Highly efficient blue electrophosphorescent devices with a new series of host materials: polyphenylene-dendronized oxadiazole derivatives

Shiyan Chen, Xinjun Xu, Yunqi Liu,* Wenfeng Qiu, Gui Yu, Xiaobo Sun, Hengjun Zhang, Ting Qi, Kun Lu, Xike Gao, Ying Liu and Daoben Zhu*

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A new series of oxadiazole derivatives **TPO**, **PPO**, **MTPO**, **MPPO**, **BTPO**, and **BPPO** have been designed and synthesized in high yields by a convenient synthetic procedure. A single crystal structure of **TPO** exhibited that this polyphenylene-dendronized material has a sterically crowded structure which efficiently prevents π - π stacking and endows it with good thermal stability. The photophysical properties of the materials show strong emission between 376 and 390 nm in the films. In addition, good reversible reductive waves in the cyclic voltammograms implied that these materials might have good electron transport properties. Blue electrophosphorescent devices fabricated using these materials as the host materials and iridium(III)bis[4,6-di-fluorophenyl-pyridinato- $N, C^{2'}$]picolinate as the blue phosphorescent dopant emitter show very high efficiencies. A maximum luminance of 4484 cd m⁻² and an external quantum efficiency of 6.20% were achieved under ambient conditions.

Introduction

Organic light-emitting diodes (OLEDs) have been widely recognized as a technology for flat panel display products and for solid state white-light sources in potential lighting industries. Electrophosphorescent OLEDs have the potential of offering 100% internal quantum efficiencies due to their ability to use both the singlet and triplet excitons for emission, so they have rapidly developed in recent years. The only way to realize efficient electrophosphorescent OLEDs is to choose suitable host materials which allow for exothermic energy transfer between a host excited state and a lower energy guest unoccupied orbital, and in turn results in an energetically favorable excited state transition between molecules.¹⁻³ To date, a few works about efficient green or red electrophosphorescent OLEDs with high electroluminescence (EL) efficiencies have been reported.³⁻²⁰ As we know well, it is easy to find suitable host materials to favor the triplet level of the green or red electrophosphorescent materials which have relatively low triplet levels. But, it is very difficult to find high energy host materials for blue electrophosphorescent OLEDs due to their high triplet levels. The blue-light-emitting phosphorescent EL performance is far from perfect.²¹⁻²⁴ However, designing effective host materials for blue electrophosphorescent OLEDs is a great challenge. The reason is that the host materials must have rather large energy gaps. Usually, enlargement of the energy gap can be realized by decreasing the extent of conjugation of the molecule, that is to say, the molecule size should be constrained. Nevertheless, to obtain

the morphologically stable and uniform amorphous thin films with typical processing techniques, we have to consider increasing the steric bulk of the molecules. Therefore, an exquisite and flexible molecular design is highly desired to satisfy these conflicting requirements for the host materials of blue electrophosphorescent OLEDs.^{6,25}

Most of the current highly fluorescent materials used as emissive materials in OLEDs are good p-type (hole-transporting) materials. They, however, have generally small electron affinities and poor electron-transporting properties. Compared with organic hole-transporting materials, electron-transporting materials with low electron injection barriers and high electron mobilities for improving the performance and the durability of the devices are also required. The use of electrondeficient heterocyclic small molecules or polymers as a separate electron-transporting layer or as a blend component in conjunction with the emissive material has been proved very useful in improving balanced injection and recombination in OLEDs.²⁶⁻²⁹ In this work, we report the synthesis of a new series of host materials with large band gaps adopting an oxadiazole moiety, which has been reported to have good electron-transporting properties.^{30,31} In addition, we introduce polyphenyl rings to increase the thermal properties and amorphous properties of the materials, since sterically crowded polyphenylphenyl (tetraphenylphenyl and pentaphenylphenyl) moieties have been reported as effective bulky groups used in light-emitting materials.^{32–34} It is a successful example if the dendrons can inhibit the formation of molecular aggregation or π - π stacking in the solid state. We investigated the photophysical, thermal, electrochemical properties of the compounds. The blue electrophosphorescent OLEDs employing these compounds as the host materials and one of the best known triplet-state blue-light emitters, iridium(III)bis[4,6-difluorophenyl-pyridinato- $N, C^{2'}$]picolinate (FIrpic), as the dopant were described as well.

Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, P. R. China. E-mail: liuyq@mail.iccas.ac.cn; Fax: +86-10-62559373; Tel: +86-10-62613253.





Scheme 1 The synthetic route of the target compounds. Reagents and conditions: (i) (a) trimethylsilylacetylene, Pd(PPh₃)₂Cl₂/CuI, THF/Et₃N, rt, 12 h, (b) K₂CO₃, CH₂Cl₂/CH₃OH, rt, 1 h. (ii) Phenylacetylene, Pd(PPh₃)₂Cl₂/CuI, THF/Et₃N, 50 °C, 18 h. (iii) Tetraphenylcyclopentadienone, m-xylene, reflux, 12 h (TPO, MTPO, BTPO); tetraphenylcyclopentadienone, biphenyl ether, reflux, 12 h (PPO, MPPO, BPPO).

Results and discussion

Synthesis and thermal properties

The new series of materials were designed and synthesized via the procedure described in Scheme 1. First, Sonogashira coupling of the oxadiazole derivatives 1a-c with trimethylsilvlacetylene and phenylacetylene gave alkylenes 2a-c and **3a-c**, respectively. Then, the final products were synthesized by the Diels-Alder reaction of 2a-c or 3a-c with tetraphenylcyclopentadienone with an overall yield of 80%. The benefits of a convenient synthetic procedure and relatively high yields are very promising in OLED materials. In addition, due to their excellent solubility of the target compounds in common organic solvents such as dichloromethane (CH2Cl2), trichloromethane (CHCl₃), toluene and tetrahydrofuran (THF), the separation and purification processes were very easy. Thus, characterization such as MALDI-TOF mass spectroscopy, elemental analysis, and NMR spectroscopy, especially ¹³C NMR spectroscopy is easily accomplished.

The thermal properties of the compounds were determined by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) measurements and the data are summarized in Table 1. We observed a glass transition temperature (T_g) of 121 °C and 191 °C for **TPO** and **BTPO**, respectively. Other compounds showed no obvious T_{g} . In addition, it should be noticed that there is no indication of melting in the DSC curve for BPPO. Their thermal decomposition temperatures ($T_{\rm d}$ s) are in the range 427–489 °C. The

results demonstrate that all compounds have excellent amorphous glass state stability. The ability to form morphologically stable and uniform amorphous films and good thermal stability should be beneficial to the device prepared by a vacuum-deposition method.

Crystal structure and optical properties

Single crystals of **TPO** suitable for X-ray crystallography were grown by layer-diffusion of hexane to their CH₂Cl₂ solution, and the X-ray single crystal determination provides an insight into structure-property relationships. As shown in Fig. 1(a), the phenyl rings a, b and the oxadiazole ring are almost coplanar with dihedral angles of only 13.4° and 3.0° , respectively. However, the central phenyl ring c and the five phenyl rings attached to it are not coplanar with dihedral angles of 48.6° , 50.2° , 64.9° , 66.4° and 67.8° , respectively. The

Table 1 The data of the optical and the thermal properties of the compounds

				λ^{abs}_{max}/nm		λ^{em}_{max}/nm			
Compounds	$T_{\rm g}/^{\circ}{\rm C}$	$T_{\rm m}/^{\circ}{\rm C}$	$T_{\rm d}/^{\circ}{\rm C}$	Solution	Film	Solution	Film	$\Phi_{\rm FL}$	
PPO TPO MPPO MTPO BPPO BTPO	 191	349 215 353 271 	452 465 427 447 489 476	301 305 308 312 313 317	301 306 309 313 313 313	367 376 370 376 375 381	376 380 383 384 379 390	0.91 0.77 0.85 0.88 0.77 0.87	

(a)

 $(b) \qquad (b) \qquad (b) \qquad (c) \\ (b) \\ (b) \\ (b) \\ (c) \\ (c)$

Fig. 1 Crystal structure (a) and the molecular packing pattern (b) of **TPO**. Hydrogen atoms are omitted for clarity.

steric interaction between the phenyl rings is so clearly evident that the molecules in the crystal lattice pack in a relatively loose way. Furthermore, from the molecular packing of **TPO** [Fig. 1(b)], we observed that the head (the phenyl rings a) of the molecule is oriented to the central phenyl ring c of the neighboring molecule with a relatively large dihedral angle 59.9°. It is evident that there is no π - π stacking in the solid state in the present **TPO** model compound. The result is consistent with the discussion in the optical properties.

The electronic absorption spectra of the compounds were examined in CHCl₃ (Fig. 2) and in the solid films. The data are listed in Table 1. In Fig. 2, two absorption bands are observed for all of the compounds. One band at about $\lambda_{max} = 240$ nm can be assigned to the π - π * transition of the phenyl ring, and another band at about $\lambda_{max} = 320$ nm can be assigned to



the π - π^* absorption of the oxadiazole skeleton. The remarkable increase in absorption intensity at shorter wavelength

We also examined the fluorescence spectra of the compounds in CHCl₃ (Fig. 3) and the solid films. The data are listed in Table 1. They all show the most emission in the ultraviolet (UV) region (below 400 nm), and the fluorescence quantum yields in CHCl₃ solution were measured to be more than 77% for all compounds using quinine in 1.0 M H₂SO₄ ($\Phi_{313} = 0.48$) as a calibration standard.³⁵ The values are very unusual for organic UV emitters. Furthermore, in the solid state, photoluminescence (PL) is also very high because the arrangement of the sterically crowded tetra- or pentaphenylphenyl polycycle provides satisfying effects on inhibiting molecular aggregation. Photoluminescence spectra of the materials in the films are only red-shifted by 4–13 nm compared to those in solution, indicating that the aggregation is suppressed.

Electrochemical properties

Fig. 4 shows the reduction cyclic voltammograms of the compounds and the data are listed in Table 2. They all exhibit good reversible cathodic reduction couples at about $-2.0 \text{ V} (E_{1/2})$, and compounds **BPPO** and **BTPO** show extra



Fig. 2 Normalized electronic absorption (at the maximum of the longest wavelength) of the compounds in CHCl₃.



Fig. 3 Normalized fluorescence emission spectra of the compounds in CHCl₃.



Fig. 4 Cyclic voltammograms of all compounds (1 mM) in 0.1 M Bu_4NPF_6 -THF, scan rate 50 mV s⁻¹.

Compounds	${E_{1/2}}^{1/2}$ /V	${E_{1/2}}^{2/}$ V	$E_{\rm red}^{\rm onset}$ /V	$E_{\rm HOMO}/eV$	$E_{ m LUMO}/eV$	$\frac{E_{\rm g}}{{ m eV}}$
PPO TPO MPPO MTPO BPPO BTPO	-2.07 -1.96 -2.14 -2.04 -2.07 -1.94	-2.39 -2.23	-1.98 -1.90 -2.08 -1.96 -2.01 -1.88	-5.92 -5.94 -5.73 -5.83 -5.76 -5.83	-2.23 -2.31 -2.13 -2.25 -2.20 -2.33	3.69 3.63 3.60 3.58 3.56 3.50

reduction couples at -2.39 and -2.23 V, respectively. This result suggests that these materials may have good charge transport properties. We observed that the reduction value of PPO, MPPO, and BPPO shifts more negative than that of TPO, MTPO, and BTPO. This phenomenon may come from the better symmetry and stability of PPO, MPPO, and BPPO. The difference in the effective conjugation as revealed in their absorption spectra might also cause the difference in their reduction potentials. Therefore, the series of pentaphenylphenyl oxadiazole derivatives are more difficult to be reduced than the series of tetraphenylphenyl ones. The energy levels of all compounds were calculated using the ferrocene (E_{FOC}) value of -4.8 eV^{36} as the standard, while the E_{FOC} was calibrated to be 0.59 V versus the Ag/AgCl electrode in a ferrocene solution. So the electron affinity (EA) (LUMO level) derived from the onset reduction potentials (EA = E_{red}^{onset} + 4.21 eV) are -2.20

to -2.33 eV. The observed reversible reductive process suggests that these compounds have a potential for electrontransporting properties. The value is higher in some sort than that of tris(8-hydroxyquinolinolato)aluminium (Alg₃) $(-2.85 \text{ eV})^{37}$ (the representative electron-transporting material). HOMO-LUMO gaps (Eg) of these compounds were calculated by the equation: $E_{\rm g} = 1240/\lambda_{\rm onset}$ eV, where the λ_{onset} denotes the onset of UV absorption, and the E_{g} values are over 3.5 eV (Table 2). Based on the LUMO energy levels and the band gaps, the HOMO levels of the compounds are between -5.73 and -5.94 eV. The values are lower than that of 4,4'-bis{4-[N-(1-naphthyl)-N-phenylamino]phenyl}biphenyl (NPB) (-5.46 eV) (the representative hole-transporting material).³⁷ It is very favorable for our device fabrication in the subsequent section. Furthermore, these materials have relatively high band gaps, which is very promising in the host materials of blue, green or red organic electrophosphorescent devices.

Electroluminescent properties

We explored the performance characteristics of the devices using these compounds as the host and FIrpic as the dopant. The data are listed in Table 3. As shown in Fig. 5a, the PL spectra of the thin films (host:FIrpic) show an emission at 480 nm with a shoulder emission at 500 nm which is consistent with the EL spectra (Fig. 5b) of the devices. From the EL spectra, no host emission at about 380 nm was observed which demonstrated complete energy transfer from the host to the dopant molecules. The emission from the dopant is similar to the previous reports.^{20,21} In addition, an undesired weak emission of the hole-transporting material NPB was observed at about 420 nm, which indicates that the devices need to be further optimized. The current-voltage-luminance (I-V-L) characteristics and the external quantum efficiency versus current density characteristics of the devices are shown in Fig. 6a and 6b, respectively. Obviously, the best performance was achieved for the device using BTPO as the host material with a maximum luminance of 4484 cd m⁻² and an external quantum efficiency of 6.20%. The result can be attributed to the lower energy barrier of electron injection compared with those of other compounds (the lowest LUMO level of BTPO in these compounds is show in Table 2). Further optimization of the devices such as varying the thickness of the layers, adopting a hole-blocking layer material other than 2,9dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP), substituting FIrpic with other blue emitters, or modifying the electrode to enhance the electron/hole-injection to realize more efficient energy transfer from host to dopant, eliminating other

Table 3 EL data of the devices. L_{max} = maximum luminance, $\eta_{\text{c.max}}$ = maximum current efficiency, $\eta_{\text{ext, max}}$ = maximum external quantum efficiency.

Compounds	Turn-on voltage/V	Peak position/nm	$L_{\rm max}$ /cd m ⁻² , voltage/V	$\eta_{\rm c.max}/{\rm cd}~{\rm A}^{-1}$	$\eta_{\rm ext,max}$ (%)	CIE x, y
РРО	4.82	481	5113, 15.0	5.02	2.61	0.18, 0.37
ТРО	4.97	481	3749, 17.0	4.00	2.08	0.18, 0.37
MPPO	4.97	481	4136, 16.0	7.71	4.00	0.20, 0.38
MTPO	4.83	483	5999, 16.0	10.8	5.59	0.19, 0.42
BPPO	4.68	481	2846, 15.5	6.72	3.49	0.18, 0.34
BTPO	4.19	484	4484, 14.0	11.9	6.20	0.19, 0.44



Fig. 5 The PL spectra of the thin films (host:FIrpic) and the EL spectra of the devices.

emission thus increasing the device performance and realizing pure blue emission will be further pursued in future studies. Furthermore, these materials would be good UV emitters for their high band gaps and high fluorescence quantum yields, and the work will be reported in the future.

Conclusions

In summary, a new series of polyphenylene-dendronized oxadiazole derivatives has been synthesized via an easy synthetic procedure with high yields. Analysis of the single crystal structure of the model compound shows that it is very efficient to prevent the π - π aggregation by introducing the polyphenylphenyl to the materials. In addition, the materials have high thermal properties and relatively high band gaps of over 3.5 eV. They all show the most emissions in the UV region and have high fluorescence quantum yields. Blue electrophosphorescent devices fabricated using these materials as host materials and FIrpic as the dopant show very high efficiencies. The best device performance was achieved with a maximum luminance of 4484 cd m⁻² and an external quantum efficiency of 6.20% under ambient conditions. We set up a new alternative approach to the design of stable and efficient ultraviolet-emitting materials and host



Fig. 6 Luminance *versus* applied electric field characteristics of the devices, the inset shows current density *versus* applied electric field characteristics (a) and external quantum efficiency *versus* current density characteristics of the devices (b).

materials with a high band gap for blue, green or red electrophosphorescent devices.

Experimental

Materials and instruments

Trimethylsilylacetylene, phenylacetylene and tetraphenylcyclopentadienone were purchased from Acros, and used as received. THF and triethylamine (TEA) was distilled from sodium-benzophenone under a nitrogen atmosphere. N,N'dicarbazolyl-4,4'-biphenyl (CBP) and BCP were purchased from Acros. Alq₃,³⁸ NPB,³⁹ FIrpic⁴⁰ were prepared by published methods. NPB, CBP, Alq₃ and FIrpic were purified by sublimation prior to use. All reactions were carried out under a nitrogen atmosphere.

¹H NMR and ¹³C NMR spectra were obtained on a Bruker DMX 300 or 400 NMR Spectrometer. ¹H and ¹³C chemical shifts are reported in ppm downfield from a tetramethylsilane (TMS) reference, using the residual protonated solvent resonance as an internal standard. The UV-Vis and fluorescence spectra were obtained on a Hitachi U-3010 and Hitachi F-4500 spectrometer, respectively. MS (MALDI-TOF-MS) were performed on a Bruker BIFLEX III Mass Spectrometer. Elemental analyses were carried out on a Carlo-Erba 1160 elemental analyzer. TGA was carried out using a Perkin-Elmer thermogravimeter (Model TGA7) under a dry nitrogen gas flow at a heating rate of 10 °C min⁻¹. T_g and melting temperatures (T_m) were determined by DSC at a heating rate of 10 °C min⁻¹ using a Perkin-Elmer differential scanning calorimeter (DSC7).

2-(4-Iodophenyl)-5-phenyl-[1,3,4]oxadiazole (1a). Yield: 80%. EI: m/z 348 (M⁺); ¹H NMR (CDCl₃, 300 MHz): δ = 8.14 (d, J = 7.0 Hz, 2H), 7.91 (d, J = 8.6 Hz), 7.86 (d, J = 8.6 Hz), 7.55 (d, J = 6.5 Hz, 3H).

2-(4-Iodophenyl)-5-(4-methoxyphenyl)-[1,3,4]oxadiazole (1b). Yield: 85%. EI: *m*/*z* 378 (M⁺); ¹H NMR (CDCl₃, 300 MHz): $\delta = 8.07$ (d, J = 9.0 Hz, 2H), 7.88 (d, J = 8.6 Hz, 2H), 7.84 (d, J = 7.0 Hz, 2H), 7.04 (d, J = 9.0 Hz, 2H), 3.88 (s, 3H).

2,5-Bis-(4-iodophenyl)-[1,3,4]oxadiazole (1c). Yield: 78%. EI: m/z 474 (M⁺); ¹H NMR (CDCl₃, 300 MHz): δ = 7.91 (d, J = 8.5 Hz, 4H), 7.86 (d, J = 8.6 Hz, 4H).

2-Phenyl-5-(4-ethynylphenyl)-[1,3,4]oxadiazole (2a). Compound 1a (696 mg, 2.0 mmol) and trimethylsilylacetylene (0.3 mL, 2.2 mmol) in a solution of THF (20 mL) and TEA (20 mL) were stirred at room temperature overnight under a nitrogen atmosphere with the catalyst CuI (38 mg, 0.2 mmol) and Pd(PPh₃)₂Cl₂ (70 mg, 0.1 mmol). The reaction mixture was poured on a silica pad and eluted with CH₂Cl₂. The solvent was removed, and the residue was dissolved in a mixture of 40 mL CH₂Cl₂-CH₃OH (1 : 1) and K₂CO₃ (1.38 g, 20 mmol). The reaction mixture was stirred for one hour at room temperature and then 50 mL of ethyl acetate was added. The mixture was washed with water, brine and dried with anhydrous magnesium sulfate. After removal of the solvent, a pale yellow solid 443 mg was obtained in 90% yield. EI: m/z 246 (M⁺); ¹H NMR (CDCl₃, 300 MHz): $\delta = 8.13$ (t, 4H), 7.65 (d, J = 8.2 Hz, 2H), 7.51–7.56 (m, 3H), 3.26 (s, 1H).

2-Phenyl-5-(4-phenylethynyl)phenyl-[1,3,4]oxadiazole (3a). A flame-dried flask with a magnetic stirrer was loaded with 1a (696 mg, 2 mmol), Pd(PPh₃)₂Cl₂ (70 mg, 0.1 mmol), and CuI (38 mg, 0.2 mmol). Under a nitrogen atmosphere, dry THF (20 mL) and TEA (20 mL) were added, and the mixture was stirred for 20 min, yielding a yellow transparent solution. Phenylacetylene (0.24 mL, 2.2 mmol) was added *via* a syringe and the reaction mixture was stirred vigorously for 18 h at 50 °C. After removal of the solvent, the residue was purified by flash column chromatography using CH₂Cl₂ as the eluent affording a pale yellow solid (618 mg, 96%). EI: *m/z* 322 (M⁺); ¹H NMR (CDCl₃, 300 MHz): $\delta = 8.13-8.17$ (m, 4H), 7.70 (d, J = 8.4 Hz, 2H), 7.55–7.60 (m, 5H), 7.38 (t, 3H).

2-Phenyl-5-[4-(2,3,4,5-tetraphenyl)phenyl]phenyl-[1,3,4]oxadiazole (TPO). A mixture of compound 2a (246 mg, 1.0 mmol) and tetraphenylcyclopentadienone (422 mg, 1.1 mmol) in *m*-xylene (10 mL) was stirred at 150 °C for 12 h under nitrogen atmosphere. The solvents were evaporated *in vacuo* and the resulting solid purified by column chromatography on silica gel using a mixture of CH₂Cl₂-petroleum ether (1 : 2) as the eluent. The product, 567 mg, was obtained as a white solid in 94% yield. MS (MALDI-TOF): *mlz* 603.1 (M⁺); ¹H NMR (CDCl₃, 300 MHz): $\delta = 8.13$, 8.11 (dd, $J_1 = 7.9$ Hz, $J_2 = 1.5$ Hz, 2H), 7.95 (d, J = 8.5 Hz, 2H), 7.61 (s, 1H), 7.50–7.54 (m, 3H), 7.34 (d, J = 8.2 Hz, 2H), 7.18 (brs, 5H), 6.78–6.97 (m, 15H). ¹³C NMR (CDCl₃, 75 MHz): $\delta = 164.5$, 164.4, 145.4, 142.0, 141.4, 141.0, 140.0, 139.7, 139.5, 139.2, 131.6, 131.4, 131.0, 130.6, 129.9, 129.0, 127.6, 127.1, 126.9, 126.8, 126.7, 126.4, 126.2, 125.9, 125.7, 125.4, 123.9, 121.7. Elemental analysis (%) calcd for: C₄₄H₃₀N₂O C 87.68, H 5.02, N 4.65; found: C 87.28, H 5.08, N 4.77.

2-Phenyl-5-[4-(2,3,4,5,6-pentaphenyl)phenyl]phenyl-[1,3,4]oxadiazole (PPO). Compound 3a (322 mg, 1.0 mmol), tetraphenylcyclopentadienone (422 mg, 1.1 mmol), and 10 mL of diphenyl ether were deoxygenated and then heated to reflux overnight under nitrogen atmosphere. After being cooled to room temperature, the diphenyl ether was removed under reduced pressure and the residue was purified by column chromatography using CH₂Cl₂ as the eluent affording a pale yellow solid, which was further purified by recrystallization from methanol-CH₂Cl₂ to give a white powder (624 mg, 92%). MS (MALDI-TOF): m/z 679.6 (M⁺+1); ¹H NMR (CDCl₃, 300 MHz): δ = 8.06, 8.04 (dd, J_1 = 1.8 Hz, J_2 = 7.8 Hz, 2H), 7.66 (d, J = 8.3 Hz, 2H), 7.48 (m, 3H), 7.02 (d, J = 8.2 Hz, 2H), 6.85 (brs, 25H). ¹³C NMR (CDCl₃, 100 MHz): $\delta = 164.5$, 164.1, 144.7, 140.8, 140.4, 140.2, 140.1, 140.0, 139.0, 131.9, 131.4, 131.2, 128.8, 126.7, 126.6, 126.5, 125.4, 125.2, 123.8, 120.5. Elemental analysis (%) calcd for: C₅₀H₃₄N₂O C 88.47, H 5.05, N 4.13; found: C 88.37, H 5.09, N 4.34.

2-(4-Methoxy)phenyl-5-(4-ethynyl)phenyl-[1,3,4]oxadiazole (**2b).** The procedure is analogous to that described for **2a** (yield: 90%). EI: m/z 276 (M⁺); ¹H NMR (CDCl₃, 300 MHz): $\delta = 8.06-8.10$ (m, 4H), 7.64 (d, J = 8.1 Hz, 2H), 7.03 (d, J = 8.7 Hz, 2H), 3.90 (s, 3H), 3.25 (s, 1H).

2-(4-Methoxy)phenyl-5-(4-phenylethynyl)phenyl-[1,3,4]oxadiazole (3b). The procedure is analogous to that described for **3a** (yield: 97%). EI: m/z 352 (M⁺); ¹H NMR (CDCl₃, 300 MHz): $\delta = 8.11$ (t, J = 8.3 Hz, 4H), 7.68 (d, J = 8.3 Hz, 2H), 7.57 (q, 2H), 7.38 (t, 3H), 7.05 (d, J = 8.8 Hz, 2H), 3.90 (s, 3H).

2-(4-Methoxy)phenyl-5-[4-(2,3,4,5-tetraphenyl)phenyl]phenyl-[1,3,4]oxadiazole (MTPO). The procedure is analogous to that described for **TPO** (yield: 95%). MS (MALDI-TOF): *m/z* 633.2 (M⁺),¹H NMR (CDCl₃, 300 MHz): δ = 8.04 (d, *J* = 8.7 Hz, 2H), 7.92 (d, *J* = 8.1 Hz, 2H), 7.60 (s, 1H), 7.32 (d, *J* = 8.2 Hz, 2H), 7.17 (brs, 5H), 7.00 (d, *J* = 8.7 Hz, 2H), 6.78–6.94 (m, 15H) 3.86 (s, 3H). ¹³C NMR (CDCl₃, 75 MHz): δ = 164.4, 164.1, 162.3, 145.2, 142.0, 141.4, 141.0, 140.0, 139.7, 139.5, 139.3, 131.4, 131.1, 130.6, 129.9, 128.6, 127.6, 127.1, 127.0, 126.7, 126.4, 126.1, 125.9, 125.7, 125.4, 121.8, 116.4, 114.4, 55.4. Elemental analysis (%) calcd for: C₄₅H₃₂N₂O₂ C 85.42, H 5.10, N 4.43; found: C 85.44, H 5.22, N 4.59. **2-(4-Methoxy)phenyl-5-[4-(2,3,4,5,6-pentaphenyl)phenyl]phenyl-[1,3,4]oxadiazole (MPPO).** The procedure is analogous to that described for **PPO** (yield: 95%). MS (MALDI-TOF): *m*/*z* 709.0 (M⁺ + 1); ¹H NMR (CDCl₃, 300 MHz): δ = 7.97 (d, *J* = 8.6 Hz, 2H), 7.64 (d, *J* = 8.0 Hz, 4H), 6.99 (t, *J* = 8.5 Hz, 4H), 6.85 (brs, 25H), 3.86 (s, 3H). ¹³C NMR (CDCl₃, 100 MHz): δ = 164.0, 162.1, 144.5, 140.7, 140.4, 140.2, 140.1, 140.0, 139.0, 131.9, 131.2, 128.4, 126.7, 126.5, 125.4, 125.2, 125.0, 120.6, 116.4, 114.3, 55.3. Elemental analysis (%) calcd for: C₅₁H₃₆N₂O₂ C 86.41, H 5.12, N 3.95; found: C 86.74, H 5.24, N 3.96.

2,5-Bis-(4-ethynyl)phenyl-[1,3,4]oxadiazole (2c). The procedure is analogous to that described for **2a** (yield: 94%). EI: m/z 270 (M⁺); ¹H NMR (CDCl₃, 300 MHz): δ = 8.11 (d, *J* = 8.1 Hz, 4H), 7.66 (d, *J* = 8.2 Hz, 4H), 3.27 (s, 2H).

2,5-Bis-(4-phenylethynyl)phenyl-[1,3,4]oxadiazole (3c). The procedure is analogous to that described for **3a** (yield: 90%). EI: m/z 422 (M⁺); ¹H NMR (CDCl₃, 300 MHz): ¹H NMR (CDCl₃, 300 MHz): δ = 8.15 (d, J = 8.3 Hz, 4H), 7.70 (d, J = 8.2 Hz, 4H), 7.57 (q, 5H), 7.38 (t, 7H).

2,5-Bis-[4-(2,3,4,5-tetraphenyl)phenyl]phenyl-[1,3,4]oxadiazole (BTPO). The procedure is analogous to that described for **TPO** (yield: 93%). MS (MALDI-TOF): m/z 983.4 (M⁺); ¹H NMR (CDCl₃, 300 MHz): δ = 7.92 (d, J = 8.1 Hz, 4H), 7.60 (s, 2H), 7.32 (d, J = 8.2 Hz, 4H), 7.18 (brs, 10H), 6.79–6.96 (m, 30H). ¹³C NMR (CDCl₃, 75 MHz): δ = 164.4, 145.3, 142.0, 141.4, 141.0, 139.7, 139.5, 139.2, 131.4, 131.0, 130.6, 129.9, 127.6, 127.1, 126.9, 126.7, 126.4, 126.2, 125.9, 125.7, 125.4, 121.7. Elemental analysis (%) calcd for: C₇₄H₅₀N₂O C 90.40, H 5.13, N 2.85; found: C 90.18, H 5.22, N 3.17.

2,5-Bis-[4-(2,3,4,5,6-pentaphenyl)phenyl]phenyl-[1,3,4]oxadiazole (BPPO). The procedure is analogous to that described for **PPO** (yield: 90%). MS (MALDI-TOF): m/z 1135.4 (M⁺+1); ¹H NMR (CDCl₃, 300 MHz): δ = 7.54 (d, J = 8.2 Hz, 4H), 6.95 (d, J = 8.2 Hz, 4H), 6.83 (brs, 50H), 6.79–6.96 (m, 30H). ¹³C NMR (CDCl₃, 100 MHz): δ =164.3, 144.7, 140.9, 140.1, 139.2, 132.0, 131.3, 132.0, 131.3, 126.8, 126.6, 125.6, 125.3, 125.2, 120.6 ; Elemental analysis (%) calcd for: C₈₆H₅₈N₂O C 90.97, H 5.15, N 2.47; found: C 91.10, H 5.22, N 2.90.

Cyclic voltammetry (CV) measurements

Cyclic voltammetric measurements were carried out in a conventional three-electrode cell using a glass carbon working electrode, a platinum wire counter electrode, and a Ag/AgCl reference electrode on a computer-controlled EG&G Potentiostat/Galvanostat model 283 at room temperature. Freshly distilled THF was used to prepare a solution of all compounds (1 mM) containing Bu₄NPF₆ (0.1 M) as a supporting electrolyte. A ferrocenium/ferrocene couple ($E_{1/2} = 0.59$ V) was employed as the internal reference. The glass carbon working electrode was polished before each experiment with a 0.05 µm alumina paste, N₂ bubbling was used to remove oxygen from the electrolyte solutions in the electrochemical cell.

LEDs fabrication and measurements

The substrates were indium tin oxide (ITO) coated glass with a sheet resistance of 20 Ω square⁻¹. The ITO-coated glass substrates were etched, patterned, and washed with detergent. deionized water, acetone, and ethanol in turn. The multilayered devices of configuration ITO/NPB (20 nm)/CBP (20 nm)/Host:FIrpic (3 ~ 6%) (40 nm)/BCP (20 nm)/Alq₃ (5 nm)/LiF (1 nm)/Al (100 nm) were fabricated, where NPB, CBP, BCP, and Alq₃ serve as the hole-transporting layer, the second hole-transporting layer, the hole-blocking layer, and the electron transport layer, respectively, LiF/Al acts as the cathode. The materials used as the emission and electrontransporting layers and all organic layers were successively deposited onto the ITO/glass substrates at a pressure of 3×10^{-4} Pa. The active area of the devices was about 5 mm². All device testing was carried out under an ambient atmosphere at room temperature. EL spectra of LEDs were recorded on a Hitachi F-4500 spectrophotometer. Current-voltage characteristics for the LEDs were measured with a PA meter/DC voltage source (HP4140B). The EL light output was recorded by a NewPort 2835-C multifunction optical meter.

X-Ray structure analysis

The single crystals of **TPO** were obtained from $CH_2Cl_{2^{-1}}$ hexane solutions and the data were collected on a Rigaku R-Axis Rapid IP diffractometer with graphite-monochromated Mo-K α radiation. Data were processed on a personal computer (PC) using the SHELXL-97 software package.⁴¹ The structure was solved by direct methods. All non-hydrogen atoms were refined anisotropically.

Selected crystal data of **TPO**: $C_{44}H_{30}N_2O$, M = 602.70, crystal dimensions $0.306 \times 0.156 \times 0.07$ mm, triclinic, a = 9.405(3), b = 10.934(4), c = 17.343(6) Å, $\alpha = 84.339(5)$, $\beta = 86.416(6)$, $\gamma = 70.879(5)^{\circ}$, U = 1676.0(10), T = 294 K, space group $P\bar{1}$, Z = 2, $D_c = 1.194$ g cm⁻³, F(000) = 636, 8252 reflection collected, 5833 independent ($R_{int} = 0.0316$), which were used in all calculations. The final wR(F2) was 0.1667 (all data). CCDC reference number 290529. For crystallographic data in CIF or other electronic format see DOI: 10.1039/ b705515c.

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