

Cyclometalated red iridium(III) complexes containing carbazoyl-acetylacetonate ligands:
efficiency enhancement in polymer LED devices

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Experimental Section

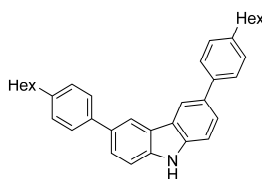
Materials

All manipulations were performed under an atmosphere of dry argon by employing usual Schlenk techniques. Solvents were carefully dried and distilled from appropriate drying agents prior to use. Commercially available reagents were used without further purification unless otherwise stated. 2-Phenylpyridine, 1-bromo-4-hexylbenzene, potassium hexamethyldisilazane, *n*-butyllithium, tetrahydrofuran, were purchased from Sigma-Aldrich. $\text{IrCl}_3 \times 3 \text{ H}_2\text{O}$, 2-ethyl-bromoacetate, *tetrakis*(triphenylphosphine)palladium(0) and pinacolone were delivered by ABCR. 2-Ethoxyethanol, 9*H*-carbazole and 2-ethoxyethanol were purchased from Acros.

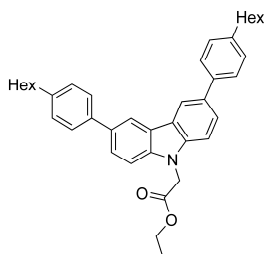
Instrumentation

^1H NMR and ^{13}C NMR spectra were acquired on a Bruker ARX 400, chemical shifts are given relative to the internal standard tetramethylsilane (Me_4Si) in CDCl_3 solutions. Chemical shifts in NMR spectra are given in Hertz (Hz; s = singlet, d = doublet, t = triplet, q = quartet, and m = multiplet). Fourier transform infrared (FT-IR) spectra were recorded on a Jasco FT/IR-4200 Fourier transform spectrometer. The UV-vis spectra were measured with a JASCO V-550 UV-vis spectrophotometer (1 cm cuvettes, CHCl_3 at concentrations of about 1×10^{-5} mol/L). The emission spectra were performed using a CARY Eclipse fluorescence spectrophotometer at concentrations of about 1×10^{-5} mol/L. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/DSC STAR System (heating rate: 10 K/min; argon; T_d @ 5% weight loss). Mass spectra were obtained using a Varian MAT 311 instrument with an electrospray source (ESI-MS), and a Varian MAT 311 instrument with an electrospray source (ESI-MS). Elemental analyses (EA) were performed on a Perkin Elmer 240 B setup.

Synthetic Methods

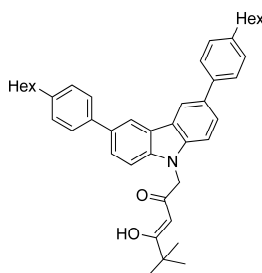


Synthesis of 3,6-bis(4-hexylphenyl)-9H-carbazole. A mixture of 4-hexylphenylboronic acid (6.0 g, 29.1 mmol) and *tetrakis*(triphenylphosphine) palladium(0) (255 mg, 1.12 mmol) was stirred in anhydrous toluene (50 mL) at RT under a nitrogen atmosphere. To this mixture, 3,6-diiodo-9H-carbazole (4.69 g, 11.2 mmol) in ethanol (15 mL) and aqueous saturated Na₂CO₃ solution (20 mL) were added one after the other. The solution was heated to reflux under argon for 3 h, cooled to ambient temperature, and poured into 2N HCl (100 mL). The mixture was subsequently extracted with chloroform (3 × 50 mL). The organic layers were combined and washed with a saturated NaHCO₃ solution (50 mL), water (10 mL) and dried over MgSO₄. The crude solid was purified by silica column chromatography (*n*-hexane/ethyl acetate, 10/3, v/v) to give white powder. Yield: (3.10 g, 58%) (Found: C, 88.68; H, 8.46; N 2.90. C₃₆H₄₁N requires C, 88.67; H, 8.47; N, 2.87); IR: ν_{max} (film)/ cm⁻¹ 3380 (N-H), 3062 (C=C-H), 2945 (C-H), 1658, 1633 (C=C), 1478, 1127, 888, 865, 861, 793 and 677; ¹H NMR: δ_{H} (600 MHz; CDCl₃; 25 °C; TMS) 0.93 (6H, m, CH₂CH₃), 1.37 (12H, s, 2 × CH₂CH₂CH₂CH₂CH₃), 2.67-2.71 (4H, dt, *J* 7.33 and 9.05, 2 × CH=CHCH₂CH₂), 7.30-7.32 (4H, d, *J* 8.08, 4 × CH=CH), 7.47 (2H, s, 2 × CH=CH), 7.64-7.69 (6H, m, 6 × CH=CH) and 8.01 (1H, s, NH); ¹³C NMR: δ_{C} (100 MHz; CDCl₃; 25 °C; TMS) 14.1, 22.6, 29.1, 31.5, 31.7, 35.6, 110.8, 118.6, 124.0, 125.4, 127.1, 128.8, 139.3 and 141.3; HRMS: *m/z* (ESI) 487.32 (C₃₆H₄₁N⁺, requires 487.32).



Synthesis of ethyl-2-(3,6-bis(4-hexylphenyl)-9H-carbazol-9-yl)acetate. 3,6-Bis(4-hexylphenyl)-9H-carbazole (1 g, 2.05 mmol) was stirred with solid dry K₂CO₃ (0.85 g, 6.15 mmol) in dry DMF (30 mL) at 70 °C for 2 hours under argon. Ethyl-2-bromoacetate (0.76 g, 4.51 mmol) was added to the dark-red solution. The resulting cloudy orange mixture was

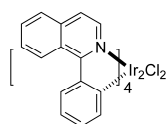
stirred for 2 h at room temperature and for 5 h at 70 °C. The reaction was quenched with water (130 mL) and cooled on ice. The crude product was filtered, washed with water, and purified by silica column chromatography (*n*-hexane/ethyl acetate, 10/3, v/v) to give a white powder. Yield: (1.56 g, 62 %). (Found: C 83.71; H 8.26; N 2.43. C₄₀H₄₇NO₂ requires C, 83.73; H, 8.26; N 2.44.); IR: $\nu_{\max}$ (film)/ cm⁻¹ 3058 (C=C-H), 2947 (C-H), 1677, 1658, 1633 (C=O, C=C), 1521, 1345, 891, 863, 852, 793 and 668; ¹H NMR: δ_{H} (600 MHz; CDCl₃; 25 °C; TMS) 0.93 (6H, m, CH₂CH₃), 1.25-1.28 (3H, dt, *J* 7.15 and 7.91, O-CH₂-CH₃), 1.35-1.43 (12H, m, 2 × CH₂CH₂CH₂CH₂CH₃), 1.68-1.73 (4H, m, 2 × CH₂CH₂CH₂), 2.68-2.71 (4H, dt, *J* 7.53 and 9.03, 2 × CH=CHCH₂CH₂), 4.23-4.26 (2H, m, OCH₂CH₃), 5.02 (2H, s, COCH₂), 7.30-7.32 (4H, d, *J* 7.91, 4 × CH=CH), 7.38-7.40 (2H, d, *J* 8.66, 2 × CH=CH), 7.64-7.66 (4H, d, *J* 7.91, 4 × CH=CH), 7.72-7.74 (4H, d, *J* 8.66, 4 × CH=CH) and 8.35 (2H, s, 2 × CH=CH); ¹³C NMR: δ_{C} (100 MHz; CDCl₃; 25 °C; TMS) 14.1, 22.6, 29.1, 31.6, 31.8, 35.6, 45.0, 61.7, 108.7, 118.9, 123.9, 125.6, 127.2, 128.8, 133.4, 139.3, 140.4, 141.4 and 168.5; HRMS: *m/z* (ESI) 573.40 (C₄₀H₄₇NO₂⁺, requires 573.36).



Synthesis of 1-(3,6-bis(4-hexylphenyl)-9H-carbazol-9-yl)-5,5-dimethylhexane-2,4-dione (4). To a solution of 3,3-dimethylbutan-2-one (0.183 g, 1.83 mmol) in THF (20 mL), KHMDS (3.9 mL of a 0.5 M solution in toluene, 1.95 mmol) was added drop-wise at 0 °C. Subsequently, the solution was stirred at room temperature for 1 h. After this time, ethyl-2-(3,6-bis(4-hexylphenyl)-9H-carbazol-9-yl)acetate (0.7 g, 1.22 mmol) in THF (20 mL) was added drop-wise and the resulting reaction mixture was stirred at room temperature for 12 h. Afterwards, the mixture was poured into water and acidified with diluted hydrochloric acid. The organic layer was extracted with CHCl₃ (3 × 50 mL) and washed with water, then dried with anhydrous sodium sulfate. The solvent was removed by reduced pressure. The crude product was purified by silica column chromatography (*n*-hexane/ethyl acetate, 10/3, v/v) to give a red powder. Yield: (0.62 g, 80 %). (Found: C, 84.21; H, 8.46; N, 2.27. C₄₄H₅₃NO₂ requires C, 84.17, H, 8.51, N, 2.23.); IR: $\nu_{\max}$ (film)/ cm⁻¹ 3058 (C=C-H), 2951 (C-H), 1676, 1658, 1641 (C=O, C=C), 1488, 1276, 889, 873, 848, 781 and 689; ¹H NMR: δ_{H} (600 MHz; CDCl₃; 25 °C; TMS) 0.94 (6H, m, CH₂CH₃), 1.04 (6H, m, 3 × CCH₃), 1.35-1.43 (12H, m, 2 ×

CH₂CH₂CH₂CH₂CH₃), 1.71 (4H, m, 2 × CH₂CH₂CH₂), 2.69-2.72 (4H, dt, *J* 7.53 and 9.03, 2 × CH=CHCH₂CH₂), 5.07 (1H, s, COCHC), 5.46 (2H, s, COCH₂N), 7.32-7.33 (4H, d, *J* 8.28, 4 × CH=CH), 7.41-7.43 (2H, d, *J* 8.28, 2 × CH=CH), 7.66-7.68 (4H, d, *J* 7.91, 4 × CH=CH), 7.75-7.76 (2H, d, *J* 8.28, 2 × CH=CH) and 8.34 (2H, s, 2 × CH=CH); ¹³C NMR: δ_c(100 MHz; CDCl₃; 25 °C; TMS) 14.1, 22.6, 25.8, 26.3, 27.1, 29.1, 31.5, 31.7, 35.6, 38.8, 48.9, 108.9, 118.8, 123.9, 125.6, 127.1, 128.9, 133.4, 139.1, 140.4, 141.4 and 200.3; HRMS: *m/z* (ESI) 627.40 (C₄₄H₅₃NO₂⁺, requires 627.41).

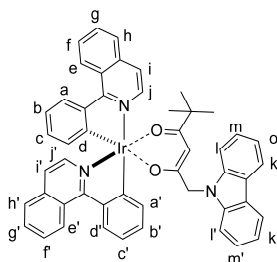
General procedure of cyclometalated [Ir^{III}(C[^]N)₂-μ-Cl]₂. Iridium(III) trichloride hydrate was combined with the C[^]N ligand 1-phenylisoquinoline (pic), dissolved in a mixture of 2-ethoxyethanol (30 mL) and water (10 mL). The mixture was stirred for 24 h under reflux. The solution was cooled to room temperature, and the precipitate was collected on a glass filter frit. The precipitate was washed with ethanol (30 mL) and dichloromethane (20 mL).



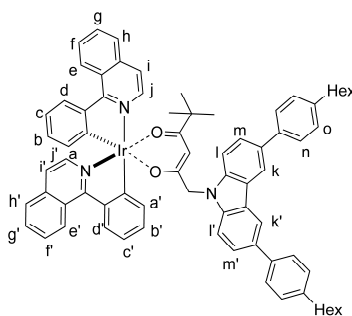
Synthesis of [Ir^{III}(pic)₂-μ-Cl]₂. Iridium(III) trichloride hydrate (233 mg, 0.78 mmol) and pic (400 mg, 1.95 mmol) afforded an orange-red powder. Yield: (336 mg, 78%). (Found: C, 56.22; H, 3.21; N, 4.42. C₆₀H₄₀C₁₂Ir₂N₄ requires C, 56.64, H, 3.17, N, 4.42.); IR: ν_{max}(film)/cm⁻¹ 3049 (C=C-H), 1676, 1658, 1641, 1587 (C=N, C=C), 1392, 1179, 910, 867, 838, 792 and 688; ¹H NMR: δ_H(600 MHz; dimethylsulfoxide-d₆; 25 °C; TMS) 5.58-5.60 (2H, d, *J* 7.33, 2 × CH=CH), 6.33-6.35 (2H, d, *J* 7.32, 2 × CH=CH), 6.63-6.67 (2H, t, *J* 7.07 and 8.58, 2 × CH=CH), 6.78-6.81 (2H, t, *J* 7.58 and 9.09, 2 × CH=CH), 6.91-6.94 (2H, t, *J* 7.33 and 8.84, 2 × CH=CH), 7.00-7.04 (2H, t, *J* 7.07 and 8.84, 2 × CH=CH), 7.82-8.04 (12H, m, 12 × CH=CH), 8.13-8.26 (8H, m, 8 × CH=CH), 8.86-8.88 (2H, d, *J* 8.59, 2 × CH=CH), 8.92-8.94 (2H, d, *J* 8.58, 2 × CH=CH), 9.59-9.61 (2H, d, *J* 6.31, 2 × CH=CH) and 9.75-9.77 (2H, d, *J* 6.31, 2 × CH=CH); MS: *m/z* (APLI-MS) 1271.20 (C₆₀H₄₀C₁₂Ir₂N₄⁺, requires 1271.19).

General procedure of [Ir^{III}(C[^]N)₂{acac}] complexes. In a 50 mL flask, the μ-chloride-bridged dimer Ir(III) complex, the acac-carbazole ligand and K₂CO₃ were mixed with 2-ethoxyethanol (30 mL) and the mixture was stirred under reflux for 3 h. After cooling to room temperature, 2-ethoxyethanol was removed under reduced pressure. The crude product was dissolved in dichloromethane (20 mL) and the obtained solid was filtered off. The

dichloromethane solution (20 mL) was concentrated under reduced pressure. Subsequently, *n*-hexane was utilized in order to precipitate the complexes and the obtained solid was filtered off. The residue was purified by silica column chromatography (*n*-hexane/ethyl acetate, 10/3, v/v), if needed, a purification on a BioBeads SX-1 column (dichloromethane) followed additionally.



[Ir^{III}(piq)₂{1-(9*H*-carbazol-9-yl)-5,5-dimethylhexane-2,4-dione}] (1). Compound [Ir^{III}(piq)₂-μ-Cl]₂ (200 mg, 0.157 mmol), 1-(9*H*-carbazol-9-yl)-5,5-dimethylhexane-2,4-dione (97 mg, 0.314 mmol) and K₂CO₃ (152 mg, 1.100 mmol) afforded after reaction and purification a red powder. Yield: (200 mg, 67%). (Found: C, 66.20; H, 4.57; N, 4.55. C₅₀H₄₀IrN₃O₂ requires C, 66.20, H, 4.44, N, 4.63.); UV/Vis: λ_{max}(Chloroform, 22 °C)/nm 478 (ε/ dm³ mol⁻¹ cm⁻¹ 2000), 291 (160000); Emission: λ_{max}(Chloroform, 22 °C)/nm 624; IR: ν_{max}(film)/ cm⁻¹ 3052 (C=C-H), 1677, 1565, 1559 (C=N, C=C), 1388, 1134, 893, 876, 867, 798 and 699; ¹H NMR: δ_H(600 MHz; CDCl₃; 25 °C; TMS) 0.52 (9H, s, 3 × CCH₃), 4.14-4.18 (1H, m, COCHCO), 5.03 (2H, s, COCH₂N), 6.43-6.45 (1H, d, *J* 7.83, CH=CH^{a'}), 6.53-6.55 (1H, d, *J* 7.58, CH=CH^a), 6.65-6.68 (1H, t, *J* 7.83 and 8.28, CH=CH^{b'}), 6.71-6.75 (1H, t, *J* 7.58 and 7.83, CH=CH^b), 6.89-6.93 (1H, t, *J* 8.08 and 9.09, CH=CH^{c'}), 6.96-7.00 (1H, t, *J* 8.08 and 9.09, CH=CH^c), 7.09-7.11 (2H, d, *J* 8.08, CH=CH^{n'} and CH=CHⁿ), 7.15-7.23 (6H, m, CH=CH^f, CH=CH^{f'}, CH=CH^{k'}, CH=CH^k, CH=CH^{o'} and CH=CH^o), 7.31-7.32 (1H, d, *J* 6.32, CH=CH^{h'}), 7.35-7.36 (1H, d, *J* 6.57, CH=CH^h), 7.70-7.72 (2H, m, CH=CH^{i'} and CH=CHⁱ), 7.79-7.82 (2H, m, CH=CH^{j'} and CH=CH^j), 7.90-7.92 (1H, m, CH=CH^{l'}), 7.97-7.99 (1H, m, CH=CH^l), 8.02-8.04 (2H, d, *J* 7.07, CH=CH^{m'} and CH=CH^m), 8.18-8.20 (1H, d, *J* 7.83, CH=CH^{g'}), 8.23-8.25 (1H, d, *J* 6.57, CH=CH^g), 8.29-8.31 (1H, d, *J* 7.83, CH=CH^{e'}), 8.39-8.40 (1H, d, *J* 6.57, CH=CH^e), 8.97-8.99 (1H, d, *J* 9.10, CH=CH^{i'}) and 9.08-9.10 (1H, d, *J* 8.84, CH=CHⁱ); ¹³C NMR: δ_C(100 MHz; CDCl₃; 25 °C; TMS) 14.2, 21.0, 27.4, 40.9, 51.4, 60.4, 92.2, 109.0, 118.9, 119.3, 119.6, 120.1, 120.2, 120.4, 122.8, 125.4, 126.1, 126.3, 126.7, 126.8, 127.2, 127.3, 127.5, 127.6, 128.5, 129.0, 129.4, 129.7, 130.5, 130.6, 133.8, 134.3, 137.0, 137.2, 140.5, 140.6, 146.4, 146.5, 151.9, 152.0, 169.0, 169.1, 181.1 and 196.6; MS: *m/z* (APLI-MS) 907.27 (C₅₀H₄₀IrN₃O₂⁺, requires 907.27).



Synthesis of $[\text{Ir}^{\text{III}}(\text{piq})_2\{1-(3-(4\text{-heptylphenyl})-6-(4\text{-hexylphenyl})-9H\text{-carbazol-9-yl})-5,5\text{-dimethylhexane-2,4-dione}\}]$ (2). Compound $[\text{Ir}^{\text{III}}(\text{piq})_2-\mu\text{-Cl}]_2$ (200 mg, 0.157 mmol), 1-(3-(4-heptylphenyl)-6-(4-hexylphenyl)-9H-carbazol-9-yl)-5,5-dimethylhexane-2,4-dione (197 mg, 0.314 mmol) and K_2CO_3 (152 mg, 1.100 mmol) afforded after reaction and purification a red powder. Yield: (286 mg, 72%). (Found: C, 72.42; H, 5.27; N, 3.15. $\text{C}_{74}\text{H}_{72}\text{IrN}_3\text{O}_2$ requires C, 72.40, H, 5.91, N, 3.42.); UV/Vis: λ_{max} (Chloroform, 22 °C)/nm 481 ($\epsilon/\text{dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$ 600), 299 (9500); Emission: λ_{max} (Chloroform, 22 °C)/nm 625; IR: 3049 (C=C-H), 1668, 1579, 1557 (C=N, C=C), 1388, 1116, 883, 864, 854, 783 and 647; ^1H NMR: δ_{H} (600 MHz; CDCl_3 ; 25 °C; TMS) 0.61 (9H, s, $3 \times \text{CCH}_3$), 0.96 (6H, s, $2 \times \text{CH}_2\text{CH}_3$), 1.38-1.45 (12H, m, $2 \times \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$), 1.74 (4H, s, $2 \times \text{CHCH}_2\text{CH}_2\text{CH}_2$), 2.73 (4H, s, $2 \times \text{CHCH}_2\text{CH}_2$), 4.55-4.77 (2H, m, COCH_2N), 5.22 (1H, s, COCHCO), 6.42-6.43 (1H, d, J 7.53, $\text{CH}=\text{CH}^{\text{a}}$), 6.52-6.53 (1H, d, J 7.53, $\text{CH}=\text{CH}^{\text{a}}$), 6.65-6.67 (1H, t, J 7.15 and 8.66, $\text{CH}=\text{CH}^{\text{b}}$), 6.70-6.73 (1H, t, J 7.15 and 8.66, $\text{CH}=\text{CH}^{\text{b}}$), 6.91-6.93 (1H, t, J 7.15 and 8.28, $\text{CH}=\text{CH}^{\text{c}}$), 6.96-6.98 (1H, t, J 7.53 and 8.28, $\text{CH}=\text{CH}^{\text{c}}$), 7.16-7.19 (2H, J 8.28, $\text{CH}=\text{CH}^{\text{n}}$ and $\text{CH}=\text{CH}^{\text{n}}$), 7.30-7.35 (4H, m, $\text{CH}=\text{CH}^{\text{f}}$, $\text{CH}=\text{CH}^{\text{f}}$, $\text{CH}=\text{CH}^{\text{k}}$ and $\text{CH}=\text{CH}^{\text{k}}$), 7.42-7.44 (2H, d, J 8.66, $\text{CH}=\text{CH}^{\text{o}}$ and $\text{CH}=\text{CH}^{\text{o}}$), 7.64-7.65 (2H, J 7.91, $\text{CH}=\text{CH}^{\text{h}}$ and $\text{CH}=\text{CH}^{\text{h}}$), 7.71-7.74 (4H, m, $\text{CH}=\text{CH}^{\text{i}}$, $\text{CH}=\text{CH}^{\text{i}}$, $\text{CH}=\text{CH}^{\text{l}}$ and $\text{CH}=\text{CH}^{\text{l}}$), 7.90-7.91 (2H, d, J 8.28, $\text{CH}=\text{CH}^{\text{m}}$ and $\text{CH}=\text{CH}^{\text{m}}$), 8.19-8.26 (4H, m, $\text{CH}=\text{CH}^{\text{e}}$, $\text{CH}=\text{CH}^{\text{e}}$, $\text{CH}=\text{CH}^{\text{d}}$ and $\text{CH}=\text{CH}^{\text{d}}$), 8.36-8.37 (2H, d, J 6.40, $\text{CH}=\text{CH}^{\text{e}}$ and $\text{CH}=\text{CH}^{\text{e}}$), 8.99-9.00 (1H, t, J 7.53, $\text{CH}=\text{CH}^{\text{j}}$) and 9.04-9.06 (1H, t, J 7.91, $\text{CH}=\text{CH}^{\text{j}}$); ^{13}C NMR: δ_{C} (100 MHz; CDCl_3 ; 25 °C; TMS) 14.1, 22.6, 27.5, 29.1, 31.5, 31.8, 35.6, 41.0, 51.7, 92.6, 109.3, 118.3, 119.3, 119.6, 120.2, 120.4, 123.5, 124.9, 126.1, 126.3, 126.7, 126.8, 127.0, 127.1, 127.2, 127.3, 127.5, 127.6, 128.5, 128.8, 128.9, 129.0, 129.4, 129.6, 130.5, 130.6, 132.3, 133.9, 134.3, 137.1, 137.2, 139.4, 140.4, 140.5, 140.6, 141.1, 146.5, 151.9, 169.1, 180.8 and 196.7; MS: m/z (APLI-MS) 1227.53 ($\text{C}_{74}\text{H}_{72}\text{IrN}_3\text{O}_2^+$, requires 1227.53).

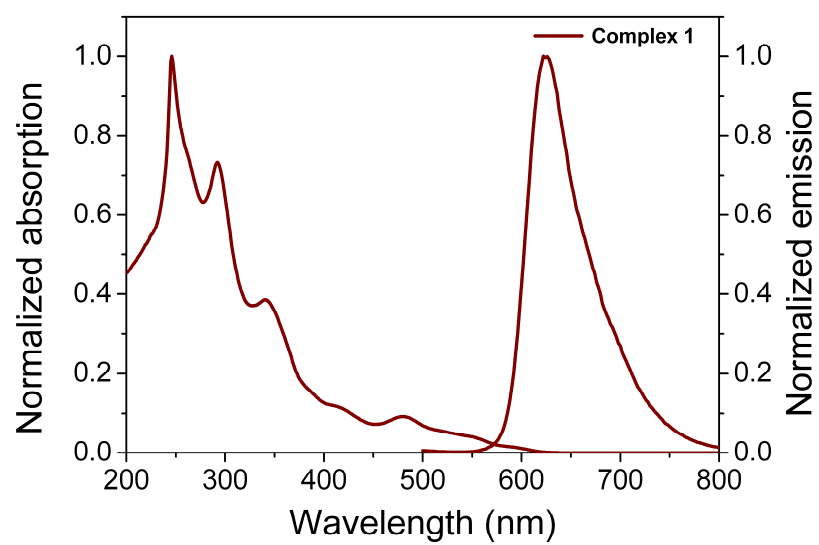


Fig S1 Absorption and emission spectra of **1** in chloroform solution (10^{-5} mol/L).

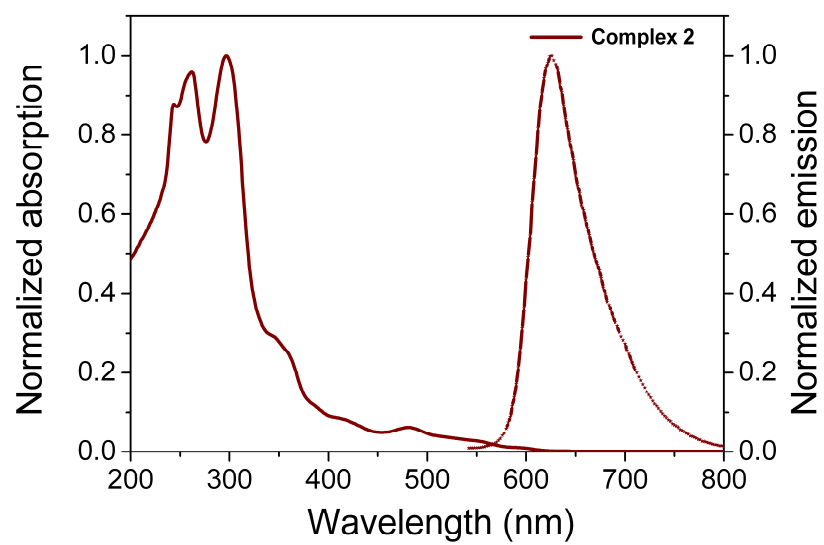


Fig S2 Absorption and emission spectra of **2** in chloroform solution (10^{-5} mol/L).

LED preparation and characterization

Light emitting diodes were fabricated in clean room environment. Upon cleaning of glass substrate with pre-coated indium tin oxide (ITO) electrodes, PEDOT:PSS was spin-coated from aqueous solution in air. After baking of PEDOT:PSS in an oven at 140 °C for 10 min samples were moved into a nitrogen glovebox. Active layer consisting of PVK:PBD doped with Iridium-coordinated complexes were spin-casted and then thermally annealed on a hotplate at 110 °C for 30 min in N₂ atmosphere. Metallic cathode composed by 5 nm of Ba and 100 nm of Al were evaporated in high vacuum conditions (10⁻⁷ mbar). Immediately after fabrication devices were transferred into a nitrogen glovebox for electrical characterization.

PVK and PBD were acquired from Sigma-Aldrich. The reference Ir-coordinated compound, [(btp)₂Ir(III)(acac)], was purchased from American Dye Source. No further purification was involved for any of the commercially available compounds.

Current-voltage characteristics (Fig S3) were acquired with Keithley 2400 source meter, the applied bias was scanned in the range of -2 to 10 V with steps 0.1V, 0.3 s per step. The shape of the IV curves did not depend on dopant molecular structure or on concentration. The light output was measured by photodiode mounted directly above sample.

The luminosity was measured using Minolta LS-110 luminance meter on devices operating at 10 V. Measurements were performed in nitrogen atmosphere to prevent degradation. To reliably estimate the device performances at least three devices were measured for every combination of dopant type and concentration. Each device was measured three times – immediately after turn on, in 30 seconds and in one minute. The obtained values of luminous efficiency were averaged out and measurement errors were estimated. The power efficiency was calculated from the luminous efficiency assuming that the devices were emitting according to the Lambertian law.

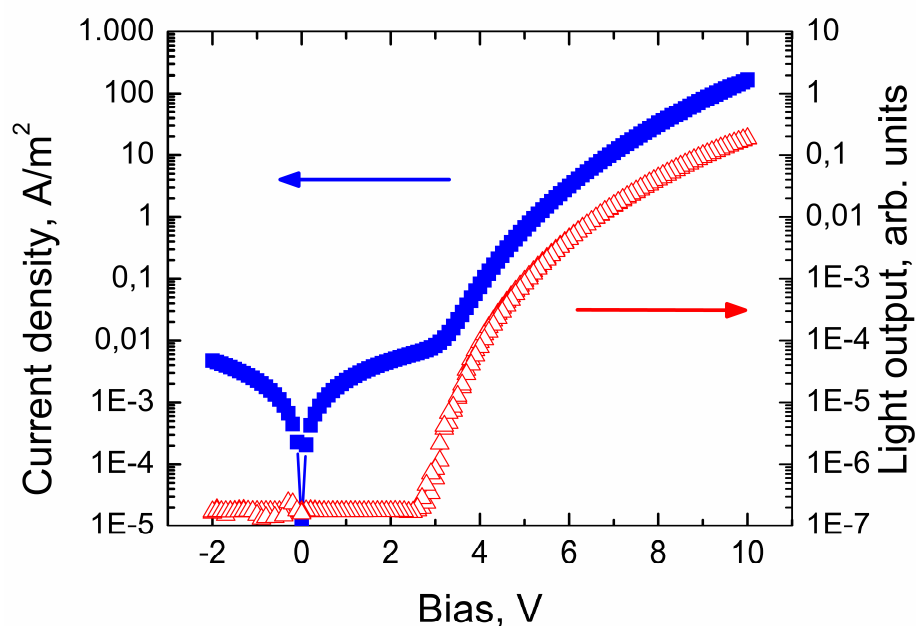


Fig S3 Typical IV curve and corresponding light output.

Electroluminescence spectra of the devices were measured under applied bias of 10 V with the Ocean Optics USB 2000 fibre optics spectrometer directly in the nitrogen glove box. For photoluminescence measurements the doped PVK:PBD blends were spin-coated on quartz substrates and kept in dynamic vacuum. PL decays were measured using an Hamamatsu Streak camera working in single sweep mode, samples were excited by the second harmonic of a Ti-Sapphire laser delivering 150 fs pulses. Steady state PL spectra were measured with an ImageEM Hamamatsu CCD detector.

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