dropwise. The mixture was stirred at that temperature for 1h and then stirred for 2h at ambient temperature. Then the solution was evaporated and the solid was dissolved in $CHCl_3$, washed twice with water. After $CHCl_3$ was evaporated, the brown solid was recrystallized with hexane. 5-bromo-N-methyloxindole (0.44 g) was prepared in 58% yield.

^{1}H-NMR (300MHz, $CDCl_3$) δ(ppm) : 7.42–7.39 (d, 1H), 7.26 (s, 1H), 6.71–6.68 (d, 1H), 3.52–3.20 (s, 2H), 3.19 (s, 3H).

Synthesis of 3,8,13-Tribromo-5,10,15-trimethyl-10,15-dihydro-5H-5,10,15-triaza-diindeno[1,2-a;1′,2′-c]fluorine (NMT-Br) (3). A mixture of 5-bromo-N-methyloxindole (5 g, 22 mmol) and $POCl_3$ (40 mL) was stirred and refluxed for 2h. After cooling, the mixture was poured into ice water, and then extracted with dichloromethane (MC) for three times. The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and concentrated. The solid was washed with MC, white solid NMT (2.6 g) was prepared. Yield was 61%.

^{1}H-NMR (300MHz, THF) δ(ppm) : 8.58 (s, 3H), 7.63–7.60 (d, 3H), 7.57–7.53 (d, 3H), 4.40 (s, 9H).

Synthesis of 5,10,15-trimethyl-10,15-dihydro-5H-5,10,15-triaza-diindeno[1,2-a;1′,2′-c]fluorine (NMT) (4). Compound NMT was synthesized according to the method described for compound NMT-Br. The white powder was purified by using column chromatography with ethyl acetate : hexane (1:10) as the eluent to afford a white solid (0.3 g, 12%).

^{1}H-NMR (300MHz, $CDCl_3$) δ(ppm) : 8.48–8.46 (d, 3H), 7.61–7.58 (d, 3H), 7.50–7.45 (t, 3H), 7.37–7.32 (t, 3H), 4.47(s, 9H).

Synthesis of 9-boroanthracene (5). 9-bromoanthracence (10.0 g, 38.9 mmol) was dissolved in anhydrous THF solution (500 mL) and stirred at −78°C. Then, 1.6 M n-BuLi (29.3 mL, 46.7 mmol) was added. Triethyl borate (9.3 mL, 54.5 mmol) was added to the reaction after 30 min. After the reaction was finished, the solution was acidified with 2 N HCl solution at room temperature and extracted with ethyl acetate and water. The organic layer was dried with anhydrous $MgSO_4$ and filtered. The solution was evaporated. The residue was redissolved in hexane and added to ethyl acetate. The precipitate was filtered and washed with hexane to obtain a beige compound (7.70 g, 89%). ^{1}H-NMR (300 MHz, $CDCl_3$): δ(ppm) = 8.47 (s, 1H), 8.14 (d, $J = 9.2$ Hz, 2H), 8.04 (d, $J = 9.8$ Hz, 2H), 7.53–7.44 (m, 4H), 5.07 (s, 2H).

Synthesis of 1-boropyrene (7). 1-Bromopyrene (1.0g, 3.56 mmol) was dissolved in anhydrous THF solution (20 mL) and stirred at −78°C. Then, 1.6 M n-BuLi (2.1 mL) was added. Triisopropyl borate (1.2 mL) was added to the reaction after 30 min. After the reaction was finished, the solution was acidified with 2 N HCl solution at room temperature and extracted with ethyl acetate and water. The organic layer was dried with anhydrous $MgSO_4$ and filtered. The solution was evaporated. The residue was redissolved in hexane and added to ethyl acetate. The precipitate was filtered and washed with hexane to obtain a beige compound (0.63 g, 72%).

^{1}H-NMR (300 MHz, DMSO): δ(ppm) = 8.72-8.69 (d, 1H) 8.60 (s, 2H) 8.30-8.15 (m, 7H) 8.06-8.04 (t, 1H).

Synthesis of 3,8,13-Tri-anthracen-9-yl-5,10,15-trimethyl-10,15-dihydro-5H-5,10,15-triaza-diindeno[1,2-a;1′,2′-c]fluorine (NMT-An) (6). NMT-Br (0.3 g, 0.48mmol), 9-boroanthracene (0.42g, 1.89mmol), $Pd_2(dba)_3$ (0.04 g), sodium-tert-butoxide (0.36 g), and tri-tert-butylphosphine (0.08 g) were added to anhydrous ortho-xylene (90 mL) solution. Then 9-boroanthracene (0.42 g) was added to reaction mixture at 80°C. The mixture was heated to 80°C for 5 h under nitrogen. After the reaction was finished, the reaction mixture was extracted with xylene and water. The organic layer was dried with anhydrous $MgSO_4$ and filtered. The solution was evaporated. The yellow powder was purified by using column chromatography with $CHCl_3$: n-hexane as the eluent to afford a yellow solid (0.2g, 46%).

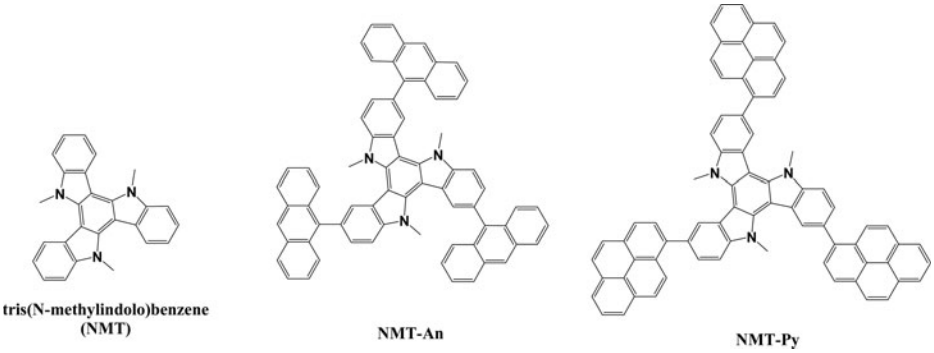
^{1}H-NMR (300 MHz, THF): δ(ppm) = 8.67 (s, 3H), 8.59 (s, 3H), 8.12–8.10 (d, 6H), 7.88–7.85 (d, 6H), 7.77–7.44 (d, 3H), 7.49–7.44 (m, 9H), 7.36–7.30 (m, 6H) 4.45 (s, 9H).

Synthesis of 5,10,15-Trimethyl-3,8,13-tri-pyren-1-yl-10,15-dihydro-5H-5,10,15-triaza-diindeno[1,2-a;1′,2′-c]fluorine (NMT-Py) (8). Compound NMT-Py was synthesized according to the method described for compound NMT-An. The beige powder was purified by using column chromatography with ethyl acetate : n-hexane as the eluent to afford a yellow solid (0.45g, 9.5%).

^{1}H-NMR (300 MHz, THF): δ(ppm) = 8.88 (s, 3H), 8.48–8.45 (d, 3H), 8.35–8.33 (d, 3H), 8.26–8.16 (m, 15H), 8.13–8.09 (d, 3H), 8.06–8.00 (t, 3H), 7.83–7.80 d, 3H), 7.75–7.72 (d, 3H), 4.60 (s, 9H).

Results and Discussion

Triphenylene-fused triazatruxene derivatives have HOMO values of 4.9–5.2 eV and good hole carrier mobility of 0.03–0.8 cm^2/Vs^7. NMT which is one of these derivatives has HOMO value of 5.03 eV and can be used as HTL material in OLED applications. As shown in Scheme 1, NMT has a propeller structure fused with carbazole. Considering optical properties of NMT in Fig. 1, PL maximum peak in solution state is 401 nm and shows sharp deep blue. In film state, unique emission peak appears at 414 nm along with excimer peak at 454 nm. While rigid structure of NMT increases carrier mobility, it may form excimer by allowing for packing in film state under optical properties.

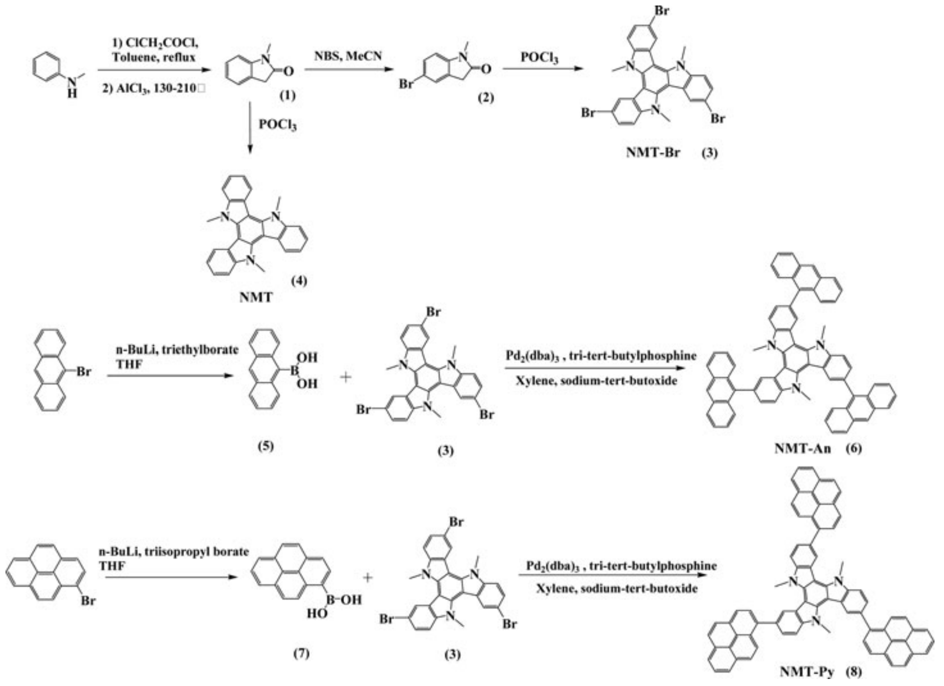


tris(N-methylindolo)benzene (NMT)

NMT-An

NMT-Py

Scheme 1. Chemical structures of the synthesized compounds.



Scheme 2. Synthetic routes of NMT, NMT-An and NMT-Py.

Using NMT with good hole mobility as the core, anthracene and pyrene as emitting materials were substituted to synthesize NMT-An and NMT-Py, EML materials with HTL characteristics. According to Fig. 1, while NMT-An and NMT-Py show narrow emission similar to NMT in solution state, excimer peak also appears in film state.

NMT-An and NMT-Py, new emitting materials based on HTL moiety, were applied to OLED device as EML materials. Energy levels of the materials used in the device are shown as a diagram in Fig. 2(a). Comparing between device 1 and device 4 in Fig. 2(b) and Table 1, NMT-An used as EML has luminance efficiency of 2.06 cd/A, which is higher than 0.5 cd/A of NMT-Py. As for the reason, electron injection at Alq3 may be more difficult for

Table 1. Optical, electrical and thermal properties of the synthesized compounds

Compound	Solution[a] UVmax (nm)	Film[b] UVmax (nm)	Solution[a] PL max (nm)	Film[b] PL max (nm)	HOMO (-eV)	LUMO (-eV)	$\triangle E_{exp}$[c] (eV)	T_d (°) (°)
NMT	319	325	401	414, 454	5.03	1.76	3.27	380
NMT-An	326, 369	329, 394	400	477, 545	5.38	2.63	2.75	500
NMT-Py	346	349	461	489, 613	5.08	2.27	2.81	529

[a] Solution in THF (1.00×10^{-5}M).
[b] Film on glass.
[c] Experimental band gaps.

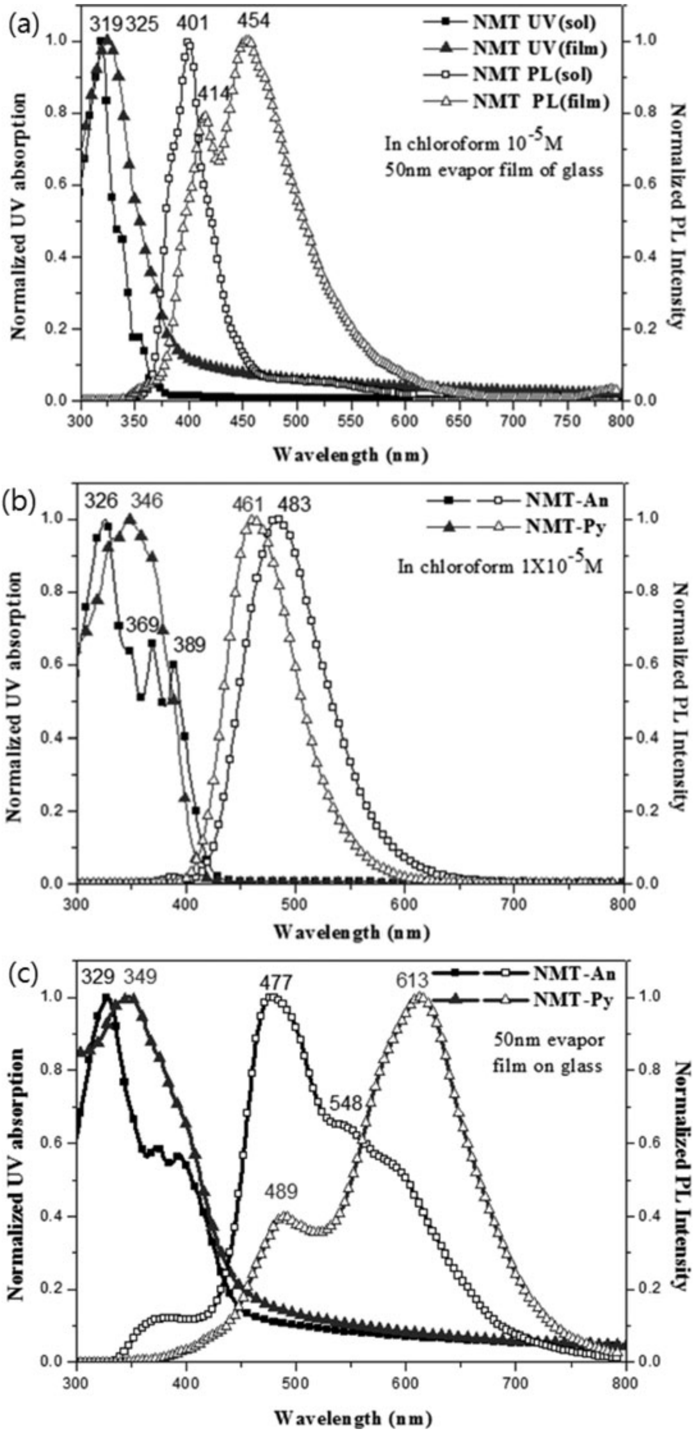


Figure 1. UV-visible absorption spectra and PL spectra of the synthesized materials: (a) NMT in chloroform solution (1.00 $\times 10^{-5}$ M) and the thin film state, (b) NMT-An and NMT-Py in chloroform solution (1.00 $\times 10^{-5}$ M), (c) NMT-An and NMT-Py in the thin film state.

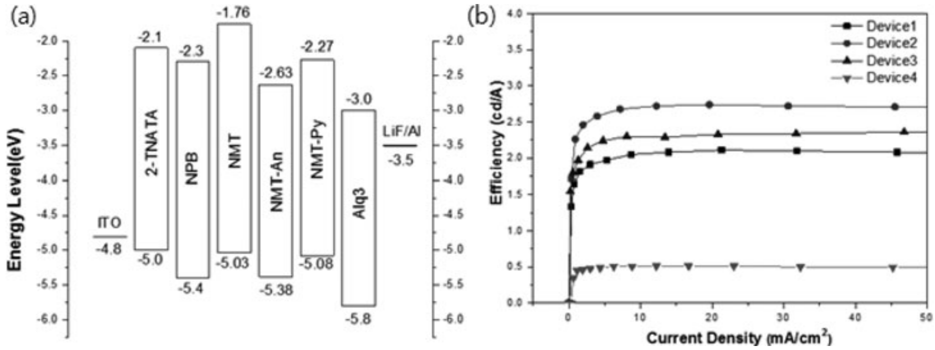


Figure 2. EL characteristics of devices using the synthetic materials as EML: (a) energy diagrams of the compounds, (b) luminance efficiency against current density.

NMT-Py than NMT-An due to high LUMO as shown in Fig. 2(a). In addition, excimer peak is found in film PL of both NMT-An and NMT-Py. When the original peak of materials is compared to excimer peak, original peak is larger for NMT-An and excimer peak is larger for NMT-Py. This means that NMT-Py can show low efficiency from excimer quenching in the device.

In the DFT calculations of Fig. 3, twist angle of the NMT core and substituent is 78° for NMT-An and 56° for NMT-Py. While the two compounds have rigid structure and form excimer based on good packing, NMT-Py has smaller twisted angle between NMT and pyrene compared to NMT-An, more strongly inducing excimer formation based on better packing. A device that uses relatively efficient NMT-An as EML and NMT as HTL in place of NPB is represented by device 2.

When NMT is applied as HTL instead of NPB, NMT has high LUMO value of 1.76eV and can increase efficiency by performing the role of an electron blocking. In fact, luminance efficiency of device 2 is 2.67 cd/A, which is about 30% higher than efficiency of device1. Device3 includes NMT-An one layer of same thickness as EML and HTL. Compared to device1 where NPB was used as HTL, luminance efficiency was increased by about 11%. These results imply that the synthesized NMT-An can be used as EML as well as HTL material without the need of other HTL materials.

Table 2. EL performances of multi-layered devices

	Volt(V)	L.E.(cd/A)	P.E.(lm/W)	E.Q.E.(%)	CIE (x,y)	El_{max}(nm)
Device 1	7.64	2.06	0.93	0.90	(0.38, 0.48)	502,550
Device 2	6.77	2.67	1.38	1.07	(0.40, 0.50)	510,561
Device 3	7.17	2.29	1.10	0.94	(0.41, 0.51)	510,562
Device 4	8.69	0.50	0.02	0.49	(0.39, 0.59)	628

Device1: ITO / 2-TNATA (60 nm) / NPB (15 nm) / NMT-An (35 nm) / Alq3 (20 nm) / LiF / Al
Device2: ITO / 2-TNATA (60 nm) / NMT (15 nm) / NMT-An (35 nm) / Alq3 (20 nm) / LiF / Al
Device3: ITO / 2-TNATA (60 nm) / NMT-An (50 nm) / Alq3 (20 nm) / LiF / Al
Device4: ITO / 2-TNATA (60 nm) / NPB (15 nm) / NMT-Py (35 nm) / Alq3 (20 nm) / LiF / Al

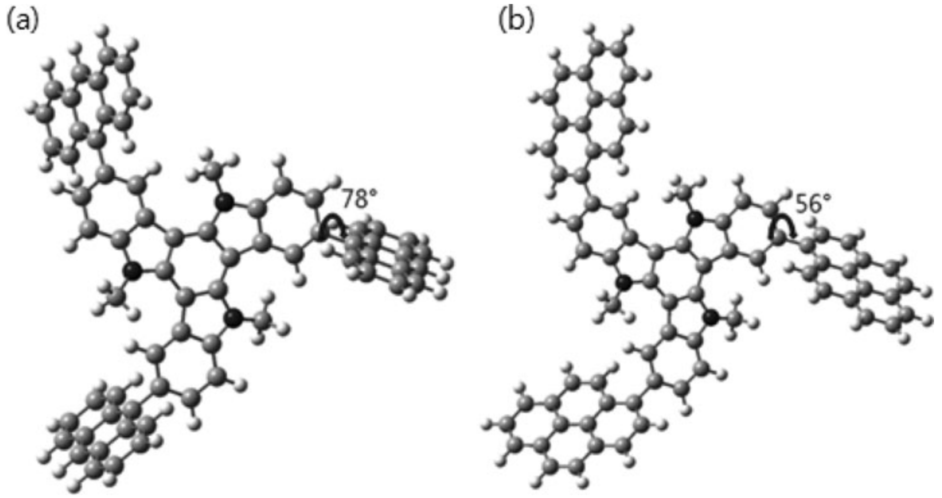


Figure 3. Molecular structures of the NMT-An (a) and NMT-Py (b) optimized by B3LYP/6-311G(d).

Conclusion

NMT-An and NMT-Py compounds that can be simultaneously applied to HTL and EML to simply the fabrication process of OLED devices, were successfully synthesized. Among the synthesized compounds, NMT-An shows higher EL efficiency and lower operating voltage compared to NMT-Py. Luminance efficiency of the device that used NMT-An as EML without HTL was increased by about 11% compared to the device that used NPB as HTL material.

Funding

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