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1,4-bis(2,2-diphenylethenyl)benzene as an efficient emitting material for organic light emitting diodes

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Abstract. We report on the photophysical properties of 1,4-bis(2,2-diphenylethenyl)benzene (PEB) in a solution and a solid state. A poor blue photoluminescence efficiency of PEB in a solution dramatically increases in the deposited film. We explain such properties in terms of molecular dynamics and degrees of intramolecular freedom in various molecular environments. PEB as an electron-transport and emitting layer in organic light-emitting diodes (OLEDs) shows bright blue-green electroluminescence (EL) with the peak wavelength at $\lambda_{\text{max}} \sim 495$ nm. The maximum external EL quantum efficiency of $\eta_{\text{EL}} = 2.5$ % and maximum luminance of 41600 cd/m² in the optimized device were obtained, indicating that PEB possesses superior electron-transport ability.

Keywords: electroluminescence, electrical transport characteristics, OLED, 1,4-bis(2,2-diphenylethenyl)benzene (PEB).

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1. Introduction

Organic light emitting diodes (OLEDs) have become one of the most attractive research areas in recent years. Wide possibilities of various molecular structures through organic synthesis, simple and low temperature processability and low cost, attributed to organic materials, show their high potential and promising feature as a next-generation display [1-4]. Since the organic multilayer electroluminescence (EL) diode was reported in 1987 [5], the OLED characteristics have been progressively improved. Various device structures, organic materials and fabrication techniques have been widely developed [6-8].

Among various emitting materials, one of the promising candidates is an arylethene and stilbene based π -conjugated system [9-14]. Some of π -conjugated compounds such as stilbene and poly(arylenevinylene)s (1,2-diarylethene-based π -systems) have already revealed their high potential as the OLED materials [9, 15-18] due to their excellent fluorescence properties [9]. Many arylethene derivatives have photoluminescence

(PL) in a visible region; the PL spectrum and the PL efficiency significantly depend on the substituents and their position and these derivatives emit intense PL even in a solid state [9, 19-21].

The blue-green emitting 1,4-bis(2,2-diphenylethenyl)benzene (PEB) shown in Fig. 1 is the simplest material in this family containing styrene units and can be a good model compound to understand basic photophysical and electrical properties. As it was reported before, PEB is highly fluorescent and can be used as a dopant in blue emitting OLEDs [16, 22-23]. OLED with PEB dispersed into a polystyrene (PS) matrix showed pure blue emission with the external EL quantum efficiency of $\eta_{\text{EL}} = 0.25$ % [22]. Further, OLED using PEB blended with rubrene in a PS matrix demonstrated white emission with $\eta_{\text{EL}} = 0.3$ % [23]. Although the PL efficiency of PEB in a solid film was found to be high [16], the EL efficiencies of OLEDs with the spin-coated emitting layer containing PEB were rather low [22-23].

In this work, we report on the fundamental photophysical properties of PEB in a solution and a solid state. We also study the EL and carrier transport

characteristics of PEB using various OLED structures. A high efficiency OLED with PEB as an electron-transport and emitting layer is demonstrated.

2. Experimental section

PEB was synthesized according to the preparation method described below. All reactions were carried out under an atmosphere of nitrogen with freshly distilled solvents, unless otherwise noted. Silica gel (Daiso gel IR-60) was used for column chromatography. NMR spectra were recorded on JEOL Lambda 500 instrument. To a DMF solution (25 mL) of terephthalaldehyde (268 mg, 2.0 mmol), 0.663 g of dimethyl diphenylmethylphosphonate and 0.449 g of potassium *t*-butoxide were added. The solution was stirred at room temperature for 12 hours. After being transferred to a separation funnel, ethyl acetate was added to mixture. NaCl solution was used to wash the organic phase for 3 times to remove DMF. Then, the organic layer was washed with brine and dried over MgSO₄. After evaporation, the residue was subjected to column chromatography on silica gel (hexane / CH₂Cl₂ = 10:1) to give 1,4-bis(2,2-diphenylethenyl)benzene (PEB) (0.617 g, 71 %) as yellow solid. H NMR (500 MHz, CDCl₃) δ 6.79 (s, 4H), 6.86 (s, 2H), 7.14-7.20 (m, 4H), 7.25-7.34 (m, 16H). C NMR (125 MHz, CDCl₃) δ 127.42, 127.45, 127.57, 127.86, 128.16, 128.60, 129.15, 130.35, 135.88, 140.35, 142.49, 143.46.

To investigate the molecular aggregation properties of PEB, the degassed solutions with various PEB concentrations of 10⁻⁶ ~ 10⁻² M in dehydrated chloroform (CHCl₃) and toluene (CH₃C₆H₅) were prepared for PL measurements. Neat PEB films were deposited in vacuum (10⁻⁴ Pa) on pre-cleaned quartz, glass and ITO substrates, respectively. The substrates were cleaned using a standard cleaning procedure and exposed to UV-ozone before vacuum deposition. The thicknesses of the deposited films were measured with Stylus Profiler DEKTAK 6M.

The highest occupied molecular orbital (HOMO) level of the deposited films was measured with an ultraviolet photoelectron spectroscopy (AC-1, Riken Keiki Co.). The absorption spectra of the degassed solutions and deposited films were recorded using a UV-VIS-NIR recording spectrophotometer UV-3100 (Shimadzu Co.). The PL spectra were measured using Spectrofluorometer FP-6500-A-51 (Jasco Co.). The absolute PL efficiency (Φ_r) of degassed solutions and neat films under argon flow was measured using an integrating sphere [24] with 325 nm excitation source (Xe lamp) and multi-channel spectrometer (Hamamatsu PMA-11) as the optical detector.

To understand the carrier transport and EL properties of PEB, we prepared three types of OLED structures (Fig. 1): Type **(I)**: ITO(110 nm) / α-NPD(50 nm) / PEB(50 nm) / Mg:Ag(100 nm) / Ag(20 nm); Type **(II)**: ITO(110 nm) / α-NPD(50 nm) /

PEB(20 nm) / Bphen(30 nm) / Mg:Ag(100 nm) / Ag(20 nm); and Type **(III)**: ITO(110 nm) / α-NPD(50 nm) / PEB(10 nm) / Alq₃(50 nm) / Mg:Ag(100 nm) / Ag(20 nm). Here, 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (α-NPD) as a hole-transport layer (HTL), aluminum (III) tris(8-hydroxyquinoline) (Alq₃) as an electron-transport layer (ETL), and 4,7-diphenyl-1,10-phenanthroline (Bphen) as an ETL and hole-blocking (HBL) layer were used for OLEDs (Fig. 1). A magnesium silver (Mg:Ag) alloy layer (10:1) capped with a silver layer was deposited on the top of the organic layers. Current density-voltage-luminance (DVL) characteristics were measured using a semiconductor parameter analyzer (Agilent, HP4155C) with an optical power meter (Newport, Model 1835-C).

3. Results and discussion

3.1. Photoluminescent properties of PEB in a solution and a solid state

Table and Fig. 2 summarize the optical properties of PEB in a neat film and in solutions with the PEB concentrations of 10⁻⁶ ~ 10⁻² M in chloroform and toluene, respectively. These PEB solutions indicate strong absorption with the maxima at λ_{a,max} ~ 355 nm corresponding to the 0 → 0* transition. The absorption spectrum of the 50 nm-thick PEB film showed the identical absorption maximum at λ_{a,max} = 356 nm (Fig. 2).

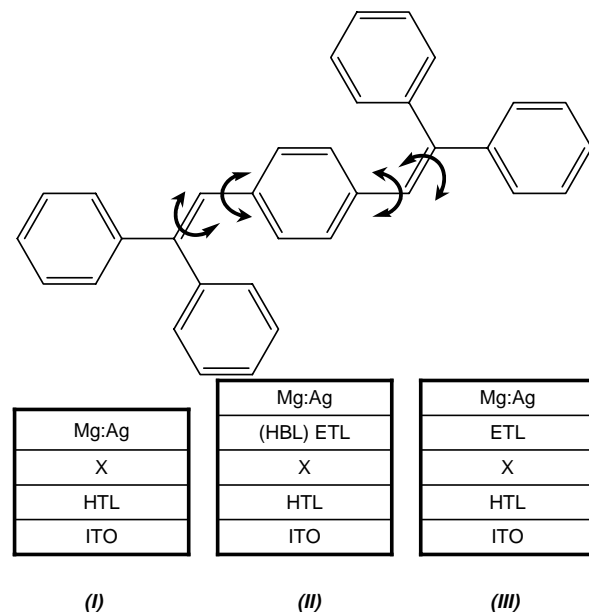


Fig. 1. PEB molecular structure with indication of possible intermolecular rotations around the single and double bonds. The types of OLED structures: **(I)** – ITO(110 nm) / α-NPD(50 nm) / PEB(50 nm) / Mg:Ag(100 nm) / Ag(20 nm); **(II)** – ITO(110 nm) / α-NPD(50 nm) / PEB(20 nm) / Bphen(30 nm) / Mg:Ag(100 nm) / Ag(20 nm); **(III)** – ITO(110 nm) / α-NPD(50 nm) / PEB(10 nm) / Alq₃(50 nm) / Mg:Ag(100 nm) / Ag(20 nm).

Table. Photophysical properties of PEB in solution and deposited film.

	Solution			Neat film	X mol % PEB: CBP (doped film)
	Molar concentration (M)	In chloroform	In toluene		
HOMO (eV)				5.8	
LUMO (eV)				2.9	
E_g (eV)	10^{-6}	3.1	3.1	2.9	
	10^{-5}	3.1	3.1		
	10^{-4}	3.1	3.1		
	10^{-3}	2.9	3.0		
	10^{-2}	2.8	3.0		
Φ_f (%)	10^{-6}	4.5 \pm 0.5	21.0 \pm 0.5	57.0 \pm 0.5	89.0 \pm 0.5* 90.5 \pm 0.5**
	10^{-5}	4.0 \pm 0.5	18.0 \pm 0.5		
	10^{-4}	4.0 \pm 0.5	18.0 \pm 0.5		
	10^{-3}	4.0 \pm 0.5	17.5 \pm 0.5		
	10^{-2}	3.5 \pm 0.5	17.5 \pm 0.5		
η_{EL} (%)				0.012 (I) 2.5 (II) 1.1 (III)	1.1* (II) 1.1** (II)
		354	358	356	359* 359**
$\lambda_{f, \max}$ (nm)	10^{-6}	456, 467	452, 468	471	471* 471**
	10^{-5} - 10^{-2}	467~470	468		
$\lambda_{EL, \max}$ (nm)				492 (I) 497 (II) 493 (III)	477* (II) 484** (II)

(I), (II) and (III) denote type of the OLED structures.

* 0.23 mol. %; ** 4.70 mol. %

In a diluted chloroform or toluene solutions of 10^{-6} M, PEB showed blue fluorescence with vibronic structures having two PL maxima at $\lambda_{f, \max} \sim 454$ nm and ~ 467 nm corresponded to the $0^* \rightarrow 0$ and $0^* \rightarrow 1$ transitions, respectively, and a weak shoulder at $\lambda_f \sim 494$ nm ($0^* \rightarrow 2$ transition). With an increase of the PEB concentration, a slight red shift of the PL peaks was observed. The PL spectra of the $10^{-5} \sim 10^{-2}$ M solutions showed the PL maximum corresponding to the $0^* \rightarrow 1$ transition and also two shoulders at 456 and 494 nm. Further, the PL spectrum of the PEB neat film showed more intense red shift compared with those of the spectra in the $10^{-5} \sim 10^{-2}$ M solutions. The film showed bright blue-greenish emission with a main maximum at $\lambda_{f, \max} = 471$ nm ($0^* \rightarrow 1$ transition) and two shoulders at ~ 456 nm ($0^* \rightarrow 0$ transition) and 493 nm ($0^* \rightarrow 2$ transition).

The PL efficiencies of PEB in the $10^{-6} \sim 10^{-2}$ M chloroform solutions were as low as $\Phi_f = 3 \sim 5$ % and was almost independent on the concentration (Table). On the other hand, the PL efficiencies of PEB in the $10^{-6} \sim 10^{-2}$ M toluene solutions showed much higher values of $\Phi_f = 17 \sim 21$ % and a slight decrease of the PL efficiency with an increase of the concentration. On the

other hand, the PL efficiency of the deposited film was $\Phi_f = 57$ %, indicating dramatic increase in the solid state compared with those in the solutions. This can be explained in terms of degrees of the intramolecular freedom of PEB in the solutions and solid state. PEB can be well dissolved in a chloroform solution and have a freedom in the intramolecular rotations as shown in Fig. 1. PEB contains stilbene units which can transform from trans to cis and vice versa under the optical excitation. The trans-configuration of stilbene is radiative, while cis-configuration is completely non-emissive. As it was found before [22], the trans-trans configuration in PEB is optically most emissive, although it can be flipped into less emissive cis-trans or cis-cis PEB configurations under the optical excitation. Thus, the prevention of the intramolecular rotations and stabilization of the trans-configuration are necessary to obtain high PL efficiency. In case of the toluene solution, we suppose that PEB have less freedom for the intramolecular rotation due to the higher viscosity of toluene ($\delta = 0.68$ Centistokes at 20 °C) compared with chloroform ($\delta = 0.38$ Centistokes at 20 °C).

To confirm the above consideration, we prepared the "solid solution" of a co-deposited film of 4,4'-N,N'-

dicarbazole-biphenyl (CBP) doped with 1 ~ 2 wt% PEB. The PL spectrum of 1 ~ 2 wt% PEB: CBP co-deposited film was similar to those in the chloroform and toluene solutions, demonstrating the same maximum at $\lambda_{f,max} = 471$ nm and two weak shoulders at 456 and 494 nm, respectively. It indicates that the PEB molecules are well dispersed in the CBP host matrix and no PEB molecular aggregation occurs. The PL efficiency was significantly high compared with these in the solutions and the neat film, showing $\Phi_f = (89 \sim 91) \pm 0.5\%$ (Table). Thus, the CBP host matrix well prevents the intramolecular rotation in PEB, leading to the significant increase of the radiative decay process.

3.2. Electroluminescent properties of PEB

All OLEDs showed blue-green EL with the maximum at $\lambda_{EL,max} = 492$ nm corresponding to the $0^* \rightarrow 2$ transition

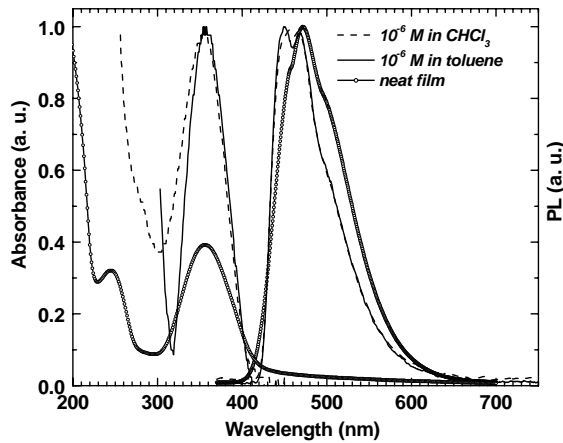


Fig. 2. Absorption and PL spectra of PEB in a neat film and in 10^{-6} M chloroform and toluene solutions.

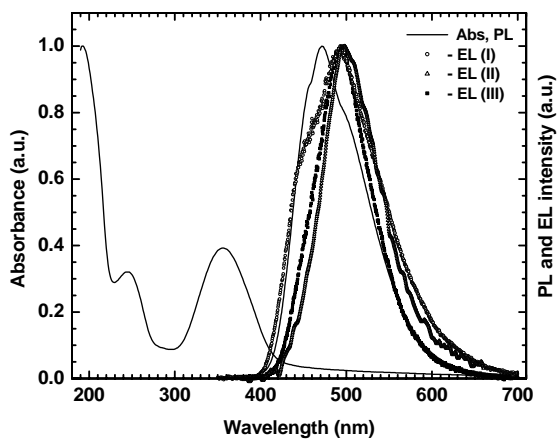


Fig. 3. EL spectra in OLED devices (I, II and III), and PL and absorption spectra of PEB in a neat film.

(Fig. 3). OLEDs with the Type (I) structure showed inferior device characteristics. The low external EL quantum efficiency of $\eta_{EL} = 0.012\%$ with maximum luminance of ~ 31 cd/m² and poor reproducibility were observed due to the crystallization of the PEB layer during the metal deposition (Figs 3-5). Also, relatively high energy barrier of ~ 0.85 eV at the PEB/MgAg interface may limit efficient electron injection (Fig. 4).

The OLEDs of Type (II) with Bphen as an additional electron-transport and hole-blocking layer showed good reproducibility and pronounced OLED characteristics with $\eta_{EL} = 2.5\%$ and the maximum luminance of 41600 cd/m² (Figs. 4 and 5). The EL spectrum showed the maximum at $\lambda_{EL,max} = 493$ nm corresponding to the $0^* \rightarrow 3$ transition in PEB (Fig. 3). Here, we observed no crystallization of the PEB layer due to the presence of the overlaid Bphen layer. The small electron injection barrier of $\Delta E = 0.1$ eV from

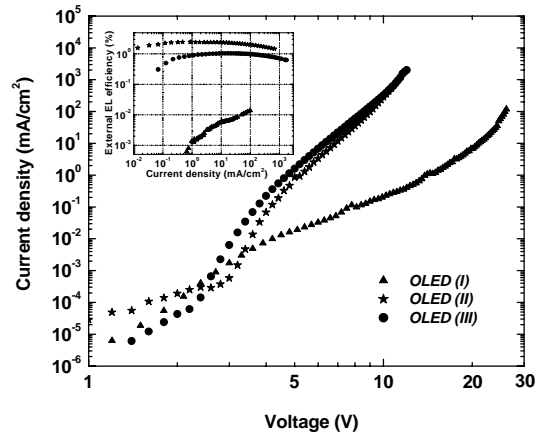


Fig. 4. Current density-voltage (DV) characteristics of OLEDs (I, II and III). The corresponding external EL efficiency-current density (η_{EL} -J) characteristics are shown in the insert.

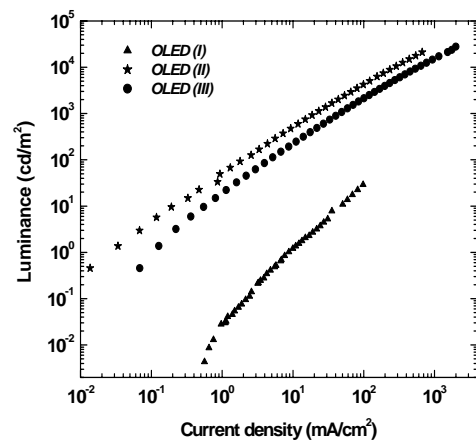


Fig. 5. Luminance-current density characteristics of OLEDs (I, II and III).

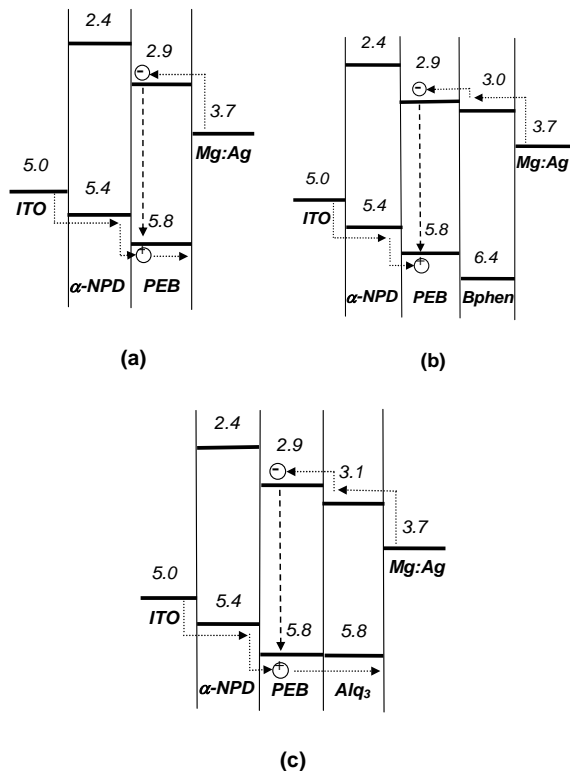


Fig. 6. Energy diagrams in OLEDs (I (a), II (b) and III (c)).

Bphen into the PEB layer would also provide efficient electron injection (Fig. 6b). To clarify the major carriers in PEB, Type (III) OLED having an Alq₃ ETL was examined (Fig. 6c). The EL spectrum was similar to the Type (II) devices, showing the greenish emission with the maximum at 493 nm, indicating that EL is due to PEB layer, since the Alq₃ emission locates at $\lambda_{EL,max} \sim 510$ nm. Thus, we can conclude that the PEB layer efficiently transports electrons.

4. Conclusions

The photophysical and EL properties of PEB were investigated. The very weak blue PL of PEB in a solution was dramatically increased in a solid state. We explained such PEB behavior in the terms of degrees of freedom in the intramolecular rotations between cis- and trans-configuration. The prevention of the intramolecular rotations leads to the dramatic increase of Φ_f . The OLEDs with PEB as an emitting layer showed blue-greenish EL with the maximum $\eta_{EL} = 2.5\%$. PEB was identified as an efficient electron-transport and emitting material in OLEDs.

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