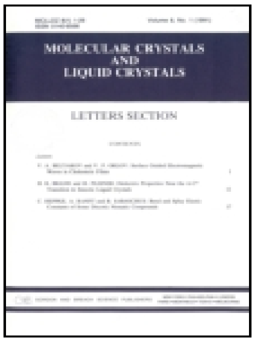

Molecular Crystals and Liquid Crystals

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Synthesis and Electroluminescence Property of New Hexaphenyl Benzene Derivatives Including Emitting Materials for OLED

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Three new emitting compounds of 5P-VCB, 5P-VAn and 5P-VPy for OLED based on hexaphenylbenzene moiety were synthesized. Physical properties by the change of the substitution groups of the synthesized materials were systematically examined. Photoluminescence spectrum of the synthesized materials showed maximum emitting wavelengths of about 420∼487 nm in solution state and 452∼488 nm in film state, indicating blue emission color. OLED devices were fabricated by the synthesized compounds using vacuum deposition process as an emitting layer. Current efficiencies and CIE values of 5P-VCB, 5P-VAn and 5P-VPy were 1.76, 0.38 and 7.91 cd/A and (0.15, 0.07), (0.20, 0.31) and (0.20, 0.36), respectively.

Keywords blue emission; carbazole; anthracene; pyrene; hexaphenylene

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.[1–3] Most of the conjugated organic molecules have been reported as red, green, and blue electroluminescence (EL).[4] It is required for those red, green, and blue emitters to show high EL efficiency, good thermal properties, long lifetime, and pure color coordinates (1931Commission Internationale de l′Eclairage (CIE)) in order to be applied to large full-color displays. A red light-fluorescence emitter with CIE coordinates of (0.66, 0.34) and a long lifetime of more than 600,000 h at 24 cd/A has recently been developed. A green light fluorescence emitter with CIE coordinates of (0.34, 0.62) and a lifetime of 400,000 h at 78cd/A has also been achieved.[5] However, the best official results for a blue-light emitter are a short lifetime of only 10,000 h at 9.0 cd/A and CIE coordinates of (0.14, 0.12) with fluorescence materials.[6] Thus, the development of a blue emitter with

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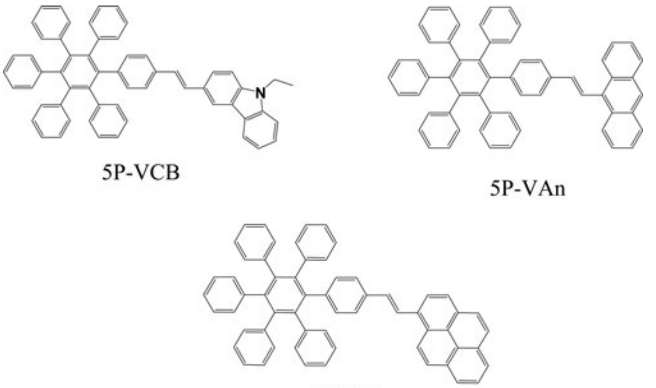
high color purity, high efficiency, and a long lifetime is an extremely challenging research topic. Most existing studies of emitters use molecules with excellent fluorescence characteristics such as anthracene[7,8] and pyrene[9,10] as core or side moieties. Many studies have investigated the use of anthracene and pyrene as blue core moiety since they have high photoluminescence (PL) and EL efficiencies. However, these molecules can easily form excimers through packing because anthracene and pyrene have flat molecular structure that reduce EL efficiency and degrade color purity.[11]

In this work, new emitting compounds based on hexaphenylbenzene group are designed and synthesized as shown in scheme 1. Carbazole, anthracene and pyrene moieties as an emitting group were introduced into main core structure. Also, the change of emission wavelength as well as device efficiency was evaluated according to the different side group.



5P-VCB

5P-VAn

5P-VPy

Scheme 1. Chemical structures of hexaphenyl derivatives.

Experimental

Reagents and solvents were purchased as reagent grade and used without further purification. Pentaphenylphenyl-4-diethylphosphomethylbenzene (**4**) and pentaphenyl(4-methylphenyl)-benzene triphenylphosphonium bromide (**5**) were synthesized by the previously reported method [12]. All reactions were performed using dry glassware under nitrogen atmosphere. Analytical TLC was carried out on Merck 60 F254 silica gel plate and column chromatography was performed on Merck 60 silica gel (230–400 mesh). Melting points were determined on an Electrothemal IA 9000 series melting point apparatus and are uncorrected. NMR spectra were recorded on a Varian Mercury-400 (400 MHz) spectrometer with TMS peak as reference. UV/Vis spectra were recorded on a Jasco V-550 spectrometer. MALDI-TOF MS spectra were recorded with an Applied Biosystems Voyager-DE-STR. Elemental analyses were performed with a Perkin-Elmer 2400 analyzer. The optical absorption spectra were obtained by HP 8453 UV-VIS-NIR spectrometer. Thermal properties of the compounds were measured by thermogravimetric analysis (TGA) and differential scanning calorimeter (DSC) using a SDT2960 and DSC2910 (TA Instruments). Voyager-DE-STR, elemental analysis was performed with a Perkin-Elmer 2400 analyzer. Perkin Elmer luminescence spectrometer LS50 (Xenon flash tube) was used for PL spectroscopy. Surface analyzer AC-2 (RIKEN KEIKI) was used for work function measurement. EL devices were fabricated as the following structure : ITO/ 2-TNATA 60nm/ NPB 15nm/

emitting layer(EML) 35nm/ TPBi 20nm/ LiF 1nm/ Al 200nm, 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), 1,3,5-tri(1-phenyl-1H-benzo[d]imidazol-2-yl)phenyl (TPBi) 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.

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Synthesis

Synthesis of hexaphenylbenzene-based compounds 1, 2, and 3. Preparation of compounds **1** and **2** was carried out by typical Wittig-Horner-Emmons type reactions of aromatic aldehydes 6 and 7 with hexaphenylbenzene phosphonate **4**[12] **to** give **1** and **2** in 29.1% and 42.6% yield, respectively. On the other hand, Wittig reaction of aldehyde **8** with ylide **5** produced **3** in 36.0% yield.

4{2(9-anthracenyl)ethenyl}phenylpentaphenylbenzene (1). [5P-VAn]

Amixture of hexaphenylbenzene phosphonate (**4**) (1.62 g, 1.82 mmol) and NaH (52 mg, 2.18 mmol) in DMF (10 ml) was stirred at room temperature for 1h, and 9-anthracenecarboxaldehyde(6) (0.38 g, 1.82 mmol) added to the mixture and then stirred for 24 h. The reaction mixture was quenched with water (500 ml). The resulting solids were filtered and dried(at 45°C, 1 day). The crude product was recrystallized from methanol to give **1** (0.39 g, 29.1%) in a yellow solid. M.p 292°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.30 (s, 1H), 8.22 (d, J = 7.2 Hz, 1H), 7.94 (d, J = 7.2 Hz, 2H), 7.64 (d, J = 7.6 Hz, 2H), 7.38 (m, 4H), 7.30 (d, 2H), 6.94-6.86 (m, 9H), 6.86-6.76 (m, 14H), 6.68 (d, J = 8.2 Hz, 2H), 6.63 (m, 2H). MS (MALDI-TOF): m/z for $C_{58}H_{40}$ Calcd 736.90 Found 736.29 Anal. Calcd.: C, 94.53 H, 5.47 Found: C, 94.35%; H, 5.65%.

4{2(1-Pyrenyl)ethenyl}phenylpentaphenylbenzene (2). [5P-VPy]

A mixture of hexaphenylbenzene phosphonate (**4**) (1.50 g, 1.69 mmol) and NaH (49 mg, 2.03 mmol) in DMF (20 ml) was stirred at room temperature for 1 h, and 1-pyrenecarboxaldehyde (7) (0.39 g, 1.69 mmol) added to the mixture and then stirred for 24 h. The reaction mixture was quenched with water (500 ml). The resulting solids were filtered and dried(at 45°C, 1 day). The crude product was recrystallized from methanol to give **2** (0.55 g, 42.6%) in a yellow solid. M.p 340°C. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.42 (d, J = 7.6 Hz, 1H), 8.22 (d, J = 7.2 Hz, 1H), 8.16 (d, J = 7.2 Hz, 2H), 8.12 (d, J = 7.6 Hz, 1H), 8.08 (d, J = 8.4 Hz, 1H), 8.04 (s, 2H), 8.00 (d, J = 7.8 Hz, 1H), 7.22 (d, J = 7.8 Hz, 2H), 7.13 (d, J = 8.2 Hz, 1H), 6.90∼6.80 (br, m, 28H). MS (MALDI-TOF): m/z for $C_{60}H_{40}$ Calcd 760.92 Found 760.12 (M^+). Anal. Calcd : C, 94.70%; H, 5.30%. Found: C, 94.43%; H, 5.57%.

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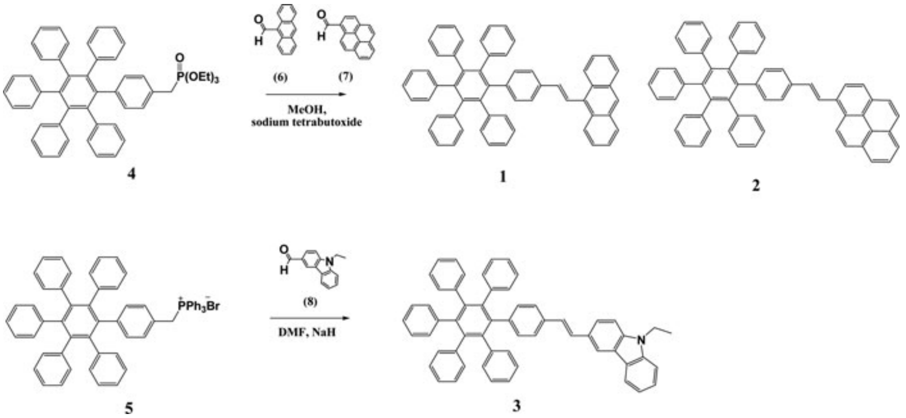
4{2(9-Ethyl-9H-carbazol-3-yl)ethenyl}phenylpentaphenylbenzene (3). [5P-VCB]

A mixture of the phosphonium bromide (**5**) (1.40 g, 1.57 mmol), 9-ethyl-9H-carbazole-3-carboxaldehyde (**8**) (0.42 g, 1.89 mmol) and sodium tert-butoxide (0.76 g, 7.85 mmol) in methanol 30 ml) was refluxed for 24 hours. After cooling to room temperature, the mixture was quenched with water (500 ml) and then extracted with dichloromethane. The solvent was evaporated under reduced pressure, and the residue was chromatographed on silica gel with dichloromethane/hexane (1:2) to give **3** (0.43 g, 36.0%) in a yellow solid. M.p 340 ºC. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.10$ (d, J = 7.6 Hz, 2H), 7.04-7.59 (m, 12H), 6.90 (m, 25H), 4.20 (q, 2H), 1.40 (t, 3H). MS (MALDI-TOF): m/z for $C_{58}H_{43}N$ Calcd 753.93. Found 753.36 (M^+). Anal. Calcd for $C_{58}H_{43}N$: C, 92.39%; H, 5.75%; N, 1.86%. Found: C, 92.27%; H, 5.84%; N, 1.89%.

Results and Discussion

Chemical structures of the three synthesized compounds are shown in Scheme 1, and synthetic methods are summarized in Scheme 2. Carbazole, anthracene and pyrene were substituted with vinyl group into hexaphenylbenzene (HPB) moiety, a star shaped bulky size group. Optical properties of the synthesized compounds are shown in Table 1. In 5P-VCB, carbazole group was introduced to HPB. UV-Visible (UV-Vis.) absorption peaks exhibited 335 nm in solution state. 5P-VAn is a molecule in which anthracene was introduced and showed UV-Vis. absorption peaks at 390 nm. 5P-VPy substituted with pyrene showed UV-Vis. maximum values at 386 nm. 5P-VCB in film state showed UV-Vis. absorption peaks at 347 nm. 5P-VAn and 5P-VPy had UV-Vis. maximum peaks at 395 nm and 386 nm, respectively. (see Fig 1, 2) The three synthesized compounds had extremely small change in UV-Vis. absorption peak of 10 nm or less between solution state and film state. 5P-VCB in solution state showed PL maximum value at 420 nm, and 5P-VAn and 5P-VPy exhibited PL maximum values at 487 nm and 434, 445 nm, respectively. In film state, 5P-VCB showed PL maximum value at 452 nm, 5P-VAn at 483 nm and 5P-VPy at 488 nm. (see Fig 3, 4)



Scheme 2. Synthetic routes of synthesized compounds

In case of 5P-VCB, PL maximum appeared in deep blue region. However, although 5P-2An and 5P-2Py contain anthracene and pyrene which are deep blue chromophores, they showed PL maximum values at 483 nm and 488 nm. It can be explained by considering

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Table 1. Optical properties of synthesized materials

Compound	Solution UV [(a)] (nm)	Film UV [(b)] (nm)	Solution PL [(a)] (nm)	Film PL [(b)] (nm)
5P-VCB	335	347	420	452
5P-VAn	390	395	487	483
5P-VPy	386	386	434, 445	488

a: $CHCl_3$ solution (2.5×10^{-5} M), b: Film thickness is 50nm

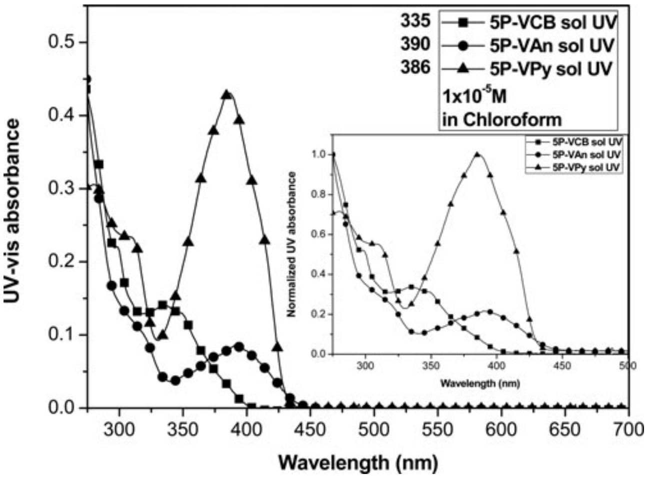

Figure 1. UV-Visible absorption spectra and normalized spectra (inset) of 5P-2VCB, 5P-VAn, 5P-VPy in $CHCl_3$ solution (1×10^{-5}M).

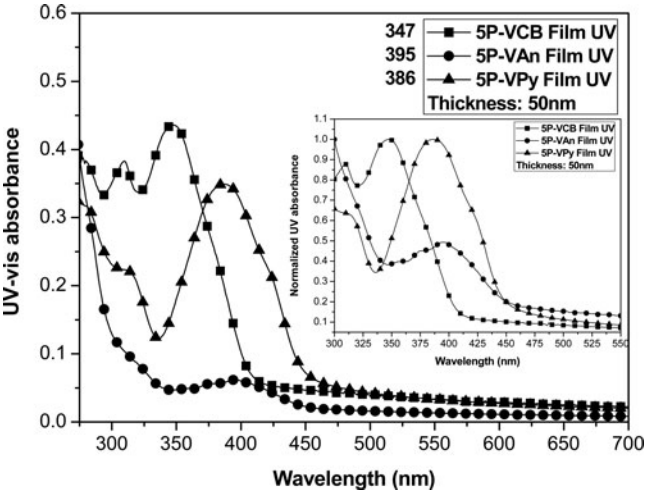

Figure 2. UV-Visible absorption spectra and normalized spectra (inset) of 5P-VCB, 5P-VAn, 5P-VPy in film state (thickness: 50 nm).

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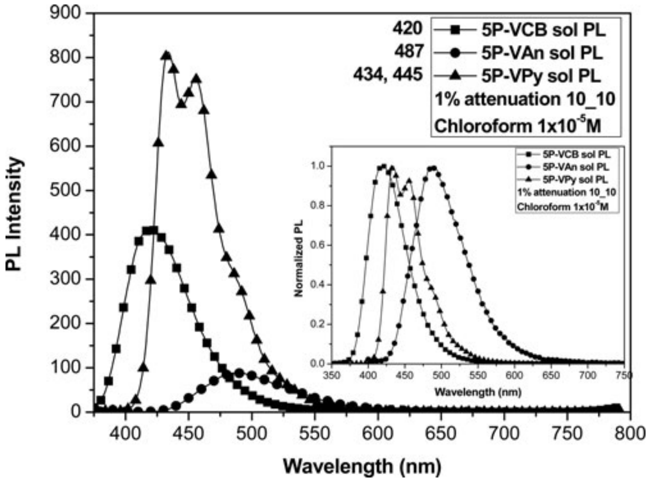

Figure 3. PL spectra and normalized spectra (inset) of 5P-2VCB, 5P-VAn, 5P-VPy in $CHCl_3$ solution (1×10^{-5}M).

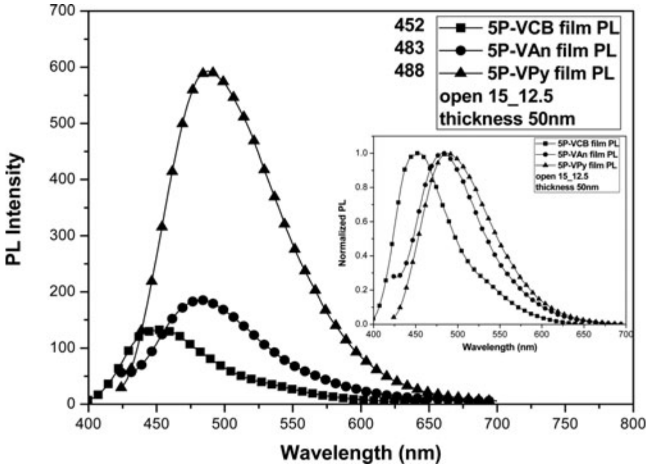

Figure 4. PL spectra and normalized spectra (inset) of 5P-VCB, 5P-VAn, 5P-VPy in film state (thickness: 50 nm).

the electron density in Fig 5. Electrons are distributed in the vinyl group substituted into 9-position of anthracene and 1-position of pyrene. Such electron distribution increased conjugation length of emitting core that directly affects emission, which caused emission wavelength to appear in bluish green.

DSC and TGA analyses to determine the thermal properties of the synthesized molecules were carried out (see Table 2). High T_d values indicate that the material morphology will not easily be changed by the high temperatures generated during the operation of OLED devices, and are closely correlated with long OLED device life-time. Three compounds showed high T_d of 409, 306 and 429°C. Energy levels of three synthesized compounds such as HOMO, LUMO, and band gap were estimated by ultraviolet photon spectroscopy of AC-2 and optical absorption spectroscopy. (see Table 2) 5P-VCB had

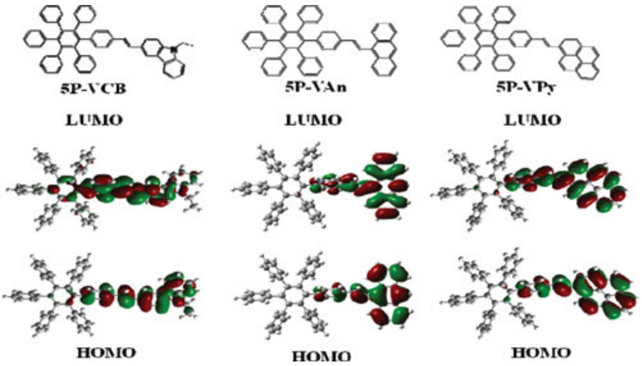

Figure 5. Optimized molecular structures of synthesized compounds.

Table 2. Thermal properties and energy levels of synthesized compounds

Compound	HOMO (eV)	LUMO (eV)	Band gap (eV)	Tg °C	Tm °C	Td °C
5P-VCB	5.54	2.49	3.05	—	340	449
5P-VAn	5.70	2.97	2.73	—	292	426
5P-VPy	5.43	2.68	2.75	—	340	467

HOMO and band gap values of −5.54 eV and 3.05 eV. 5P-VAn and 5P-VPy showed HOMO values of −5.70 eV and −5.43 eV, and band gap values of 2.73 eV and 2.75 eV, respectively. Band gap was decreased and emission wavelength was red-shifted according to the change from carbazole group to anthracene and pyrene.

OLED devices of three compounds as an EML were fabricated as ITO/2-TNATA 60 nm/NPB 15 nm/EML 35 nm/TPBi 20 nm/LiF 1 nm/Al 200 nm. All organic films were prepared by thermal evaporation under high vacuum of 10^{-6} torr.(see Table 3)

Figurer 6 shows I-V-L characteristics and current efficiency of three devices. It exhibits current density and luminance according to the applied voltage. I-V-L curves of three compounds showed typical diode characteristics. The related efficiency data was also summarized in Table 3. Comparing current efficiency (C.E.) of three devices, 5P-VPy had higher current efficiency such as 7.91 cd/A than two compounds of 5P-VCB and 5P-VAn. 5P-VPy device had low operating voltage such as 7.06 V compared to the operating voltage of 5P-VCB and 5P-VAn. The high operating voltage of 5P-VCB and 5P-VAn was based on

Table 3. Optical EL performance of multilayered devices with the synthesized compounds at 10 mA/cm^2

Compound	Volt (v)	C.E (cd/A)	P.E (lm/W)	CIE (x, y)	EL max	Film PL
5P-VCB	9.02	1.76	0.67	(0.150, 0.073)	447	452
5P-VAn	10.93	0.38	0.12	(0.202, 0.310)	484	483
5P-VPy	7.06	7.91	4.04	(0.201, 0.360)	484	488

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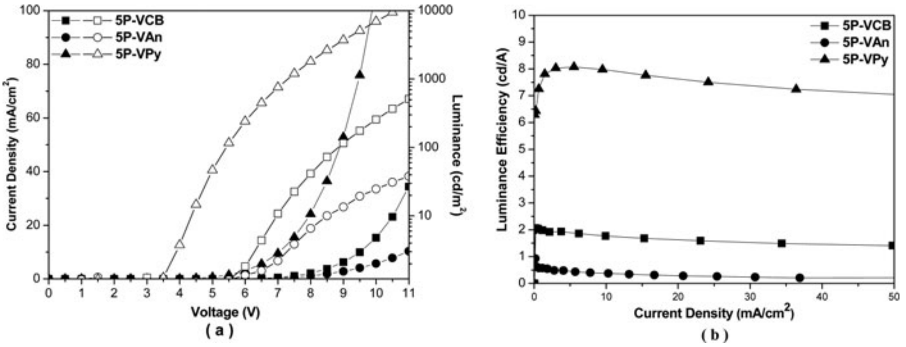

Figure 6. I-V-L graphs (a) and current efficiency (b) of synthesized compounds Device structure: ITO/ 2-TNATA 60 nm/ NPB 15 nm/ EML 35 nm/ TPBi 20 nm/ LiF / Al.

higher LUMO level of 5P-VCB and deep HOMO level of 5P-VAn which can be increased energy barrier between ETL and HTL than 5P-VPy compounds.

CIE values of 5P-VCB, 5P-VAn and 5P-VPy showed beep blue and sky blue color such as (0.15, 0.07), (0.20, 0.31) and (0.20, 0.36), respectivily.

Conclusion

We demonstrated new fluorescence compounds based on hexaphenyl benzene derivatives. Those chemical structures can be varied by side groups of aliphatic and aromatic moiety. Three model compounds were designed and synthesized. Pyrene groups can improve EL property such as current efficiency and operating voltage. CIE values of 5P-VCB, 5P-VAn and 5P-VPy showed beep blue and sky blue color such as (0.15, 0.07), (0.20, 0.31) and (0.20, 0.36), respectively and exhibited current efficiency values of 1.76, 0.38, 7.91 cd/A. Also, three compounds exhibited thermal stability such as high T_d of 409°C, 306 °C and 429°C.

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