Nondoped Deep-Blue Organic Light-Emitting Diodes with Color Stability and Very Low Efficiency Roll-Off: Solution-Processable Small-Molecule Fluorophores by Phosphine Oxide Linkage

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Abstract: A series of solution-processable small molecules PO1-PO4 were designed and synthesized by linking Nphenylnaphthalen-1-amine groups to a phenyl phosphine oxide core through a π -conjugated bridge, and their thermal, photophysical, and electrochemical properties were investigated. The phosphine oxide linkage can disrupt the conjugation and allows the molecular system to be extended to enable solution processability and high glass transition temperatures (159-181 °C) while preserving the deep-blue emission. The noncoplanar molecular structures resulting from the trigonal-pyramidal configuration of the phosphine oxide can suppress intermolecular interactions, and thus these compounds exhibit strong deep-blue emission both in solution and the solid state with high photoluminescent quantum vield

Keywords: electrochemistry · electroluminescence · fluorescence · light-emitting diodes · phosphine oxides

(PLOY) of 0.88-0.99 in dilute toluene solution. Solution-processed nondoped organic light-emitting diodes featuring PO4 as emitter achieve a maximum current efficiency of $2.36 \text{ cd } \text{A}^{-1}$ with CIE coordinates of (0.15, 0.11) that are very close to the NTSC blue standard. Noticeably, all devices based on these small-molecular fluorescent emitters show striking deep-blue electroluminescent color stability and extremely low efficiency roll-off.

Introduction

Since the pioneering work on organic light-emitting diodes (OLEDs) by the Kodak^[1] and Cambridge groups,^[2] OLEDs have attracted considerable scientific and industrial attention because of their applications in flat-panel displays and solid-state lighting.^[3-12] Full-color displays require primary RGB emission of relatively equal stability, efficiency, and color purity. It is critical to develop highly efficient deepblue emission, which is defined as having blue electroluminescent (EL) emission with a CIE y coordinate of less than 0.15, because such emitters can not only effectively reduce the power consumption of a full-color OLED, but also be utilized to generate light of other colors by energy cascade to a lower-energy fluorescent or phosphorescent dopant.^[13-15] However, the performance of blue LEDs is

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often inferior to that of green and red counterparts because of the intrinsic wide bandgap of blue-emitting materials, which makes it hard to inject charges into the emitting layer.

To obtain high efficiency, phosphorescent emitters have aroused intensive interest, as they have the ability to boost the internal quantum efficiency to 100%.[16] However, the difficulties of synthesizing applicable large-bandgap dopants and host materials make blue phosphorescent systems less desirable than their fluorescent counterparts, and only a few deep-blue phosphorescent emitters with a CIE coordinate of y < 0.15 have been reported.^[17–20] Therefore, deep-blue OLEDs mainly focus on fluorescent emitters, and extensive research has been carried out to develop high-performance deep-blue fluorophores.

Commonly, thermal high-vacuum evaporation technology is used for fabrication of small molecule based OLEDs (SMOLEDs), and solution processing technology for polymer-based devices (PLEDs). The vapor deposition techniques enable complicated multilayer device architectures and give excellent devices with high efficiencies.^[21-22] However, thermal evaporation deposition has critical drawbacks including high manufacturing costs and low utilization of the expensive materials.^[23] Although solution processing limits fabrication of composite device structures because the solvent used for one layer can redissolve or damage the previous layers,^[24] it is advantageous over thermal evaporation processing in terms of its low-cost and large-area manufac-

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turing.^[25] Compared with light-emitting polymers, small molecules have advantages such as precise molecular structure and excellent chemical purity, which may greatly impact efficiency and stability of the OLEDs. Therefore, it would be a good strategy to develop SMOLEDs via a solution process.

A number of solution-processed small molecules have been reported as blue electroluminescent materials.^[26-37] However, deep-blue fluorescent SMOLEDs fabricated by spin-coating with stable color coordinates and high efficiency remain rare. It is not easy to design a small molecule that has both deep-blue emission and solution processability. Solution processability usually requires large enough molecule size, while the molecular conjugation system should not be too extended to ensure the deep-blue emission of the materials.

In this work, we designed and synthesized a series of solution-processable small molecules with phenyl phosphine oxide core and N-phenylnaphthalen-1-amine groups as end caps. The deep-blue emission of these emitters can be wellpreserved due to disruption of conjugation by the phosphine oxide linkage, even though the molecular size is enlarged. Introduction of the electron-withdrawing phosphine oxide can also improve the electron-transporting ability of the materials. Moreover, the existence of the phosphine oxide group results in a trigonal-pyramidal structure, which could effectively hinder close molecular packing in the solid state and prevent excimer formation and fluorescence quenching. All of these compounds show high fluorescence quantum yields in solution when using 9,10-diphenylanthracene (DPA) as standard. We fabricated simple double-layer devices that achieve efficient deep-blue performance of $2.36 \text{ cd } A^{-1}$ (2.06%) with CIE coordinate of (0.15, 0.11). Moreover, all devices based on these materials show excellent color stability and extremely low efficiency roll-off.

Results and Discussion

Synthesis and characterization: The synthetic routes and chemical structures of PO1-PO4 are depicted in Scheme 1. Key intermediates 1-3 were prepared from 1,4-dibromobenzene, 4,4'-dibromobiphenyl, and 2,7-dibromo-9,9-diethyl-9Hfluorene, respectively, by sequential lithium-halogen exchange with *n*BuLi, coupling with dichlorophenylphosphine, and oxidation with hydrogen peroxide. Compounds 4, 5 and 2,7-dibromo-9,9-diethyl-9H-fluorene were prepared by following reported procedures.^[38-41] Lithiation of 5 with an excess of *n*BuLi followed by treatment with trimethyl borate and hydrolysis in aqueous HCl gave 9,9-diethyl-7-[1naphthyl(phenyl)amino]-9H-fluoren-2-ylboronic acid (6). Target compounds PO1-PO4 were prepared by Suzuki cross-coupling reactions in yields of about 70%. All compounds were fully characterized by ¹H NMR, ¹³C NMR, MALDI-TOF MS, and elemental analysis.

Thermal properties: The good thermal stability of the compounds is indicated by their high decomposition tempera-



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Figure 1. TGA thermograms of **PO1–PO4** recorded at a heating rate of 10°Cmin⁻¹. Inset: DSC traces recorded at a heating rate of 10°Cmin⁻¹.

tures (T_d , corresponding to 5% weight loss) in the range of 478-555°C in the thermogravimetric analysis (Figure 1). Though PO3 and PO4 have rigid fluorene structures and higher molecular weights than PO1 and PO2, the former pair has lower T_d values than the latter. This can be attributed to decomposition of the ethyl substituents at the 9-position of fluorene rings of PO3 and PO4. Their glass transition temperatures $T_{\rm g}$, determined by differential scanning calorimetry, are between 159 and 181 °C (inset in Figure 1), which are much higher than that of 1,4-bis[(1-naphthylphenvl)amino]biphenvl (NPB, 98°C).^[42] The enhanced thermal stability may be due to the presence of the phosphine oxide group. The trigonal-pyramidal structure can cause a more crowded arrangement of the aryl groups around the P atom, prevent intermolecular packing, and improve the stability of the amorphous morphology against crystallization. The T_{g} order of PO1 < PO2, PO3 < PO4 could be attributable to the increased molecular size and molecular weight. The excellent thermal and morphological stability of these materials enables preparation of homogeneous and stable amorphous thin films through solution processing, which is crucial for operation of OLEDs.

Photophysical properties: Figure 2 shows the absorption and fluorescence spectra of **PO1–PO4** in the film state. The photophysical data of the compounds are presented in Table 1. The absorption band in the region from 270 to 310 nm can



Figure 2. UV/Vis absorption and PL spectra of PO1-PO4 in film state.



Scheme 1. Synthesis of **PO1–PO4**. a) *n*BuLi, THF, dichlorophenylphosphine, -78 °C; b) 30% H₂O₂, CH₂Cl₂; c) [Pd(PPh₃)₄], toluene, ethanol, 2M Na₂CO₃, reflux; d) i) *n*BuLi, THF, trimethyl borate, -78 °C, ii) 2M HCl, 0 °C.

be attributed to the π - π^* transition of the terminal functional aryl groups,^[43] while the absorption peaks around 355 nm for **PO1** and **PO2** and 375 nm for **PO3** and **PO4** are assigned to the π - π^* transition of the conjugated bridges between the electron-donating *N*-phenylnaphthalen-1-amine (NPA) moiety and the electron-accepting phenyl phosphine oxide (PPO) moiety. The emission maxima of the compounds in the film state, which range from 453 to 457 nm, exhibit only a small blueshift compared with those in dichloromethane solution, that is, intermolecular interactions do not occur in the solid state. The noncoplanar structure of these compounds effectively prevents close packing of constituent molecules and shields the intermolecular interactions. All of the blue emitters show relatively high photoluminescent quantum yield (PLQY) of 0.88–0.99 in dilute toluene solution with DPA ($\Phi = 0.90$) as calibration standard.

Electrochemical properties and DFT calculations: The electrochemical properties of the compounds were probed by cyclic voltammetry (CV, Figure 3). **PO1** and **PO2** exhibit irreversible oxidation waves, while **PO3** and **PO4** show reversible oxidation process. The oxidation wave around 0.5 eV could be attributed to oxidation of the terminal aryl groups, and the presence of fluorene units in **PO3** and **PO4** makes the oxidation process reversible. The HOMO energy levels estimated from the onsets of the oxidation potentials are in the range of 5.10–5.30 eV with respect to the energy level of ferrocene (4.8 eV below vacuum), which matches well with

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Table 1. Thermal, photophysical, and electrochemical data of PO1-PO4.

	PO1	PO2	PO3	PO4
$T_{\rm d}/T_{\rm g}$ [°C]	552/163	555/181	484/159	478/170
$\lambda_{abs}^{[a]}$ [nm]	279, 355	296, 354	284, 375	299, 382
$\lambda_{abs}^{[b]}$ [nm]	349	347	376	375
$(\varepsilon [M^{-1} cm^{-1}])$	(52000)	(63300)	(72700)	(84700)
$\lambda_{\rm em,max}^{[a]}$ [nm]	453	457	455	455
$\lambda_{\rm em,max}^{[b]}$ [nm]	466	471	464	466
HOMO ^[c] /LU-	5.26/2.30	5.24/2.28	5.14/2.21	5.11/2.23
$MO^{[d]}[eV]$				
$\Phi_{ ext{PL}}{}^{[e]}$	0.92 (0.35)	0.99 (0.49)	0.88 (0.46)	0.95 (0.49)

[a] Measured in film. [b] Measured in CH₂Cl₂. [c] Determined from the onset of oxidation potential. [d] Deduced from HOMO and E_g . [e] Fluorescence quantum yields in toluene solution were measured with 9,10-diphenylanthracene (Φ =0.90) as standard, and fluorescence quantum yields in solid-state films on a quartz plate by using an integrating sphere (in parentheses).



Figure 3. Cyclic voltammograms of PO1-PO4 in CH₂Cl₂ for oxidation.

that of 5.2 eV for poly(3,4-ethylenedioxythiopene):poly(styrene sulfonate) (PEDOT:PSS) and may result in efficient hole injection from PEDOT:PSS to the emissive layer. The band gaps E_g of **PO1–PO4**, estimated on the basis of the red edge of the longest absorption wavelength for the solidfilm sample, are 2.96–2.88 eV. The LUMO levels range from 2.21 to 2.30 eV, as deduced from the HOMO level and E_g (Table 1).

Density functional calculations [B3LYP; 6-31G(d)] were carried out to obtain a better understanding of the geometrical and electronic properties of the compounds. As depicted in Figure 4, HOMO and HOMO-1 of **PO1-PO4** are mainly



Figure 4. Calculated spatial distributions of the HOMO and LUMO levels of **PO1–PO4**.

located on terminal functional aryl groups, while LUMO and LUMO+1 are mainly distributed on the π -conjugated bridges. Considering the interchange between HOMO and HOMO-1 and between LUMO and LUMO+1 when the molecules vibrate, the HOMO and LUMO distributions for **PO1** and **PO2** and for **PO3** and **PO4** are similar. The terminal functional aryl groups have twisted configurations that result in a noncoplanar structure in each molecule, and all four molecules show trigonal-pyramidal structure.

Electroluminescence: To evaluate the EL performance of **PO1–PO4** as nondoped blue emitters, double-layer devices were fabricated with the configurations of indium tin oxide (ITO)/PEDOT:PSS (40 nm)/emission layer (EML, 40 nm)/1,3,5-tris(*N*-phenylbenzimidazol-2-yl)benzene (TPBI, 30 nm)/LiF (1 nm)/Al (100 nm), in which the emitter is **PO1** in device A, **PO2** in device B, **PO3** in device C, and **PO4** in device D, the emission layer was spin-coated from chlorobenzene solution on top of PEDOT:PSS, PEDOT:PSS and LiF served as hole- and electron-injecting layers, respectively, and TPBI was inserted between the EML and LiF as electron-transporting layer.

The devices based on these emitters exhibit deep-blue emission in their EL spectra with CIE coordinates of (0.15, 0.09) for device A, (0.15, 0.12) for device B, (0.15, 0.10) for device C, and (0.15, 0.11) for device D (Figure 5). The EL spectra of all materials show only slight blueshifts relative to the PL spectra of thin-film samples, which indicates that excimers or exciplexes are effectively suppressed during the EL process.

More importantly, these devices exhibit striking blue EL color stability at various driving voltages, as shown in Figure 5. With increasing driving voltage from 4 to 9 V, the EL spectra of all these devices remain nearly unchanged, and the CIE coordinates show only slight changes, and this suggests a remarkable voltage-independent and stable EL spectrum. The excellent color stability can be attributed to the noncoplanar conformation, which may suppress close packing of molecules in the solid state and improve the morphological stability by resisting crystallization and morphological transition induced deterioration during device operation.

Figure 6 shows the current density-voltage-brightness (J-V-L) characteristics, and efficiency versus current density curves of the devices, and the device data are summarized in Table 2. All of these devices display a low turn-on voltage around 4 V, which can be attributed to the small injection barriers in the devices. A schematic energy-level diagram of these devices is presented in Figure 7. The electron-injection barriers at the EML/TPBI junction are about 0.4–0.5 eV, while the hole injection barriers at the PEDOT:PSS/EML junction are smaller than 0.1 eV. These small injection barriers into the emission layer.

The best EL performance is achieved by **PO4** with a maximum current efficiency $\eta_{c,max}$ of 2.36 cd A⁻¹, a maximum power efficiency $\eta_{p,max}$ of 1.86 Lm W⁻¹, and a maximum ex-



Figure 5. Normalized EL spectra of devices a) A, b) B, c) C, and d) D recorded at various driving voltages.

ternal quantum efficiency $\eta_{\text{ext,max}}$ of 2.06%, which is comparable with the best device performances in the literature for solution-processed small-molecular nondoped deep-blue OLEDs.^[26-27,30,32-37] For example, Ma et al. reported fluorene-based small molecule TCPA-6, and fabricated a deep-blue device with $\eta_{\text{c,max}} = 1.35 \text{ cd A}^{-1}$ and CIE coordinates of (0.16, 0.05);^[26] Huang et al. reported pyrene-functioned fluorene 2PPPF and obtained a deep-blue emitting OLED with $\eta_{\text{c,max}} = 1.13 \text{ cd A}^{-1}$ and CIE coordinates of (0.16, 0.10);^[30] Park et al. obtained a deep-blue emitting OLED with



Figure 6. a) Current density–voltage–brightness (J-V-L) characteristics for devices A–D. b) Current efficiency and power efficiency. c) EQE versus current density curves for devices A–D.



Figure 7. Energy-level diagrams for devices A-D.

 $\eta_{c,max}$ =1.15 cd A⁻¹ and CIE coordinates of (0.159, 0.105) by utilizing anthracene-derived compound PCAN as emitter.^[34]

Notably, the efficiency of device D remains at 2.01% (2.32 cd A^{-1}) on increasing to the practical brightness of 100 cd m⁻². Even at a much higher brightness of 1000 cd m⁻², the external quantum efficiency is still 1.87% with a roll-off

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Table 2. Electroluminescence characteristics of the devices.

Device	$V_{ m on} [{ m V}]^{[a]}$	$L_{\rm max} [{\rm cd} {\rm m}^{-2}]^{[{\rm b}]}$, voltage [V]	$\eta_{\rm c} [{\rm cd} {\rm A}^{-1}]^{[{\rm c},{\rm f}]}$	$\eta_{\mathrm{p}}[\mathrm{lm}\;\mathrm{W}^{-1}]^{[\mathrm{d,f}]}$	$\eta_{\mathrm{ext}}[\%]^{[\mathrm{e,f}]}$	CIE $(x, y)^{[g]}$
A	4.1	5913, 9.1	1.78, 1.69, 1.76	1.11, 1.08, 0.91	1.79, 1.70, 1.77	0.15, 0.09
В	4.1	5892, 9.3	1.84, 1.79, 1.79	1.11, 1.06, 0.86	1.54, 1.50, 1.50	0.15, 0.12
С	4.1	4575, 9.1	1.72, 1.72, 1.67	1.19, 1.10, 0.86	1.66, 1.66, 1.61	0.15, 0.10
D	3.9	5650, 8.9	2.36, 2.32, 2.15	1.86, 1.55, 1.18	2.06, 2.01, 1.87	0.15, 0.11

[a] Turn-on voltage, recorded at a brightness of 1 cdm^{-2} . [b] Maximum luminance. [c] Current efficiency. [d] Power efficiency. [e] External quantum efficiency. [f] Order of measured values: maximum, then values at 100 and 1000 cdm⁻². [g] Measured at 7 V.

value of 9.2%. Although the other three devices showed inferior EL performance to the **PO4**-based device, they exhibit much lower efficiency roll-off. At a brightness of 1000 cdm⁻², the roll-off values of devices A, B, and C for η_{ext} are 1.1, 2.6, and 3.0%, respectively. The high efficiencies and low efficiency roll-off at high luminance for these devices can be attributed to the bipolar conformation of the emitters, which may result in balanced charge fluxes and a broadly distributed recombination region within the emitting layer.

Conclusion

We have designed and synthesized four deep-blue smallmolecule fluorescent emitters with solution processability. Theoretical calculations reveal that the blue emitters have noncoplanar structures resulting from the phosphine oxide core and peripheral functional aryl groups. The steric hindrance effectively suppresses close molecular packing in the solid state and prevents excimer formation and fluorescence quenching. Simple nondoped OLEDs based on spin coating of the new materials exhibit deep-blue electroluminescence. Moreover, all devices show excellent color stability, high efficiency, and very low roll-off. The PO4-based device achieves a maximum current efficiency of 2.36 cd A⁻¹ with CIE coordinates of (0.15, 0.11). Our findings provide a valuable strategy for the rational design and development of solution-processable deep-blue fluorescent materials for use in OLED displays.

Experimental Section

General information: ¹H NMR and ¹³C NMR spectra were measured on a Mercury-VX300 spectrometer. Elemental analyses of carbon, hydrogen, and nitrogen were performed on a Vario EL III microanalyzer. EI-MS spectra were recorded on VJ-ZAB-3F Mass spectrometer. MALDI-TOF mass spectra were recorded on a Bruker BIFLEX III TOF mass spectrometer. UV/Vis absorption spectra were recorded on a Shimadzu UV-2500 recording spectrophotometer. Photoluminescence spectra were recorded on a Hitachi F-4500 fluorescence spectrophotometer. The PL quantum yields of solid-state films were measured by an absolute method using the Edinburgh Instruments (FLS920) integrating sphere excited with an Xe lamp. Differential scanning calorimetry (DSC) was performed on a NETZSCH DSC 200 PC unit at a heating rate of 10°Cmin⁻¹ from room temperature to 400°C under argon. The glass transition temperature was determined from the second heating scan. Thermogravimetric analysis was performed with a NETZSCH STA 449C instrument. The

thermal stability of the samples under a nitrogen atmosphere was determined by measuring their weight loss while heating at a rate of 10°C min⁻¹ from 20 to 800 °C. Cyclic voltammetry (CV) was carried out in nitrogen-purged dichloromethane (oxidation scan) at room temperature with a CHI voltammetric analyzer. Tetrabutylammonium hexafluorophosphate (TBAPF₆) (0.1 M) was used as supporting electrolyte. The conventional three-electrode configuration consisted of a platinum working electrode, a platinum wire auxiliary electrode, and an Ag wire pseudoreference electrode with ferrocenium/ferrocene (Fc+/Fc) as internal standard. Cyclic voltammograms were obtained at scan rate of 100 mV s⁻¹. The onset potential was determined from the intersection of two tangents drawn at the rising and background current of the cyclic voltammogram. Device fabrication and measurement: The hole-injection material PE-DOT:PSS and electron-transporting material TPBI were commercially available. Commercial ITO-coated glass with sheet resistance of 10 Ω square⁻¹ was used as starting substrates. Before device fabrication, the ITO/glass substrates were precleaned carefully and treated with oxygen plasma for 2 min. PEDOT:PSS was spin-coated to smooth the ITO surface and promote hole injection, and then the emissive layer was spin-coated from chlorobenzene solution. The samples were annealed at 120°C for 30 min to remove residual solvent. The thickness of the EML was about 40 nm. Finally, an electron-transporting layer of TPBI (30 nm) and a cathode composed of lithium fluoride (LiF, 1 nm) and aluminum (Al, 100 nm) were sequentially deposited onto the substrate by vacuum deposition at 10⁻⁶ Torr. The J-V-L characteristics of the devices were measured with a Keithley 2400 Source meter and a Keithley 2000 Source multimeter equipped with a calibrated silicon photodiode. The electroluminescence (EL) spectra were measured on a JY SPEX CCD3000 spectrometer. The EQE values were calculated according to previously reported methods.^[44] All measurements were carried out at room temperature under ambient conditions.

Synthesis: 4'-[1-naphthyl(phenyl)amino]biphenyl-4-ylboronic acid (4),^[38-39] 7-bromo-9,9-diethyl-*N*-1-naphthyl-*N*-phenyl-9*H*-fluoren-2-amine (5),^[40] and 2,7-dibromo-9,9-diethyl-9*H*-fluorene^[41] were prepared by the following reported procedures.

Bis(4-bromophenyl)(phenyl)phosphine oxide (1): n-Butyllithium (2.4м in hexane, 7.9 mL, 19 mmol) was added dropwise to a solution of 1,4-dibromobenzene (4.72 g, 20 mmol) in anhydrous THF (160 mL) at -78 °C. The reaction mixture was kept at this temperature for 3 h, and then dichlorophenylphosphine (1.26 mL, 9.3 mmol) was added. The resulting mixture was stirred for a further 3 h at -78°C before quenching with 5 mL of methanol. Water was added, and the mixture was extracted with CH2Cl2, washed with water, and dried over anhydrous Na2SO4. After the solvent had been completely removed, 30% hydrogen peroxide (30 mL) and CH₂Cl₂ (60 mL) were added to the obtained residue and the mixture stirred overnight at room temperature. The organic layer was separated and washed with water and then brine. The extract was evaporated to dryness, and the residue was purified by column chromatography on silica gel with dichloromethane/methanol (30/1 v/v) as eluent to give a white solid in 70% yield (%). ¹H NMR (300 MHz, CDCl₃): $\delta = 7.68-7.58$ (m, 6H), 7.58–7.45 ppm (m, 7H); ¹³C NMR (75 MHz, CDCl₃): $\delta = 133.38$, 133.31, 132.35, 131.80, 131.77, 131.47, 131.12, 130.77, 130.43, 128.69, 128.60, 127.38, 127.36 ppm; MS (EI): *m*/*z* calcd for C₁₈H₁₃Br₂OP: 435.91, found: 435.83.

Bis(4'-bromobiphenyl-4-yl)(phenyl)phosphine oxide (2): Compound 2 was prepared in 67% yield according to a similar procedure to 1 by using 4,4'-dibromobiphenyl instead of 1,4-dibromobenzene. ¹H NMR

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(300 MHz, CDCl3): δ =7.82–7.71 (m, 6H), 7.68 (d, *J*=8.1 Hz 4H), 7.61 (d, *J*=8.7 Hz 4H), 7.54–7.45 ppm (m, 7H); ¹³C NMR (75 MHz, CDCl₃): δ =143.34, 138.52, 132.59, 132.52, 131.93, 131.70, 131.58, 130.88, 128.64, 128.50, 128.43, 126.82, 122.44 ppm; MS (EI): *m*/*z* calcd for C₃₀H₂₁Br₂OP: 587.97, found: 587.81.

Bis(7-bromo-9,9-diethyl-9H-fluoren-2-yl)(phenyl)phosphine oxide (3): Compound **3** was prepared in 81 % yield according to a similar procedure to **1** by using 2,7-dibromo-9,9-diethyl-9H-fluorene instead of 1,4-dibromobenzene. ¹H NMR (300 MHz, CDCl₃): δ =7.80–7.64 (m, 6H), 7.64–7.44 (m, 11 H), 1.99 (q, *J*=6.9 Hz 8H), 0.27 ppm (t, *J*=6.9 Hz 12 H); ¹³C NMR (75 MHz, CDCl₃): δ =152.54, 149.58, 149.50, 144.05, 138.95, 133.08, 132.39, 131.80, 131.21, 131.15, 131.08, 130.52, 130.12, 128.36, 128.28, 126.35, 126.28, 126.20, 122.36, 121.62, 119.38, 56.60, 32.28, 32.23, 8.37, 8.09 ppm; MS (EI): *m*/*z* calcd for C₄₀H₃₇Br₂OP: 724.09, found: 724.02.

 $4^{\prime\prime}, 4^{\prime\prime\prime} - (Phenylphosphoryl) bis (N-1-naphthyl-N-phenyl-1, 1^{\prime}: 4^{\prime}, 1^{\prime\prime} - terphenyl-1, 1^{\prime}: 4^{\prime}, 1^{\prime} - terphenyl-1, 1$ 4-amine) (PO1): Degassed toluene (18 mL) and ethanol (4 mL) were added to a mixture of compound 1 (0.305 g, 0.7 mmol), 4 (0.872 g, 2.1 mmol), Na2CO3 (2 м, 3.5 mL, 7 mmol), and [Pd(PPh3)4] (0.048 g, 0.042 mmol). The resulting mixture was stirred and heated to reflux at 100°C for 48 h under argon atmosphere. After cooling to room temperature, the solution was extracted with CH₂Cl₂ and the organic layer was washed with brine and water and then dried over anhydrous Na2SO4. After the solvent had been removed, the residue was purified by column chromatography on silica gel with dichloromethane/methanol (30/1 v/v) as eluent to give a yellow powder in 67% yield. ¹H NMR (300 MHz, CDCl₃): $\delta = 7.97$ (d, J = 7.8 Hz 2H), 7.92 (d, J = 6.9 Hz 2H), 7.83–7.69 (m, 12H), 7.68-7.59 (m, 8H), 7.54-7.42 (m, 9H), 7.42-7.33 (m, 4H), 7.27-7.18 (m, 6H), 7.09 ppm (t, J = 8.4 Hz 8H), 7.01–6.93 (m, 2H); ¹³C NMR $(75 \text{ MHz}, \text{ CDCl}_3): \delta = 148.36, 148.29, 144.54, 143.50, 140.78, 138.16,$ 135.56, 133.22, 132.94, 132.42, 131.48, 129.46, 128.90, 128.72, 127.83, 127.61, 127.25, 126.95, 126.79, 126.67, 126.49, 124.45, 122.60, 122.42, 121.72 ppm; elemental analysis calcd (%) for C₇₄H₅₃N₂OP: C 87.04, H 5.02, N 2.68; found: C 87.38, H 5.25, N 2.75; MALDI-TOF MS: m/z 1017.1.

4"",4""-(Phenylphosphoryl)bis(N-1-naphthyl-N-phenyl-1,1':4',1"':4'',1"''-quaterphenyl-4-amine) (**PO2**): **PO2** was prepared in 71 % yield according to a similar procedure to **PO1** by using **2** instead of **1**. ¹H NMR (300 MHz, CDCl₃): δ =7.98 (d, *J*=8.7 Hz, 2H), 7.92 (d, *J*=8.7 Hz, 2H), 7.92 (d, *J*=8.7 Hz, 2H), 7.92 (m, 25H), 7.61–7.42 (m, 12H), 7.42–7.34 (m, 4H), 7.28–7.18 (m, 6H), 7.18–7.02 (m, 8H), 7.01–6.95 ppm (m, 2H); ¹³C NMR (75 MHz, CDCl₃): δ =148.38, 148.26, 144.51, 143.59, 140.83, 140.20, 138.86, 138.74, 135.59, 133.55, 133.02, 132.90, 132.46, 132.34, 131.54, 129.44, 128.96, 128.71, 127.93, 127.80, 127.70, 127.57, 127.40, 127.20, 126.91, 126.75, 126.65, 126.47, 124.49, 122.56, 122.36, 121.83 ppm; elemental analysis calcd (%) for C₈₆H₆₁N₂OP: C 88.27, H 5.18, N 2.29; found: C 88.33, H 5.26, N 2.40; MALDI-TOF MS: *m/z* 1169.0.

N,N'-{(Phenylphosphoryl)bis[(9,9-diethyl-9H-fluorene-7,2-diyl)-4,1-phenylene]}bis(N-phenylnaphthalen-1-amine) (PO3): nBuLi (2.4м in hexane, 2.9 mL, 6.96 mmol) was added dropwise to a solution of 7-bromo-9,9-diethyl-N-1-naphthyl-N-phenyl-9H-fluoren-2-amine (5, 3.0 g, 5.8 mmol) in anhydrous THF (60 mL), at -78 °C. At this temperature, the reaction mixture was stirred for 1 h before adding trimethyl borate (0.97 mL, 8.7 mmol). After the mixture was stirred for 1 h at -78 °C, it was allowed to warm to room temperature, stirred overnight, quenched with HCl (50 mL, $2.0\,\ensuremath{\text{m}}\xspace$), and poured into a large amount of water. After extraction with diethyl ether three times, the organic portions were washed with brine before drying over anhydrous Na2SO4. The solvents were removed under reduced pressure, and boronic acid 6 was obtained (2.38 g 85%) yield). Degassed toluene (15 mL) and ethanol (4 mL) were added to a mixture of compound 1 (0.262 g, 0.6 mmol), boronic acid 6 (0.87 g, 1.8 mmol), Na₂CO₃ (2 м, 3 mL, 6 mmol), and [Pd(PPh₃)₄] (0.042 g, 0.036 mmol). The resulting mixture was stirred and heated to reflux at 100°C for 48 h under argon atmosphere. After cooling to room temperature, the solution was extracted with CH₂Cl₂ and the organic layer was washed with brine and water and then dried over anhydrous Na2SO4. After the solvent had been removed, the residue was purified by column chromatography on silica gel with dichloromethane/methanol (30/1 v/v)

as eluent to give **PO3** as a yellow powder in 69% yield (%); ¹H NMR (300 MHz, CDCl₃): δ = 7.95–7.87 (m, 4H), 7.83–7.71 (m, 10H), 7.68–7.40 (m, 16H), 7.38–7.30 (m, 4H), 7.24–7.18 (m, 5H), 7.10–7.04 (m, 6H), 6.99–6.91 (m, 4H), 1.79–2.00 (m, 8H), 0.355 ppm (t, *J*=7.2 Hz 12H); ¹³C NMR (75 MHz, CDCl₃): δ =151.56, 150.58, 148.68, 148.35, 145.23, 143.80, 141.71, 137.56, 135.27, 134.88, 132.65, 132.20, 131.92, 130.92, 129.08, 128.55, 128.35, 127.07, 126.73, 126.23, 126.04, 124.36, 121.96, 121.68, 121.35, 120.51, 119.29, 116.80, 56.11, 32.62, 8.50 ppm; elemental analysis calcd (%) for C₈₄H₆₉N₂OP: C 87.67, H 5.90, N 2.42; found: C 87.47, H 6.03, N 2.43; MALDI-TOF MS: *m/z* 1153.0.

7',7''-(*Phenylphosphoryl*)*bis*(9,9,9',9'-tetraethyl-N-1-naphthyl-N-phenyl-9H,9'H-2,2'-bifluoren-7-amine) (**PO4**): **PO4** was prepared in 64 % yield according to a similar procedure to **PO3** by using **3** instead of **1**. ¹H NMR (300 MHz, CDCl₃): δ =7.96 (d, *J*=8.1 Hz 2H), 7.91 (d, *J*=8.1 Hz 2H), 7.85–7.72 (m, 10H), 7.72–7.41 (m, 20H), 7.39–7.30 (m, 4H), 7.25–7.18 (m, 5H), 7.12–7.03 (m, 6H), 7.00–6.91 (m, 4H), 2.16–1.80 (m, 16H), 0.45–0.30 ppm (m, 24 H); ¹³C NMR (75 MHz, CDCl₃): δ =151.70, 151.64, 150.78, 149.03, 148.38, 145.40, 144.12, 142.28, 141.23, 139.45, 139.34, 135.54, 131.19, 129.36, 128.65, 127.02, 126.82, 126.58, 126.43, 126.33, 124.67, 122.10, 121.81, 121.64, 121.48, 121.00, 120.64, 119.45, 117.24, 56.89, 56.43, 32.99, 8.88 ppm; elemental analysis calcd (%) for C₁₀₆H₉₃N₂OP: C 88.61, H 6.42, N 1.87; found: C 88.30, H 6.50, N 1.94; MALDI-TOF: *m*/z 1441.1.

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Deep-blue small molecule fluorescent emitters with solution processsability were designed and synthesized by linking N-phenylnaphthalen-1-amine groups to a phenyl phosphine oxide core through a π -conjugated bridge. Solution-processed small molecule based organic light-emitting diodes featuring PO4 as emitter (see figure) achieve a maximum current efficiency of 2.36 cd A⁻¹ with CIE coordinates of (0.15, 0.11).



Electroluminescence -

C. Liu, Y. Gu, Q. Fu, N. Sun, C. Zhong, D. Ma,* J. Qin,

Nondoped Deep-Blue Organic Light-**Emitting Diodes with Color Stability** and Very Low Efficiency Roll-Off: Solution-Processable Small-Molecule Fluorophores by Phosphine Oxide Linkage

