

Electrical properties of 1,4-bis(4-(phenylethynyl)phenylethynyl)benzene and its application for organic light emitting diodes†

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We found that a phenylene ethynylene derivative, 1,4-bis(4-(phenylethynyl)phenylethynyl)benzene (BPPB), provides very high photoluminescence efficiency both in solution ($\Phi_{\text{PL}} = 95 \pm 3\%$) and thin films ($\Phi_{\text{PL}} = 71 \pm 3\%$); further, we observed blue electroluminescence (EL) of $\lambda_{\text{EL (max)}} \sim 470$ and 510 nm with an external EL efficiency of $\eta_{\text{EL}} \sim 0.53\%$ and maximum luminance of $\sim 70000 \text{ cd m}^{-2}$ at current density of $\sim 2 \text{ A cm}^{-2}$ with BPPB as an emitter; also we identified that BPPB functions as a hole transport layer in organic light emitting diodes.

Organic materials composed of aromatic groups conjugated through acetylene linkages such as (phenylethynyl)benzenes are expected to attract a lot of attention as optoelectronic materials because of their abundant π -conjugation.^{1–4} In fact, efficient charge transport, fast energy transfer, and excellent luminescence properties have been reported in some phenylethynyl compounds.^{5–9} Their highest occupied molecular orbital (HOMO)–lowest unoccupied molecular orbital (LUMO) energy gaps and emissive properties can be well controlled by tuning their effective conjugation lengths. It is also of fundamental interest to compare the photoluminescent (PL) and electroluminescent (EL) properties of the phenylene ethynylene groups with these of well characterized phenylene vinylene groups.^{4,10}

One of the interesting features of phenylene ethynylene compounds is their linear molecular structure, which potentially provides efficient π -stacking between adjacent molecules. Moreover, the triple bonds lead to coplanar and twisted molecular structures, which can change their π -conjugation.^{10–12} In the solid state, some phenyl acetylene compounds self-organize through cofacial interactions, leading to close packed molecular aggregates.¹⁰ It has been further reported that arylene ethynylene derivatives show unique intermolecular aggregation in solution and the solid state.^{13,14} Such interactions between π -electrons on phenylene and ethynylene of neighbouring molecules should greatly enhance intermolecular charge transport.

Here, we synthesized a novel phenylethynyl derivative, 1,4-bis(4-(phenylethynyl)phenylethynyl)benzene (BPPB), (Fig. 1) and

examined the optical, charge transport and EL characteristics in organic light emitting diodes (OLEDs).

BPPB was synthesized according to the following procedure. A 50 mL flask was charged with 1-iodo-4-(phenylethynyl)benzene (346 mg, 1.14 mmol), 1,4-diethynylbenzene (65 mg, 0.52 mmol), Pd(PPh₃)₄ (69 mg, 0.06 mmol) and CuI (11 mg, 0.06 mmol), diisopropylamine (3 mL), and toluene (20 mL). After being stirred at 65 °C for 12 h, the reaction mixture was cooled to room temperature and then poured into aqueous NH₄Cl. The resultant precipitate was collected by filtration. The crude product was washed with H₂O, EtOAc and CH₂Cl₂. After being dried, a pale yellow solid was obtained (214 mg, 86%). The crude product was sublimed before preparation of OLEDs. All reactions were carried out in an atmosphere of nitrogen with freshly distilled solvents, unless otherwise noted.

20–50 nm-thick neat films of BPPB were deposited in a vacuum ($\sim 10^{-4}$ Pa) on quartz, glass and ITO substrates. The substrates were chemically cleaned and exposed to UV/ozone before vacuum deposition. The thicknesses of the deposited films were measured with a Stylus Profiler (DEKTAK 6M). The HOMO level of each BPPB deposited film was measured using ultraviolet photoelectron spectroscopy (AC-1, Riken Keiki Co.). The absorption spectra were measured using a UV-VIS-NIR recording spectrophotometer (UV-3100, Shimadzu Co.). The photoluminescence (PL) spectra were measured using a spectrofluorometer (FP-6500, Jasco Co.). The absolute PL efficiency (Φ_{PL}) of the deposited neat films under the argon flow was measured using an integrating sphere with a Xe

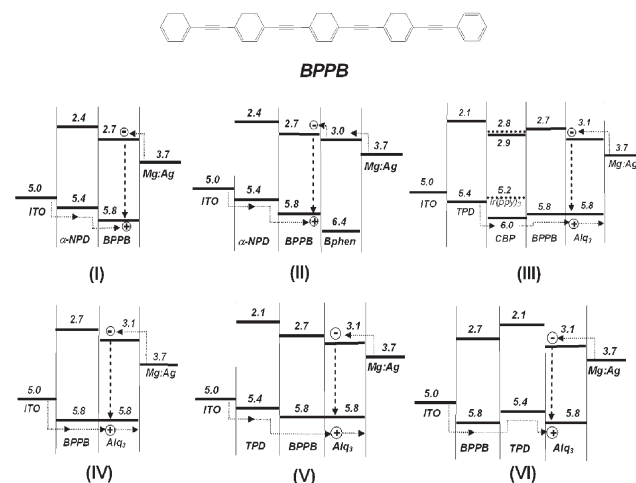


Fig. 1 Molecular structure of BPPB and energy diagrams in OLED devices (I), (II), (III), (IV), (V) and (VI).

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lamp as the excitation source and a multi-channel spectrometer (Hamamatsu PMA-11) as the optical detector.¹⁵

To understand the carrier transport and EL characteristics of BPPB, various OLED structures shown in Fig. 1 were examined:

(I): ITO (110 nm)/ α -NPD (50 nm)/BPPB (50 nm)/Mg:Ag (100 nm)/Ag (20 nm)

(II): ITO (110 nm)/ α -NPD (50 nm)/BPPB (20 nm)/Bphen (30 nm)/Mg:Ag (100 nm)/Ag (20 nm)

(III): ITO (110 nm)/TPD (50 nm)/6 wt% Ir(ppy)₃:CBP (20 nm)/BPPB (20 nm)/Alq₃ (30 nm)/Mg:Ag (100 nm)/Ag (20 nm)

(IV): ITO (110 nm)/BPPB (50 nm)/Alq₃ (50 nm)/Mg:Ag (100 nm)/Ag (20 nm)

(V): ITO (110 nm)/TPD (20 nm)/BPPB (30 nm)/Alq₃ (50 nm)/Mg:Ag (100 nm)/Ag (20 nm)

(VI): ITO (110 nm)/BPPB (20 nm)/TPD (30 nm)/Alq₃ (50 nm)/Mg:Ag (100 nm)/Ag (20 nm).

Here, 4,4'-bis(*N*-(1-naphthyl)-*N*-phenylamino)biphenyl (α -NPD) and *N,N'*-diphenyl-*N,N'*-bis(3-methylphenyl)-1,1'-biphenyl-4,4'-diamine (TPD) as a hole-transport layer (HTL), aluminium(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. Also the 4,4'-(9-carbazolyl)biphenyl (CBP) doped with 6 wt% tris(2-phenylpyridine) iridium complex (Ir(ppy)₃) was used in device (III) as an emitting layer. A magnesium silver (Mg:Ag) alloy layer (10 : 1) capped with a silver layer was deposited on the top of the organic layer. The current density–voltage–luminance (*J*–*V*–*L*) characteristics were measured using a semiconductor parameter analyzer (Agilent, HP4155C) with an optical power meter (Newport, Model 1835-C).

BPPB neat films were successfully deposited using vacuum evaporation without decomposition. The films showed transparent and uniform morphology and no visible crystallization when observed with a scanning electron microscope. The absorption spectrum showed the characteristic vibronic structure with several peaks at $\lambda_{\text{abs (max)}}$ ~ 245, 329, 353 and 382 nm (Fig. 2). The optical band gap of the BPPB solid film estimated from the absorption

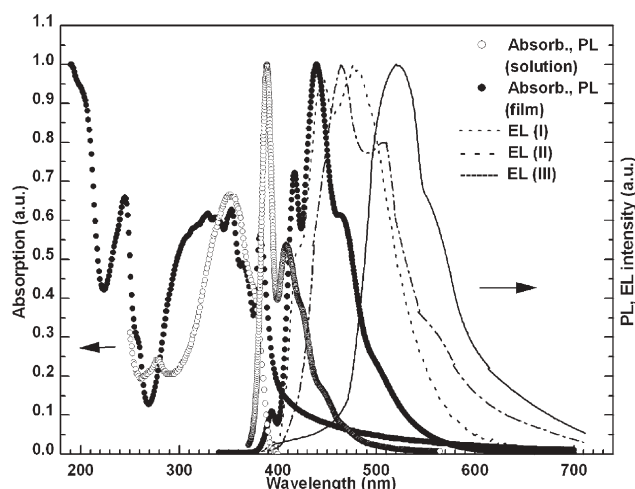


Fig. 2 EL spectra in OLED devices (I), (II) and (III). PL and absorption spectra of BPPB film are also shown.

edge was $E_g = 3.07$ eV. Upon excitation at $\lambda_{\text{ex}} = 353$ nm, the deposited film showed pure blue PL with main maximum at $\lambda_{\text{PL (max)}} \sim 440$ nm ($0^* \rightarrow 2$ transition) with three sub-peaks at $\lambda_{\text{PL}} = 394$ ($0^* \rightarrow 0$), 417 ($0^* \rightarrow 1$) and 467 nm ($0^* \rightarrow 3$) and a weak shoulder at 500 nm. The PL efficiency of the BPPB film was relatively high showing $\Phi_{\text{PL}} = 71 \pm 3\%$. In addition, the HOMO and LUMO levels of the BPPB film were 5.8 and 2.7 eV, respectively.

We also examined PL in a degassed chloroform solution at a concentration of 10^{-6} M (Fig. 2). The absorption spectrum showed the vibronic structure with main maximum at $\lambda_{\text{abs (max)}} \sim 352$ nm, sub-peak at 279 nm and a shoulder at 380 nm. Under the excitation with $\lambda_{\text{ex}} = 352$ nm, BPPB showed deep blue PL with maximum at $\lambda_{\text{PL (max)}} = 389$ ($0^* \rightarrow 0$), sub-peak at $\lambda_{\text{PL (max)}} \sim 409$ nm ($0^* \rightarrow 1$ transition), and weak shoulders at 420, 442 and 467 nm with very high $\Phi_{\text{PL}} = 95 \pm 3\%$, indicating that non-radiative decay is well suppressed due to the rigid molecular structure. In the solid film, on the other hand, since the significant spectral shift with a slight decrease of Φ_{PL} was observed, the molecular aggregation between the BPPB molecules would enhance the non-radiative decay processes such as concentration quenching.

To understand the carrier transport nature of the phenylene ethynylene unit in BPPB, we examined the OLED characteristics in six OLED structures (Fig. 1). The BPPB layer was used as an ETL in devices (I), (II) and (III) and as a HTL in devices (IV), (V) and (VI). Device (I), with BPPB as an ETL, showed very low EL efficiency of $\eta_{\text{EL}} \sim 4 \times 10^{-3}\%$ with EL maxima at $\lambda_{\text{EL (max)}} \sim 440$ and 478 nm corresponding to the characteristic $0^* \rightarrow 2$ and $0^* \rightarrow 3$ transitions of the BPPB film. This indicates occurrence of carrier recombination at the BPPB layer (Fig. 2 and 3). The maximum luminance was ~ 23 cd m⁻² at a current density of ~ 1 A cm⁻². Also, the *J*–*V* characteristics were shifted to a rather high voltage region. These poor OLED characteristics can be ascribed to the poor electron transport properties of the BPPB layer and high energy barrier for electron injection at the BPPB/Mg:Ag interface ($\delta E \sim 1.0$ eV) (Fig. 1 (I) and 3). In contrast, insertion of the additional ETL/HBL layer of Bphen (Fig. 1 (II)) significantly improved the OLED characteristics. The device emitted blue EL with $\eta_{\text{EL}} \sim 0.53\%$ with EL maxima at $\lambda_{\text{EL (max)}} \sim 470$ and 510 nm,

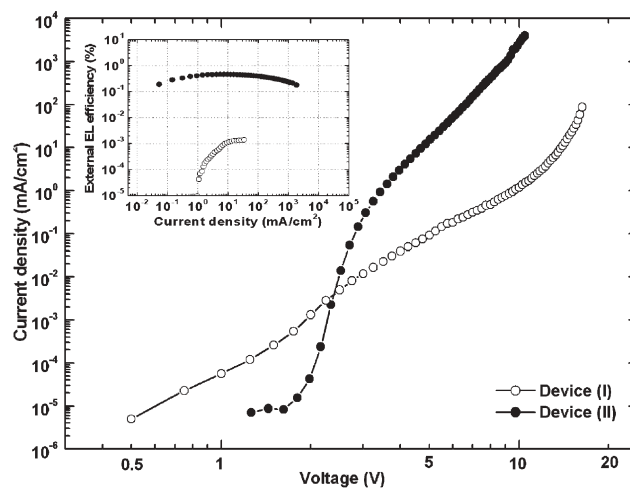


Fig. 3 Current density–voltage (*J*–*V*) characteristics in OLED devices (I) and (II). Corresponding external EL quantum efficiency–current density (η_{EL} –*J*) dependences are shown in inset.

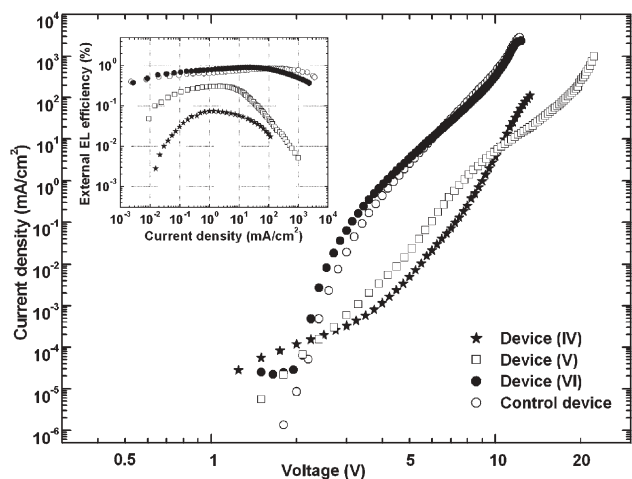


Fig. 4 Current density–voltage (J – V) characteristics of OLED devices (IV), (V) and (VI), and control device of ITO (110 nm)/TPD (50 nm)/Alq₃ (50 nm)/Mg:Ag (100 nm)/Ag (20 nm). External quantum efficiency–current density (η_{EL} – J) dependences are shown in inset.

which are characteristic emission of the BPPB layer (Fig. 2 and 3). We observed pronounced carrier injection at ~ 1.9 V, and the maximum luminance of ~ 70000 cd m⁻² at a current density of 2 A cm⁻² (see ESI†). This significant improvement is due to efficient electron injection from Bphen into the BPPB layer and successive confinement of holes at this interface (Fig. 1 (II)), which leads to efficient carrier recombination at the BPPB/Bphen interface.

To further confirm the poor electron-transport properties of BPPB, we examined a double ETL device (III). Insertion of the 20 nm-thick BPPB layer between Alq₃ and 6 wt% Ir(ppy)₃:CBP emitter layers resulted in a weak green EL based on the Alq₃ emission ($\lambda_{\text{EL (max)}}$ ~ 525 nm) with low $\eta_{\text{EL}} \sim 0.36\%$, indicating that the BPPB layer definitely transports no electrons but holes (Fig. 2).

To clarify the hole transport ability of BPPB, we further examined BPPB as a hole-transport layer in the device structures of (IV), (V) and (VI). A weak green emission with a maximum at 525 nm was observed in $\sim 0.08\%$ and $\sim 0.32\%$ external EL efficiencies in OLEDs (IV) and (V), respectively (see inset in Fig. 4). In sharp contrast to these results, the device (VI) with TPD as an intermediate HTL exhibited remarkably higher external EL efficiency ($\sim 0.9\%$). The reason for poor OLED characteristics in devices (IV) and (V) can be understood by using the energy diagram (Fig. 1 (IV) and (V)). Since the HOMO levels of BPPB and Alq₃ layers are well aligned, the holes pass through the BPPB/Alq₃ interface without substantial hole accumulation inside the BPPB layer. Thus, no net electron accumulation happens in the Alq₃ layer to result in low carrier recombination probability at the BPPB/Alq₃ interface. In a separate experiment, we directly measured the field effect mobility of BPPB in a field effect transistor (FET) structure of n⁺⁺-Si/SiO₂ (300 nm)/PMMA (500 nm)/BPPB (50 nm)/Au source–drain electrodes (40 nm) and obtained FET hole mobility of 4.5×10^{-2} cm² V⁻¹ s⁻¹ and no clear signal on electron mobility, indicating dominant hole transport nature of BPPB.

Device (VI) exhibited OLED characteristics coincident with those of a control device (ITO (110 nm)/TPD (50 nm)/Alq₃

(50 nm)/Mg:Ag (100 nm)/Ag (20 nm)) as shown in Fig. 4. This result clearly indicates that BPPB functions as an excellent hole transport layer in OLEDs in spite of a large energy barrier of ITO/BPPB interface for hole injection ($\delta E = 0.8$ eV) (Fig. 1 (VI)).

This unusual characteristic of BPPB can be explained on the basis of peculiar orientation of BPPB such as parallel orientation of the ITO surface, which enables efficient electron exchange mechanism. Since the XRD-analysis revealed the BPPB neat film to be amorphous, local orientation of some BPPB molecules on the ITO surface would enhance hole injection process. Further studies to clarify the detailed carrier injection mechanism at the interface and enhancement of the molecular orientation by increasing a substrate temperature during formation of a BPPB thin film are now in progress. We expect that increasing the domain size of BPPB and orientation will significantly enhance the electrical properties.

In summary, we demonstrated that the BPPB film has an intense pure blue PL with $\lambda_{\text{PL (max)}}$ ~ 440 nm and high $\Phi_{\text{PL}} = 71 \pm 3\%$. OLEDs with BPPB as an active layer emitted blue EL with the emission maxima at $\lambda_{\text{EL (max)}}$ ~ 470 and 510 nm and $\eta_{\text{EL}} \sim 0.53\%$. We confirmed that the phenylacetylene units in BPPB provide hole transport ability in OLEDs, which contrasts with the electron transport characteristics of the phenylvinylene units in PPV derivatives. The phenylacetylene units will be useful components in organic semiconductors to adjust carrier injection and transport characteristics.

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