Electronic Supplementary Information (ESI)

Bipolar homoleptic iridium dendrimer composed of diphenylphosphoryl and diphenylamine dendrons for highly efficient non-doped single-layer green PhOLEDs

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Experiments

1. Instrumental analysis

^{1}H NMR and ^{31}P NMR spectra were measured on a BRUKER AMX 300- or 500-MHz instrument at room temperature. ^{31}P NMR spectra were referenced to external 85% H_3PO_4 (0 ppm). Molecular masses were determined by electrospray ionization-mass spectrometry (ESI-MS) using a FINNIGAN LCQ instrument, or matrix-assisted laser desorption-ionization time-of-flight mass spectrometry (MALDI-TOF-MS) using a BRUKER DALTONICS instrument, with α-cyano-hydroxycinnamic acid as a matrix. Elemental analyses were performed on a Vario EL Ⅲ elemental analyzer. Absorption and photoluminescence emission spectra of the target compound were measured using a SHIMADZU UV-2450 spectrophotometer and a HORIBA FLUOROMAX-4 spectrophotometer, respectively. The solution PL quantum efficiency was measured by a relative method using $(ppy)_2Ir(acac)$ ($\Phi_p = 0.34$ in 2-methyltetrahydrofuran) as the standard in degassed DMSO solutions. The film PL quantum efficiency was measured with an integrating sphere under an excitation wavelength of 370 nm. The integrating sphere was purged with flowing nitrogen during the whole measuring process.[1] Phosphorescence spectra at 77 K were measured in a dichloromethane solvent. Thermogravimetric analysis (TGA) was performed on a NETZSCH STA449-F3 thermal analyzer under a nitrogen atmosphere at a heating rate of 10 °C min^{-1}. Cyclic voltammetry (CV) was performed on a CHI760D voltammetric analyzer in CH_2Cl_2 solutions (10^{-3} M) at a scan rate of 100 mV s^{-1} with a glassy carbon rod as the working electrode, a silver wire as the pseudo-reference electrode, and a platinum wire as the counter electrode. The supporting electrolyte was tetrabutylammonium perchlorate (0.1 M) and ferrocene was selected as the external standard. The highest occupied molecule orbital (HOMO) energy levels of the dendrimers were determined from the half-potential ($E_{1/2}$), according to the equation of $E_{\mathrm{HOMO}} = -(E_{1/2}^{\mathrm{oxy}\rightarrow\mathrm{SCE}} + 4.4)$ eV.[2] The solutions were bubbled with a constant nitrogen flow for 15 min before measurements. X-ray diffraction (XRD) was performed on a BRUKER D8-DISCOVER diffractometer using Cu Kα radiation.

2. Quantum chemical calculations

The molecular structures of the complexes in their neutral, cationic and anionic states were optimized by DFT method using the Becke-Lee-Yang-Parr composite exchange correlation functional (B3LYP). “Double-ξ” quality basis sets were employed for the C, H, O, N and P (6-31G) and the Ir (LANL2DZ).[3] An effective core potential (ECP) replaces the inner core electrons of Ir leaving the outer core $(5s)^2(5p)^6$ electrons and the $(5d)^6$ valence electrons of Ir (Ⅲ). Singlepoint calculations were performed at the same theoretical level. All of the calculations were accomplished with Gaussian 09 software package in vacuo without any constrained symmetry. The molecular orbitals were visualized using Gaussview 5.0. The inner reorganization energies were obtained by comparing the energies in charged and uncharged optimized configurations, for both neutral and ionized states:[4]

$$\lambda_+ = \lambda_1 + \lambda_2 = (E_0^+ - E_+^+) + (E_+^0 - E_0^0);\ \lambda_- = \lambda_3 + \lambda_4 = (E_0^- - E_-^-) + (E_-^0 - E_0^0)$$

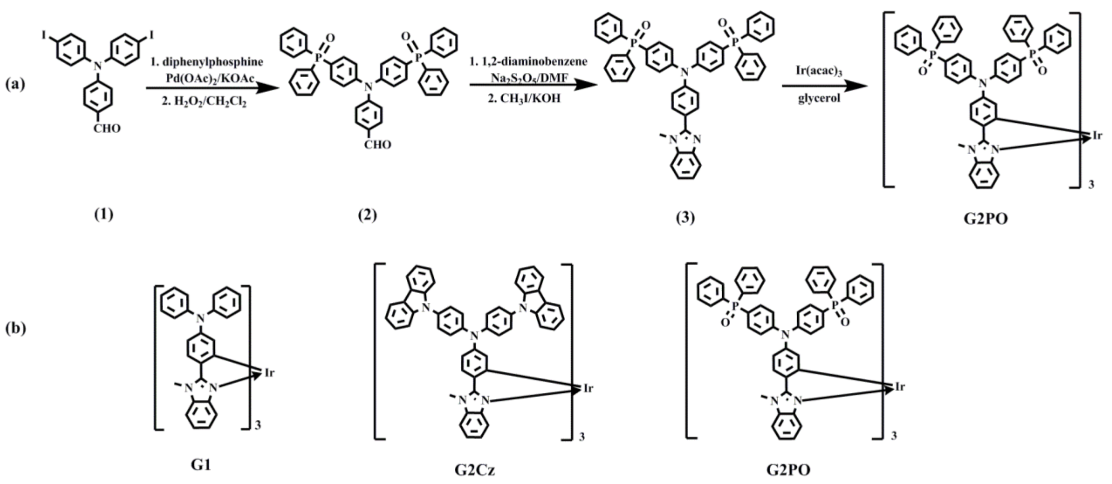
where E_+^+, E_-^- and E_0^0 denote the energy of the cationic, anionic and neutral species at their respective optimized geometries. E_0^+ and E_0^- denote the energy of the cationic and anionic species in the optimized neutral geometry respectively. Similarly, E_+^0 and E_-^0 represent the energy of the neutral molecule in the optimized cationic and anionic species geometries respectively. To compare the magnitudes of hole and electron mobility, we calculate the relative hopping rates of holes versus electrons, k_{et+}/k_{et-}, according to $(\lambda_-/\lambda_+)^{1/2}\exp[(\lambda_- - \lambda_+)/4kT]$ assuming T to be 300 K and neglecting the difference in the charge transfer integral (H_{ab}). k is the Boltzman constant.

3. Device fabrication and performance measurements

Indium-tin oxide (ITO)-coated glass substrates with a sheet resistance of 15 ohm/square underwent a wet-cleaning course in an ultrasonic bath, beginning with acetone, followed by detergent, deionized water, and isopropanol. The ITO substrates were then dried in an oven at 120 °C for 4 h, and treated with UV-ozone for 6 min before use. The PEDOT:PSS (poly(3,4-ethylenedioxythiophene) : poly(styrene-4-sulfonate)) (Bayer AG, CH8000) was diluted with deionized water at a mix ratio of 1:1 (by volume), and filtered with a 0.45 μm polyvinylidene fluoride (PVDF) syringe filter. A 40 nm PEDOT:PSS film was spin coated onto the ITO substrate and baked at 210 °C for 10 min. The substrates were then taken into a nitrogen glove box, where the emitting layer (100 nm) was spin coated onto the PEDOT:PSS layer from 1,2-dichloroethane solution and annealed at 120 °C for 30 min. The substrate was then transferred into an evaporation chamber, where the Cs_2CO_3/Al bilayer cathode was evaporated at evaporation rates of 0.2 and 10 Å s^{-1} for Cs_2CO_3 and Al, respectively, under a pressure of 1×10^{-3} Pa. The current-density-voltage and brightness-voltage curves of the devices were measured using a Keithley 4200 semiconductor characterization system and a calibrated silicon photodiode. The electroluminescent (EL) spectra were collected with a Photo Research PR705 Spectrophotometer. All measurements of the devices were carried out in ambient conditions. Assuming a Lambertian emission profile, the forward viewing external quantum efficiency (EQE) was calculated using the luminance efficiency, EL spectra and photopic luminosity function.

4. Materials

All reagents were used as purchased without further purification. All manipulations involving air-sensitive reagents were performed under a dry nitrogen atmosphere. The intermediate 4-[bis(4-iodophenyl)amino]benzaldehyde (1)[5] was prepared according to the literature procedures.



Scheme S1. (a) Synthetic route of G2PO. (b) Molecular structures of the dendrimers G1, G2Cz and G2PO.

4-[bis[4-(diphenylphosphoryl)phenyl]amino]benzaldehyde (2)

4-[bis(4-iodophenyl)amino]benzaldehyde (1) (8.84 g, 16.84 mmol), potassium acetate (3.97 g, 40.42 mmol), diphenylphosphine (7.84 g, 42.10 mmol) and palladium acetate (7.6 mg, 33.68 μmol) were dissolved in 24 mL dimethylacetamide and the solution was refluxed under a nitrogen atmosphere for 4 h. After cooling to room temperature, the mixture was poured into water (200 mL) and extracted with CH_2Cl_2 (3 × 50 mL). Then, 16 mL hydrogen peroxide (30%) was added slowly and the mixture was stirred for 3 h. After the solvent had been removed, the residue was purified by column chromatography on silica gel with ethyl acetate/methanol (25:1) as the eluent to give the product in a yield of 65 %. ^{1}H NMR (300 MHz, DMSO-d$_6$): 9.87 (s, 1H), 7.82 (d, J = 8.4 Hz, 2H), 7.67-7.55 (m, 24H), 7.26-7.18 (q, 6H). ^{31}P NMR (121MHz, DMSO-d$_6$): δ 24.96. MS (ESI): m/z 672.2 $[M-H]^-$. Anal. calcd (%) for $C_{43}H_{33}NO_3P_2$: C, 76.66; H, 4.94; N, 2.08. Found: C, 76.54; H, 4.89; N, 2.14.

1-Methyl-2-[4-bis[4-(diphenylphosphoryl)phenyl]aminophenyl]-1H-benzimidazole (3)

A mixture of 1, 2-diaminobenzene (1.30 g, 12.0 mmol), compound 2 (6.72 g, 10.0 mmol), sodium metabisulfite (1.90 g, 10.0 mmol), and DMF (40 mL) was heated at 80 °C for 12 h. After cooling to room temperature, the mixture was poured into water (400 mL) for extraction with ethyl acetate (3 × 100 mL). The organic extracts were washed with brine (100 mL) and dried over anhydrous sodium sulfate. After the solvent had been removed, the residue was purified by column chromatography on silica gel with dichloromethane/methanol (20:1) as the eluent to give the intermediate 2-[4-bis[4-(diphenyl- phosphoryl)phenyl]aminophenyl]-1H-benzimidazole in a yield of 73%. ^{1}H NMR (300 MHz, DMSO-d$_6$): 8.14 (d, J = 8.5 Hz, 2H), 7.67-7.54 (m, 26H), 7.28 (d, J = 8.5 Hz, 2H), 7.22-7.19 (m, 6H). ^{31}P NMR (121MHz, DMSO-d$_6$): δ 24.99. MS (ESI): m/z 762.2 $[M+H]^+$. Anal. calcd (%) for $C_{49}H_{37}N_3O_2P_2$: C, 77.26; H, 4.90; N, 5.52. Found: C, 77.21; H, 4.96; N, 5.46.

2-[4-bis[4-(diphenylphosphoryl)phenyl]aminophenyl]-1H-benzimidazole (3.81 g, 5.0 mmol) was dissolved in acetone (40 mL) containing potassium hydroxide (1.40 g, 25.0 mmol). The mixture was cooled in an ice bath while iodomethane (1.42 g, 10.0 mmol) was added in a drop-wise manner. The reaction was allowed to return to room temperature and stirred for an additional 12 h at which time the reaction mixture was filtered to remove the potassium hydroxide. The solvent was removed under reduced pressure and the residue in 100 mL chloroform was washed with brine (50 mL) and dried over anhydrous sodium sulfate. After the solvent had been removed, the residue was purified by column chromatography on silica gel with dichloromethane/methanol (15:1) as the eluent to give the product in a yield of 79%. ^{1}H NMR (300 MHz, DMSO-d$_6$): 7.85 (d, J = 8.5 Hz, 2H), 7.67-7.54 (m, 26H), 7.30-7.22 (q, 8H), 3.88 (s, 3H). ^{31}P NMR (121MHz, DMSO-d$_6$): δ 25.02. MS (ESI): m/z 798.2 [M+Na]$^+$. Anal. calcd (%) for $C_{50}H_{39}N_3O_2P_2$: C, 77.41; H, 5.07; N, 5.42. Found: C, 77.50; H, 4.96; N, 5.49.

Dendrimer G2PO.

Under a nitrogen atmosphere, compound 3 (0.65 g, 0.84 mmol) and Ir(acac)$_3$ (0.10 g, 0.21 mmol) were heated to 230 °C in glycerol (25 mL) for 24h. Then the reaction mixture was cooled to room temperature and water (250 mL) was added. After extraction with CH_2Cl_2 (3 × 80 mL), the organic phase was dried over anhydrous $MgSO_4$ and the solvent was then removed under reduced pressure. The residue was obtained as a crude product, which was chromatographed on a silica column by using dichloromethane/ methanol (12:1) as the eluent to produce a pure sample in a yield of 16 %. ^{1}H NMR (500 MHz, DMSO-d$_6$): 7.66 (d, J = 8.2 Hz, 3H), 7.52-7.50 (m, 30H), 7.43-7.38 (m, 18H), 7.32-7.26 (m, 24H), 7.11 (t, J = 7.5 Hz, 3H), 6.94 (d, J = 7.9 Hz, 3H), 6.69 (m, 15H), 6.12 (d, J = 8.2 Hz, 3H), 6.06 (s, 3H), 5.72 (d, J = 7.5 Hz, 3H), 4.05 (s, 9H). ^{31}P NMR (121MHz, DMSO-d$_6$): δ 24.42. MALDI-TOF-MS (m/z): Calcd. for $C_{150}H_{114}IrN_9O_6P_6$: 2516.68, found: 2515.69. Anal. calcd (%) for $C_{150}H_{114}IrN_9O_6P_6$: C, 71.59; H, 4.57; N, 5.01. Found: C, 71.32; H, 4.73; N, 4.81.

5. Thermal and phase properties

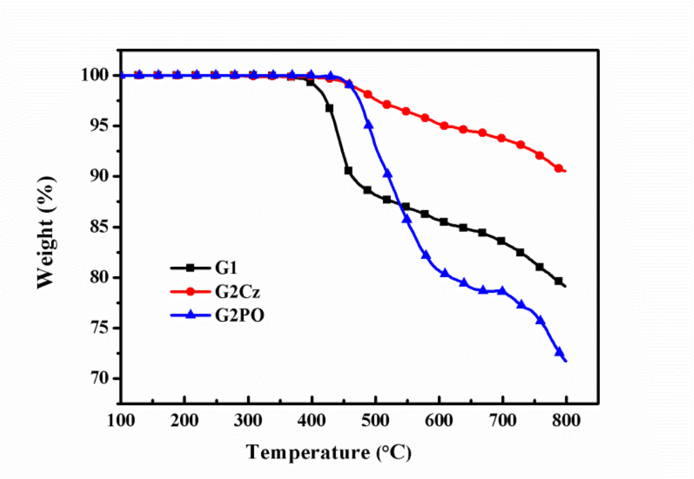


Fig. S1 TGA curves of the complexes recorded under a nitrogen atmosphere.

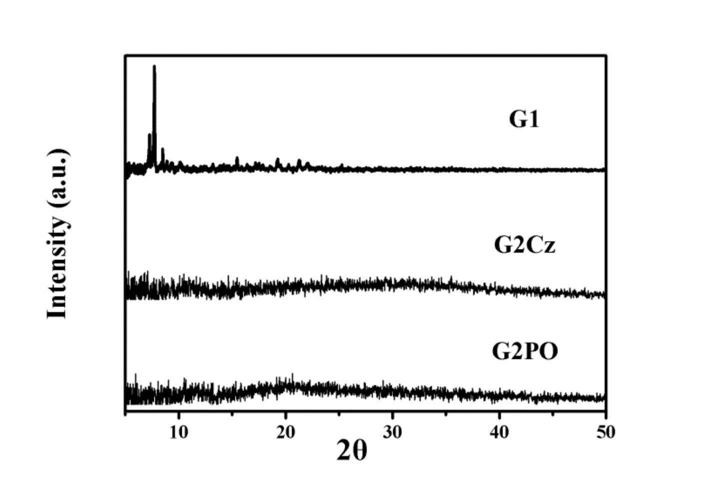


Fig. S2 XRD spectra of the complexes.

6. Cyclic voltammetry

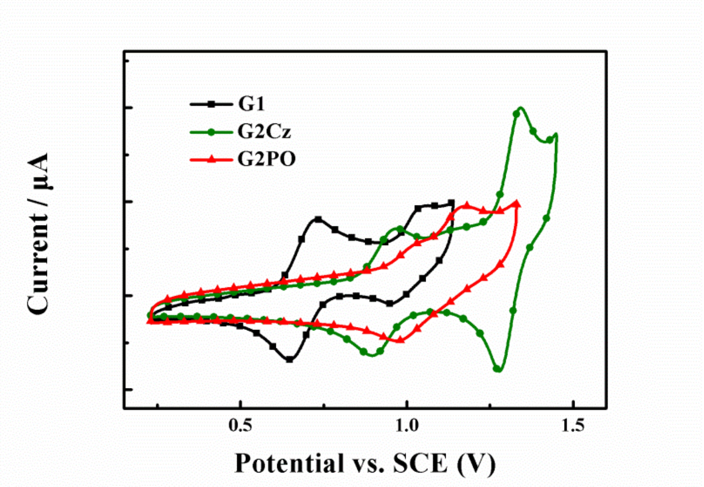


Fig. S3 CV curves of the complexes (*versus* saturated calomel electrode (SCE)).

Table S1 The photophysical, electrochemical, and thermal data of the complexes

complex	λ_{abs}[a] [nm] (log ε)	λ_{em} [nm]	Φ_p	HOMO/E_g[d] [eV]	T_1[f] [eV]	T_d [°C]
G1	233(4.8), 317(4.7), 359(4.8), 397(4.7), 450(4.0), 500(2.7)	517[a]/526[b]	0.52[c]/0.28[b]	-5.08/2.37	2.41	436
G2Cz	235(5.5), 294(5.1), 343(5.1), 399(4.8), 453(4.0), 501(2.8)	515[a]/526[b]	0.60[c]/0.50[b]	-5.32/2.37	2.42	609
G2PO	229(5.2), 354(5.0), 397(4.8), 452(3.9), 501(3.1)	516[a]/520[b]	0.75[c]/0.65[b]	-5.38/2.40	2.41	490

[a] In CH_2Cl_2 solutions (1 × 10^{-6} mol/L). ε denotes the molar extinction coefficients. [b] Neat film data measured at 298K. The film Φ_p was measured with an integrating sphere under an excitation wavelength of 370 nm. The integrating sphere was purged with flowing nitrogen during the whole measuring process. [c] In degassed DMSO solutions. The solution Φ_p was measured versus $(ppy)_2Ir(acac)$ (Φ_p = 0.34 in 2-methyltetrahydrofuran) [d] The HOMO and the optical gap (E_g) were determined from the half-potential ($E_{1/2}$) and absorption data.[6] [f] In CH_2Cl_2 glass at 77K.

7. Quantum chemical calculations

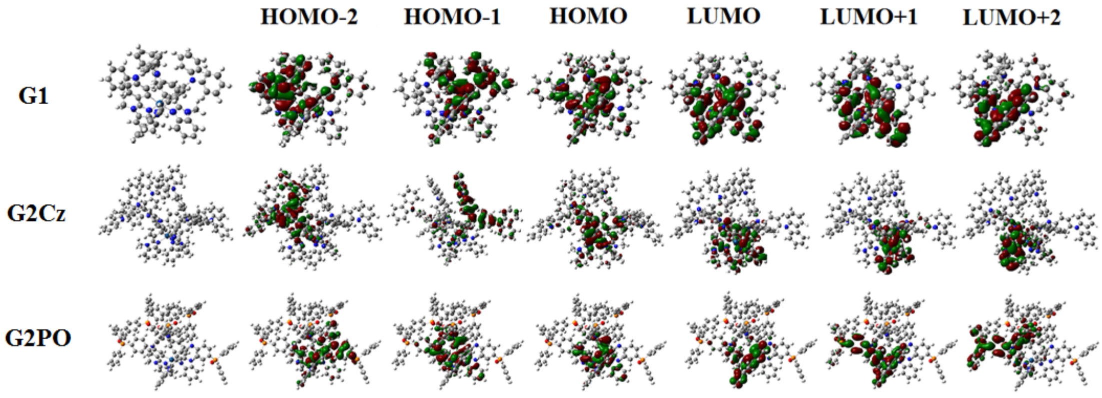


Fig. S4 Selected frontier orbitals for the complexes.

Table S2 The calculated reorganization energies (in eV) and Connolly solvent excluded volumes (in Å^3) of the dendrimers

	λ_1	λ_2	λ_+	λ_3	λ_4	λ_-	k_{et+}/k_{et-}	CSEV
G2Cz	0.0787	0.0740	0.153	0.123	0.100	0.223	2.37	1965
G2PO	0.129	0.159	0.288	0.0987	0.113	0.212	0.41	2236

8. Electroluminescent properties

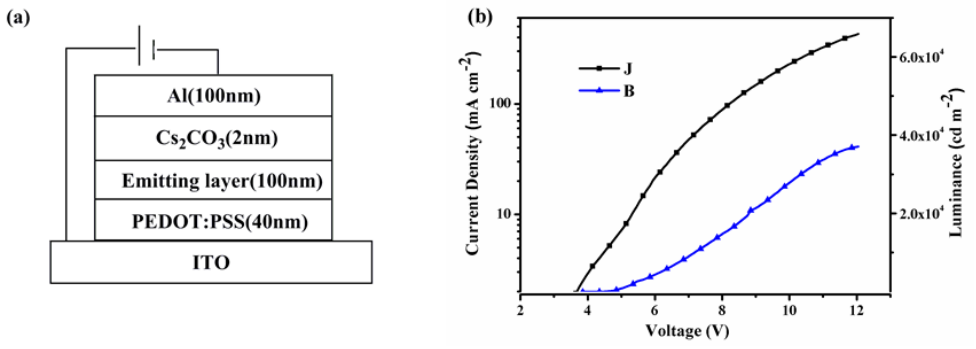


Fig. S5 (a) EL device configuration and (b) J–V–B characteristics for the device from G2PO.

Table S3 Device performances of the PhOLEDs

	V_{on} ^{a} [V]	$\eta_{c,\,max}$ ^{b} [cd A^{-1}]	$\eta_{ext,\,max}$ ^{c} [%]	λ_{em} ^{d} [nm]	CIE ^{d} (x, y)	γ	k_{et+}/k_{et-} or k_{et-}/k_{et+}
G2Cz	4.3	18.3	6.1	524	0.38, 0.58	0.61	2.37
G2PO	4.6	21.6	7.2	522	0.35, 0.60	0.55	2.44

^{a} Recorded at 1 cd m^{-2}. ^{b} Maximum current efficiency. ^{c} Maximum external quantum efficiency. ^{d} Data were measured at 8 V.

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