

Highly Luminescent Phosphine Oxide-Containing Bipolar Alkynylgold(III) Complexes for Solution-Processable Organic Light-Emitting Devices with Small Efficiency Roll-Offs**

*Chin-Ho Lee, Man-Chung Tang, Wai-Lung Cheung, Shiu-Lun Lai, Mei-Yee Chan, Vivian Wing-Wah Yam**

[*] Mr. C.-H. Lee, Dr. M.-C. Tang, Mr. W.-L. Cheung, Dr. S.-L. Lai, Dr. M.-Y. Chan, Prof. V. W.-W. Yam*

Department of Chemistry, The University of Hong Kong, Pokfulam Road, Hong Kong, P. R. China.

Fax: +(852) 2857-1586; Tel: +(852) 2859-2153

E-mail: wwyam@hku.hk

Electronic Supplementary Information

Experimental Section	3
<i>Materials and Reagents</i>	3
<i>Physical Measurements and Instrumentation</i>	3
<i>OLED Fabrication and Characterization</i>	4
<i>Synthesis and Characterization</i>	5
Figures and Tables	10
References	20

Experimental Section

Materials and Reagents

Tetra-*n*-butylammonium hexafluorophosphate (Aldrich, 98 %) was recrystallized for more than three times from hot absolute ethanol before use. Triethylamine was distilled over calcium hydride before use. $\text{tBuC}^{\text{N}}(\text{C}_6\text{H}_4\text{Br})^{\text{C}}\text{tBu}$ was synthesized by Kröhnke Cyclization.¹ The alkynes were synthesized according to literature method.² All other reagents were of analytical grade and were used as received. All reactions were performed under anaerobic conditions using standard Schlenk techniques under nitrogen atmosphere unless specified otherwise.

Physical Measurements and Instrumentation

Electronic absorption spectra were obtained by using a Cary 60 UV-visible spectrophotometer (Agilent technology) equipped with a xenon flash lamp. ^1H , $^{13}\text{C}\{^1\text{H}\}$, $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker AVANCE 400, 500 or 600 (400 MHz, 500 MHz and 600 MHz for ^1H respectively; 100 MHz, 125 MHz and 150 MHz for ^{13}C respectively; 162 MHz and 202 MHz for ^{31}P respectively) Fourier-transform nuclear magnetic resonance (NMR) spectrometers with chemical shifts reported relative to tetramethylsilane, with the residual NMR solvent peak used as internal reference (δ 7.26 ppm for chloroform, δ 5.32 ppm for dichloromethane, δ 1.72 or δ 3.58 ppm for tetrahydrofuran). Splitting of the ^{13}C signal due to ^{31}P - ^{13}C coupling was not determined; instead all of them were reported as individual singlet peaks. Positive electron-impact (EI) mass spectra were recorded on a Thermo Scientific DFS High Resolution Magnetic Sector Mass Spectrometer. Positive matrix assisted laser desorption ionization (MALDI) spectra were recorded on Bruker ultraXtreme using dithranol matrix. High-resolution electrospray ionization (ESI) mass spectra were recorded on a Bruker maXis II High Resolution LC-QTOF Mass Spectrometer. IR spectra were recorded as KBr disk on a Bio-Rad FTS-7 FTIR spectrometer (4000–400 cm^{-1}). Elemental analyses for the metal complexes were performed on the Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences in Beijing. Steady-state excitation and emission spectra were recorded on a Spex Fluorolog-3 model FL3-211 fluorescence spectrofluorometer equipped with a Hamamatsu R2658P photomultiplier tube (PMT) detector or

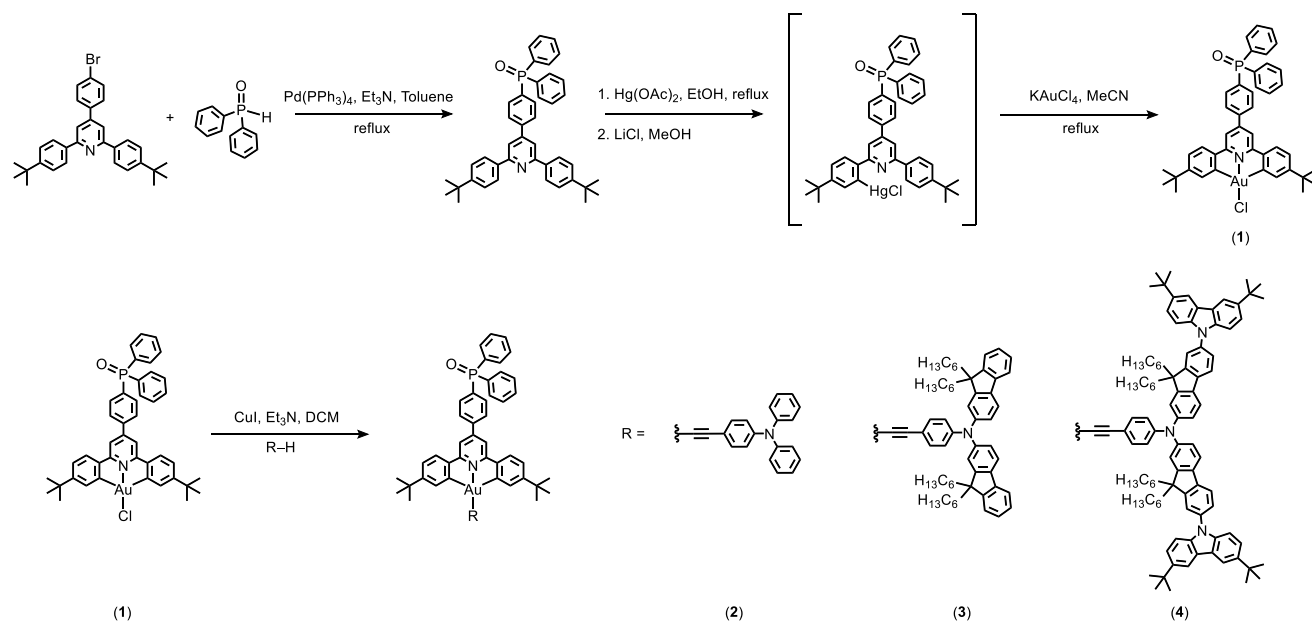
a Horiba Fluoromax-4 fluorescence spectrofluorometer equipped with a R928P PMT detector. Solid-state photophysical measurements were carried out with the solid sample loaded in a quartz tube inside a quartz-walled Dewar flask. Liquid nitrogen was placed into the optical Dewar flask for low temperature (77 K) photophysical measurements. Excited-state lifetimes of solution, solid and glass samples, in the microsecond regime, were measured using a conventional laser system. The excitation source used was the 355-nm output (third harmonic, 8 ns) of a Spectra-Physics Quanta-Ray Q-switched GCR-150 pulsed Nd:YAG laser (10 Hz). Luminescence decay signals were detected by a Hamamatsu R928 photomultiplier tube, recorded on a Tektronix Model TDS-620A (500 MHz, 2 GS s⁻¹) digital oscilloscope, and analyzed by using a program for exponential fits. The excited-state lifetimes in solution state, in the nanosecond regime, were measured with Edinburgh Instruments LP980 spectrometer, while the excited-state lifetimes of thin film samples were measured on a Hamamatsu C11367 Quantaaurus-Tau Compact Fluorescence Lifetime Spectrometer. Relative luminescence quantum yields were measured by the optical dilute method reported by Demas and Crosby.³ A degassed solution of [Ru(bpy)₃]Cl₂ in degassed acetonitrile ($\Phi_{\text{lum}}=0.06$, excitation wavelength at 436 nm) was used as the reference,³ while absolute photoluminescence quantum yields (PLQYs) of the thin films were measured on a Hamamatsu C11347 Absolute PLQY Measurement System. E₀₋₀ energy was estimated from the intersection of the UV-visible absorption spectrum and the emission spectrum at cryogenic temperature. Cyclic voltammetric measurements were performed by using a CH Instruments, Inc. model CHI 620E electrochemical analyzer. All solutions for electrochemical measurements were purged with pre-purified argon gas prior to measurement. Thermal analyses were performed with the Q50 TGA (TA instruments), in which the decomposition temperature, T_d, is defined as the temperature at which the sample shows a 5 % weight loss.

OLED Fabrication and Characterization

Solution-processable OLEDs with the configuration of indium-tin-oxide (ITO)/poly(ethylenedioxythiophene):poly(styrene sulfonic acid) (PEDOT:PSS; 70 nm)/emissive layer (60 nm)/tris(2,4,6-trimethyl-3-(pyridine-3-yl)phenyl)borane (3TPyMB; 5 nm)/1,3,5-tri[(3-pyridyl)-phen-3-yl]benzene (TmPyPB; 30 nm)/LiF (0.8 nm)/Al (100 nm) were fabricated, in which the emissive layer was formed by mixing gold(III) complex with *N,N'*-dicarbazolyl-3,5-

benzene (MCP) and 4,4',4''-tris(carbazol-9-yl)triphenylamine (TCTA) to prepare 1 mL solution in chloroform via a spin-coating technique. High-purity 3TPyMB, TmPyPB, MCP and TCTA (> 99.5 % HPLC) were purchased from Luminescence Technology Corp. and were used as received. Current density–voltage–luminance characteristics of devices were simultaneously measured by a programmable Keithley 2420 source meter and a PR-655 colorimeter. All the devices were measured under ambient conditions without encapsulation.

Synthesis and Characterization



Scheme S1. Synthetic route of cyclometalating ligands and complexes **1–4**.

Synthesis of cyclometalating ligand

A mixture of $t\text{Bu}^{\wedge}\text{N}(\text{C}_6\text{H}_4\text{Br})^{\wedge}\text{C}^t\text{Bu}$ (2.00 g, 4.00 mmol) and diphenylphosphine oxide (0.77 g, 3.80 mmol) was degassed in a two-necked flask. Anhydrous degassed toluene (50 mL) was added. $\text{Pd}(\text{PPh}_3)_4$ (0.44 g, 0.38 mmol) was added, followed by Et_3N (1.70 mL). The mixture was then refluxed. Upon completion of reaction, the mixture was concentrated. It was then purified by column chromatography to give a yellowish orange solid. The product was further recrystallized

from a solution of dichloromethane and diethyl ether to give ${}^t\text{BuC}^{\wedge}\text{N}(\text{C}_6\text{H}_4\text{P}(\text{O})\text{Ph}_2)^{\wedge}\text{C}^t\text{Bu}$ as a white solid (70 %).

${}^t\text{BuC}^{\wedge}\text{N}(\text{C}_6\text{H}_4\text{P}(\text{O})\text{Ph}_2)^{\wedge}\text{C}^t\text{Bu}$: Yield: 70 %. ${}^1\text{H}$ NMR (400 MHz, chloroform-*d*, δ / ppm): δ 8.15–8.10 (d, $J = 8.5$ Hz, 4H), 7.89–7.82 (m, 6H), 7.77–7.70 (m, 4H), 7.62–7.47 (m, 10H), 1.39 (s, 18H); ${}^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz, chloroform-*d*, δ / ppm): δ 157.76, 152.58, 149.01, 142.81, 138.25, 136.56, 133.07, 132.96, 132.29, 132.25, 132.24, 132.19, 132.00, 128.82, 128.69, 127.49, 127.36, 127.03, 125.82, 116.76, 34.86, 31.45; ${}^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, chloroform-*d*, δ / ppm): δ 28.69; MS (positive EI): m/z 619.2 [M^+]; HRMS (positive EI): calcd for $\text{C}_{43}\text{H}_{42}\text{NOP}$ [M^+]: m/z 619.2999, found m/z 619.3002.

Synthesis of chlorogold(III) complexes (1)

Chlorogold(III) complexes were synthesized by a modification of the literature method.⁴ A mixture of ${}^t\text{BuC}^{\wedge}\text{N}(\text{C}_6\text{H}_4\text{POPh}_2)^{\wedge}\text{C}^t\text{Bu}$ (1 g, 1.60 mmol) and $\text{Hg}(\text{OAc})_2$ (561 mg, 1.76 mmol) was refluxed in EtOH (20 mL) overnight. Then it was cooled to room temperature and LiCl (68 mg, 1.60 mmol, dissolved in 5 mL MeOH) was added to the mixture. The mixture was then stirred at room temperature for 30 minutes. After adding chloroform, the mixture was washed with brine and dried over anhydrous MgSO_4 . It was then filtered and concentrated. The mixture was purified by passing it through a short silica gel column with ethyl acetate as eluent. The concentrated mixture was used directly for the next step. The mixture was combined with KAuCl_4 (0.68 g, 1.80 mmol) in another round-bottomed flask and were refluxed in acetonitrile (20 mL) solution overnight. Then it was cooled down and filtered to give a yellow solid. The yellow solid was dissolved in dichloromethane and eluted through a small silica gel pad with ethyl acetate. The eluent was concentrated to give the desired product **1** as a yellow solid (53 %).

$[\text{Au}\{{}^t\text{BuC}^{\wedge}\text{N}(\text{C}_6\text{H}_4\text{P}(\text{O})\text{Ph}_2)^{\wedge}\text{C}^t\text{Bu}\}\text{Cl}]$ (**1**): Yield: 53 %. Pale yellow solid. ${}^1\text{H}$ NMR (600 MHz, dichloromethane-*d*₂, δ / ppm): δ 7.89–7.85 (m, 4H, $\text{O}=\text{P}-\text{C}_6\text{H}_4-$), 7.84 (d, $J = 2.0$ Hz, 2H, $-\text{C}_6\text{H}_3-$ of the $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 7.74–7.69 (m, 4H, $-\text{C}_6\text{H}_5$ of phosphine oxide), 7.62 (td, $J = 7.6$ Hz, 1.4 Hz, 2H, $-\text{C}_6\text{H}_5$ of phosphine oxide), 7.54 (td, $J = 7.6$ Hz, 2.8 Hz, 4H, $-\text{C}_6\text{H}_5$ of phosphine oxide), 7.45 (s,

2H, $-\text{C}_5\text{H}_2\text{N}-$ of $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 7.40 (d, $J = 8.1$ Hz, 2H, $-\text{C}_6\text{H}_3-$ of the $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 7.22 (dd, $J = 8.1$ Hz, 2.0 Hz, 2H, $-\text{C}_6\text{H}_3-$ of the $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 1.33 (s, 18H, $-\text{tBu}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, dichloromethane- d_2 , δ / ppm): δ 170.90, 165.39, 156.09, 154.90, 145.45, 140.90, 136.28, 135.61, 133.41, 133.34, 133.28, 132.76, 132.75, 132.56, 132.49, 130.88, 129.28, 129.20, 128.26, 128.18, 125.59, 124.74, 115.28, 36.00, 31.47; $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, dichloromethane- d_2 , δ / ppm): δ 27.08; HRMS (positive ESI): Found: m/z 850.2279 $[\text{M}+\text{H}]^+$. Calcd for $\text{C}_{43}\text{H}_{41}\text{NOPAuCl}$: m/z 850.2274; Elemental analyses: Found (%): C 59.68, H 4.59, N 1.83. Calcd for $\text{C}_{43}\text{H}_{40}\text{NOPAuCl}\cdot\text{H}_2\text{O}$: C 59.49, H 4.88, N 1.61; IR (KBr): 1121 cm^{-1} $\nu(\text{P}=\text{O})$.

General synthetic procedure for the synthesis of alkynylgold(III) complexes (2–4)

To a 2-necked flask was charged with $[\text{Au}\{\text{tBuC}^{\wedge}\text{N}(\text{C}_6\text{H}_4\text{P}(\text{O})\text{Ph}_2)^{\wedge}\text{C}^{\wedge}\text{tBu}\}\text{Cl}]$ (1 equiv.), alkynyl ligand (1.05 equiv.) and CuI (0.05 equiv.). The reaction mixture was degassed and then anhydrous degassed dichloromethane (50 mL/mmol chlorogold(III) compound) was added, followed by the addition of anhydrous degassed Et_3N (10 mL/mmol chlorogold(III) compound). The mixture was stirred at room temperature overnight. Then it was concentrated and purified by column chromatography to afford the target complexes.

$[\text{Au}\{\text{tBuC}^{\wedge}\text{N}(\text{C}_6\text{H}_4\text{P}(\text{O})\text{Ph}_2)^{\wedge}\text{C}^{\wedge}\text{tBu}\}(\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{NPh}_2)]$ (**2**): Yield: 90 %. Yellow solid. ^1H NMR (600 MHz, dichloromethane- d_2 , δ / ppm): δ 8.15 (d, $J = 2.1$ Hz, 2H, $-\text{C}_6\text{H}_3-$ of $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 7.90–7.83 (m, 4H, $\text{O}=\text{P}-\text{C}_6\text{H}_4-$), 7.71–7.69 (m, 2H, $-\text{C}_6\text{H}_5$ of phosphine oxide), 7.69–7.67 (m, 2H, $-\text{C}_6\text{H}_5$ of phosphine oxide), 7.62–7.58 (m, 2H, $-\text{C}_6\text{H}_5$ of phosphine oxide), 7.57–7.55 (m, 4H, $-\text{C}_6\text{H}_3-$ and $-\text{C}_5\text{H}_2\text{N}-$ of $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 7.53–7.49 (m, 4H, $-\text{C}_6\text{H}_5$ of phosphine oxide), 7.44 (d, $J = 8.6$ Hz, 2H, $-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-$), 7.32–7.27 (m, 6H, $-\text{C}_6\text{H}_5$ of triphenylamine and $-\text{C}_6\text{H}_3-$ of $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 7.12 (d, $J = 7.3$ Hz, 4H, $-\text{C}_6\text{H}_5$ of triphenylamine), 7.06 (t, $J = 7.3$ Hz, 2H, $-\text{C}_6\text{H}_5$ of triphenylamine), 6.99 (d, $J = 8.6$ Hz, 2H, $-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-$), 1.37 (s, 18H, $-\text{tBu}$); $^{13}\text{C}\{^1\text{H}\}$ NMR (150 MHz, dichloromethane- d_2 , δ / ppm): δ 167.61, 165.50, 155.87, 154.46, 148.10, 147.36, 146.89, 141.59, 136.02, 135.35, 133.87, 133.41, 133.34, 133.28, 132.71, 132.53, 132.47, 129.87, 129.26, 129.18, 128.18, 128.10, 125.59, 125.22, 124.37, 123.70, 123.42, 120.79, 115.26, 101.69, 92.10, 35.83, 31.52; $^{31}\text{P}\{^1\text{H}\}$

NMR (162 MHz, dichloromethane- d_2 , δ / ppm): δ 26.82; MS (positive MALDI): m/z 1083.395 [M+H]⁺; Elemental analyses: Found (%): C 69.06, H 5.11, N 2.52. Calcd for C₆₃H₅₄N₂OPAu•0.5H₂O: C 69.29, H 5.08, N 2.57; IR (KBr): 1121 cm⁻¹ ν (P=O), 2146 cm⁻¹ ν (C≡C).

[Au{^tBuC^N(C₆H₄P(O)Ph₂)^CBu} {C≡C–C₆H₄–N(C₁₃H₇(C₆H₁₃)₂)}] (**3**): Yield: 80 %. Orange solid. ¹H NMR (600 MHz, tetrahydrofuran- d_8 , δ / ppm): δ 8.23 (d, J = 2.2 Hz, 2H, –C₆H₃– of C^NC), 8.05 (dd, J = 8.2 Hz, 2.2 Hz, 2H, O=P–C₆H₄–), 7.94–7.88 (m, 4H, –C₅H₂N– of C^NC and O=P–C₆H₄–), 7.78–7.72 (m, 6H, –C₆H₅ of phosphine oxide and –C₆H₃– of C^NC), 7.66 (d, J = 7.4 Hz, 2H, –C₁₃H₇(C₆H₁₃)₂–), 7.64 (d, J = 8.2 Hz, 2H, –C≡C–C₆H₄–), 7.57 (td, J = 7.5 Hz, 1.4 Hz, 2H, –C₆H₅ of phosphine oxide), 7.50 (td, J = 7.5 Hz, 2.7 Hz, 4H, –C₆H₅ of phosphine oxide), 7.45 (d, J = 8.7 Hz, 2H, –C₁₃H₇(C₆H₁₃)₂–), 7.34 (d, J = 7.4 Hz, 2H, –C₁₃H₇(C₆H₁₃)₂–), 7.31–7.25 (m, 6H, –C₆H₃– of C^NC and –C₁₃H₇(C₆H₁₃)₂–), 7.22 (t, J = 7.4 Hz, 2H, –C₁₃H₇(C₆H₁₃)₂–), 7.11–7.06 (m, 4H, –C≡C–C₆H₄– and –C₁₃H₇(C₆H₁₃)₂–), 1.99–1.90 (m, 8H, –CH₂– and –CH₃), 1.38 (s, 18H, –^tBu), 1.21–1.07 (m, 24H, –CH₂–), 0.84–0.61 (m, 20H, –CH₂– and –CH₃); ¹³C{¹H} NMR (150 MHz, tetrahydrofuran- d_8 , δ / ppm): δ 168.48, 166.20, 155.47, 155.16, 152.93, 151.37, 148.00, 147.84, 147.74, 142.11, 141.80, 137.64, 137.34, 136.68, 135.01, 134.33, 134.30, 133.65, 133.58, 133.46, 132.93, 132.87, 132.68, 132.66, 129.42, 129.34, 128.63, 128.55, 127.70, 127.22, 126.13, 124.41, 123.71, 123.50, 122.15, 121.35, 120.01, 119.94, 115.67, 101.37, 93.24, 55.98, 41.19, 36.05, 32.63, 31.70, 30.71, 24.82, 23.50, 14.54; ³¹P{¹H} NMR (162 MHz, tetrahydrofuran- d_8 , δ / ppm): δ 23.61; MS (positive MALDI): m/z 1594.814 [M+H]⁺; Elemental analyses: Found (%): C 75.37, H 7.10, N 1.94. Calcd for C₁₀₁H₁₁₀N₂OPAu•0.5H₂O: C 75.59, H 7.10, N 1.94; IR (KBr): 1121 cm⁻¹ ν (P=O), 2146 cm⁻¹ ν (C≡C).

[Au{^tBuC^N(C₆H₄P(O)Ph₂)^CBu} {C≡C–C₆H₄–N(C₁₃H₆(C₆H₁₃)₂–(^tBuCbz))₂}] (**4**): Yield: 77 %. Orange solid. ¹H NMR (500 MHz, dichloromethane- d_2 , δ / ppm): δ 8.22 (d, J = 2.0 Hz, 2H, –C₆H₃– of C^NC), 8.18 (d, J = 1.9 Hz, 4H, –C₁₂H₆N–), 7.90–7.85 (m, 6H, –C₁₃H₇(C₆H₁₃)₂–, O=P–C₆H₄– and –C₅H₂N– of C^NC), 7.73–7.69 (m, 6H, –C₁₃H₇(C₆H₁₃)₂– and –C₆H₅ of phosphine oxide), 7.64–7.59 (m, 6H, –C₆H₅ of phosphine oxide and –C₆H₃– of C^NC), 7.55–7.49 (m, 14H,

$-\text{C}_{12}\text{H}_6\text{N}-$, $-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-$, $\text{O}=\text{P}-\text{C}_6\text{H}_4-$ and $-\text{C}_6\text{H}_5$ of phosphine oxide), 7.41 (d, $J = 8.7$ Hz, 4H, $-\text{C}_{12}\text{H}_6\text{N}-$), 7.36–7.32 (m, 4H, $-\text{C}_{13}\text{H}_7(\text{C}_6\text{H}_{13})_2-$ and $-\text{C}_6\text{H}_3-$ of $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 7.18 (d, $J = 9.4$ Hz, 4H, $-\text{C}_{13}\text{H}_7(\text{C}_6\text{H}_{13})_2-$ and $-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-$), 2.03–1.91 (m, 8H, $-\text{CH}_2-$), 1.48 (s, 36H, $-\text{tBu}$ of carbazole), 1.40 (s, 18H, $-\text{tBu}$ of $\text{C}^{\wedge}\text{N}^{\wedge}\text{C}$), 1.24–1.13 (m, 24H, $-\text{CH}_2-$), 0.87–0.77 (m, 20H, $-\text{CH}_2-$ and $-\text{CH}_3$); $^{13}\text{C}\{^1\text{H}\}$ NMR (125 MHz, dichloromethane- d_2 , δ / ppm): δ 167.71, 165.64, 156.01, 154.53, 153.15, 153.02, 147.66, 147.59, 146.97, 143.40, 141.63, 140.48, 140.00, 136.79, 136.48, 133.96, 133.49, 133.41, 132.76, 132.74, 132.66, 132.59, 132.51, 129.30, 129.21, 128.15, 128.05, 125.93, 125.63, 124.48, 124.34, 124.21, 123.79, 123.40, 121.97, 121.15, 120.88, 120.65, 119.86, 116.84, 115.26, 109.87, 101.81, 92.33, 56.04, 40.81, 35.89, 35.22, 32.35, 32.27, 31.56, 30.26, 24.61, 23.17, 14.50; $^{31}\text{P}\{^1\text{H}\}$ NMR (202 MHz, dichloromethane- d_2 , δ / ppm): δ 26.80; MS (positive MALDI): m/z 2150.176 $[\text{M}+\text{H}]^+$; Elemental analyses: Found (%): C 78.04, H 7.35, N 2.60. Calcd for $\text{C}_{141}\text{H}_{156}\text{N}_4\text{OPAu}\cdot\text{H}_2\text{O}$: C 78.09, H 7.34, N 2.58; IR (KBr): 1118 cm^{-1} $\nu(\text{P}=\text{O})$, 2145 cm^{-1} $\nu(\text{C}\equiv\text{C})$.

Figures and Tables

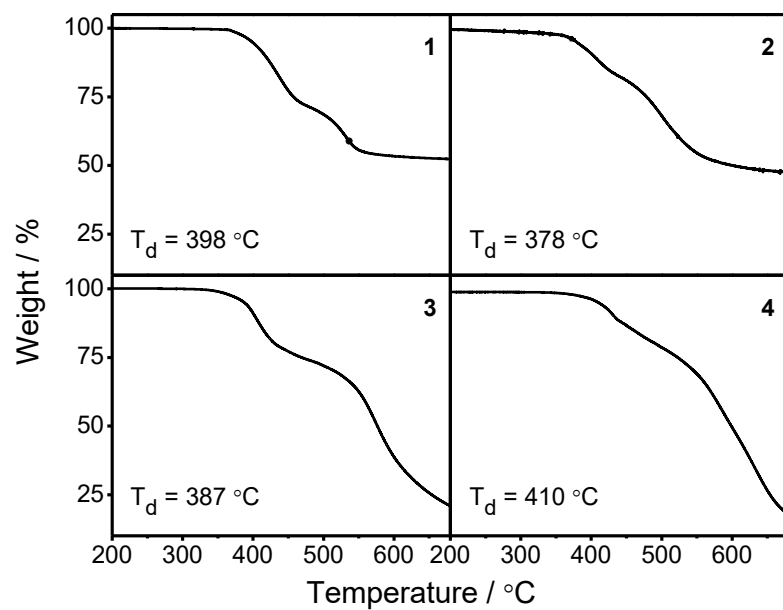


Figure S1. Thermogravimetric analysis (TGA) traces of complexes 1–4.

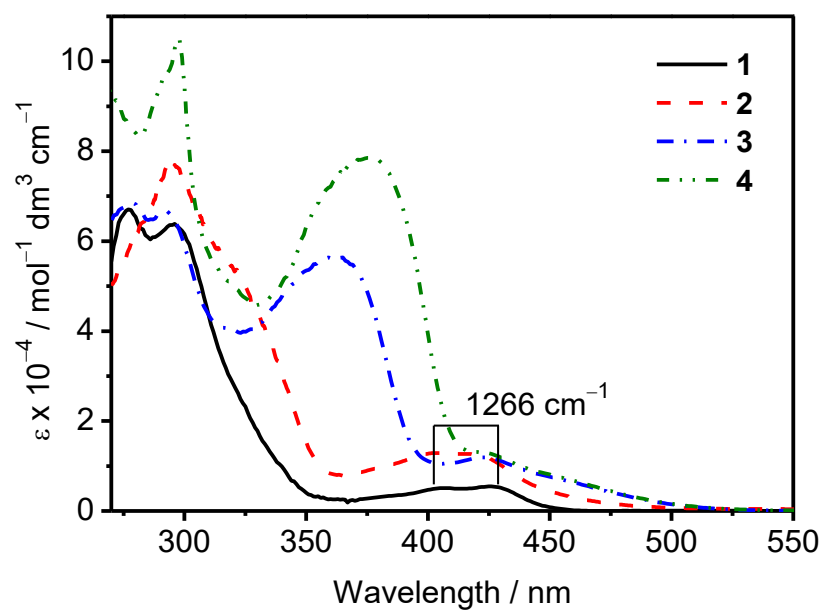


Figure S2. UV-Visible spectra for complexes 1–4 in dichloromethane solution at 298 K.

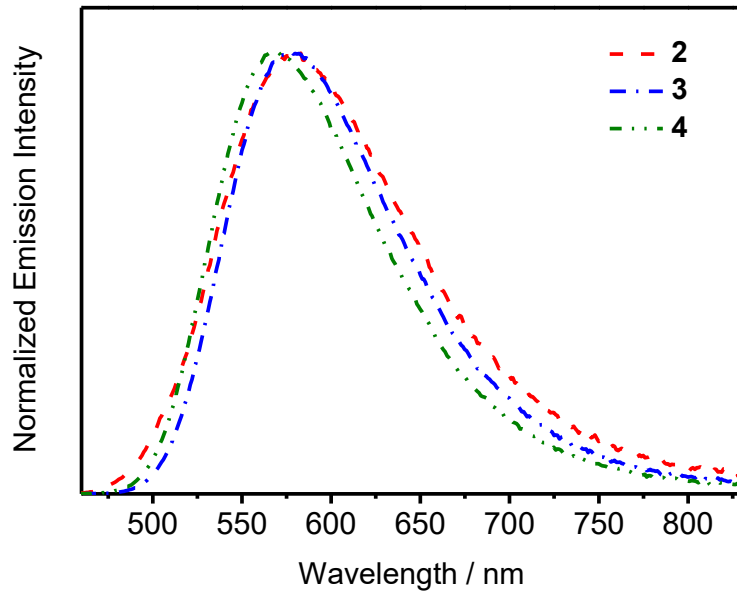


Figure S3. Emission spectra for complexes **2–4** in degassed toluene solution at 298 K.

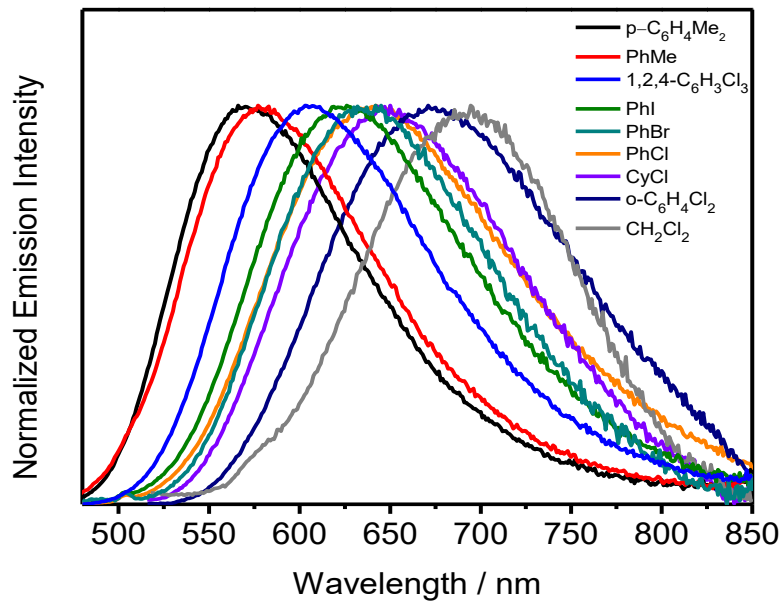


Figure S4. Solvent-dependent emission spectra of complex **2** at 298 K.

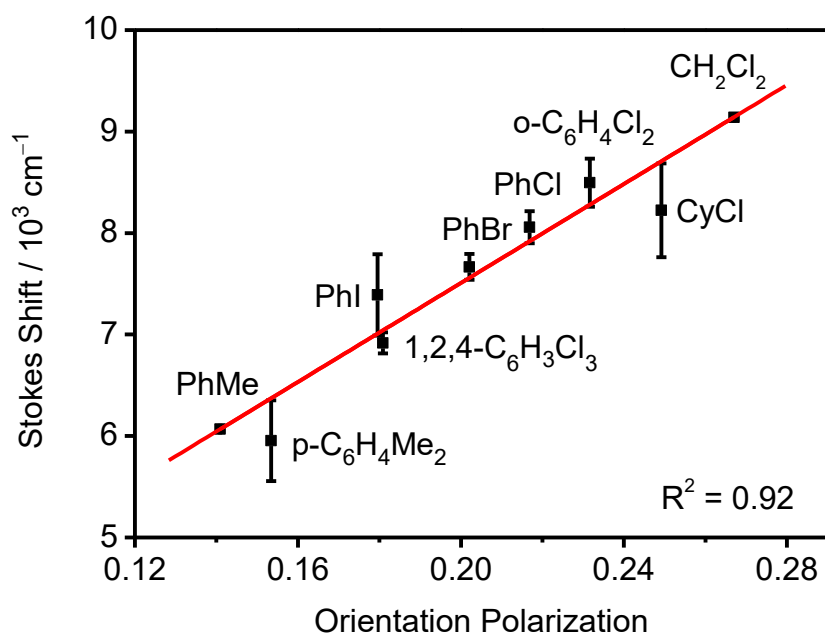


Figure S5. Lippert-Mataga plot for complex **2** at 298K.

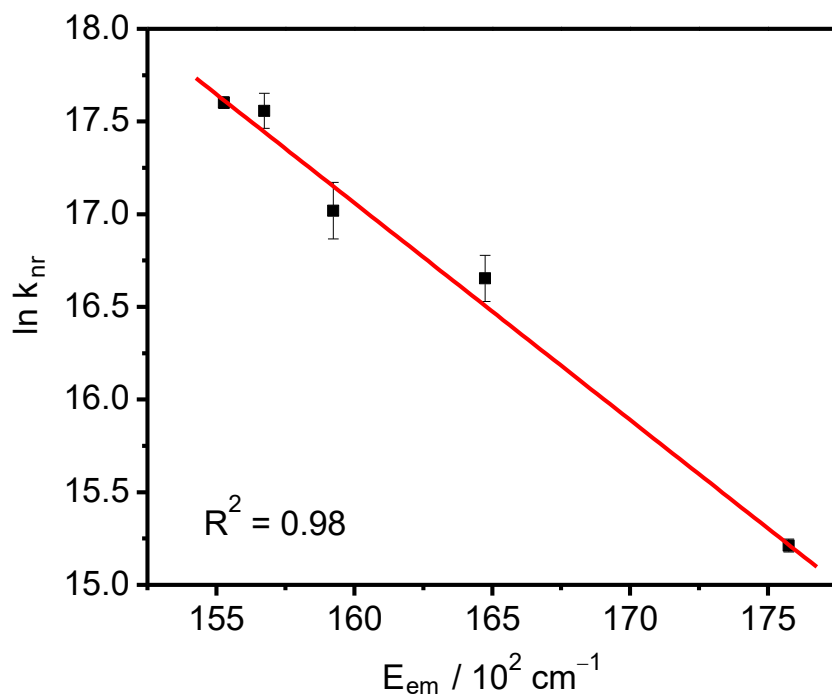


Figure S6. Plot of $\ln k_{nr}$ vs. E_{em} of complex **2** at 298 K.

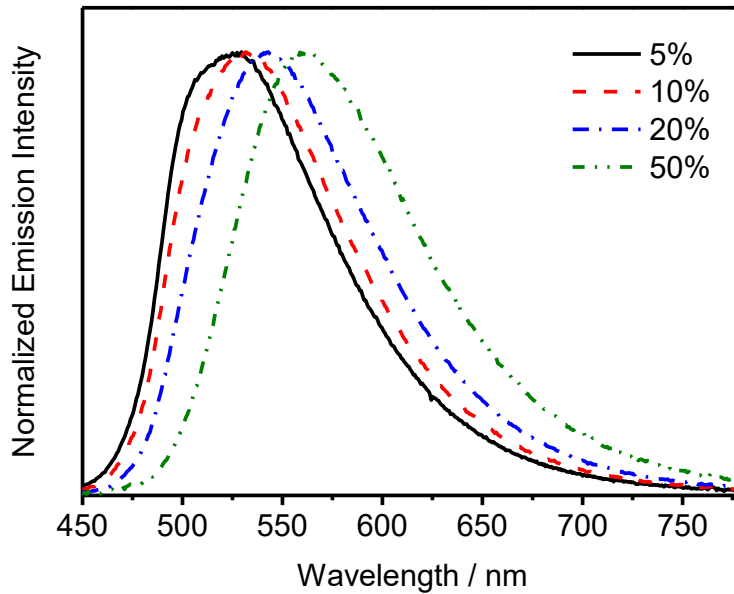


Figure S7. Concentration-dependent thin-film emission spectra of complex **2** doped in MCP:TCTA (w/w = 3:1) at 298 K.

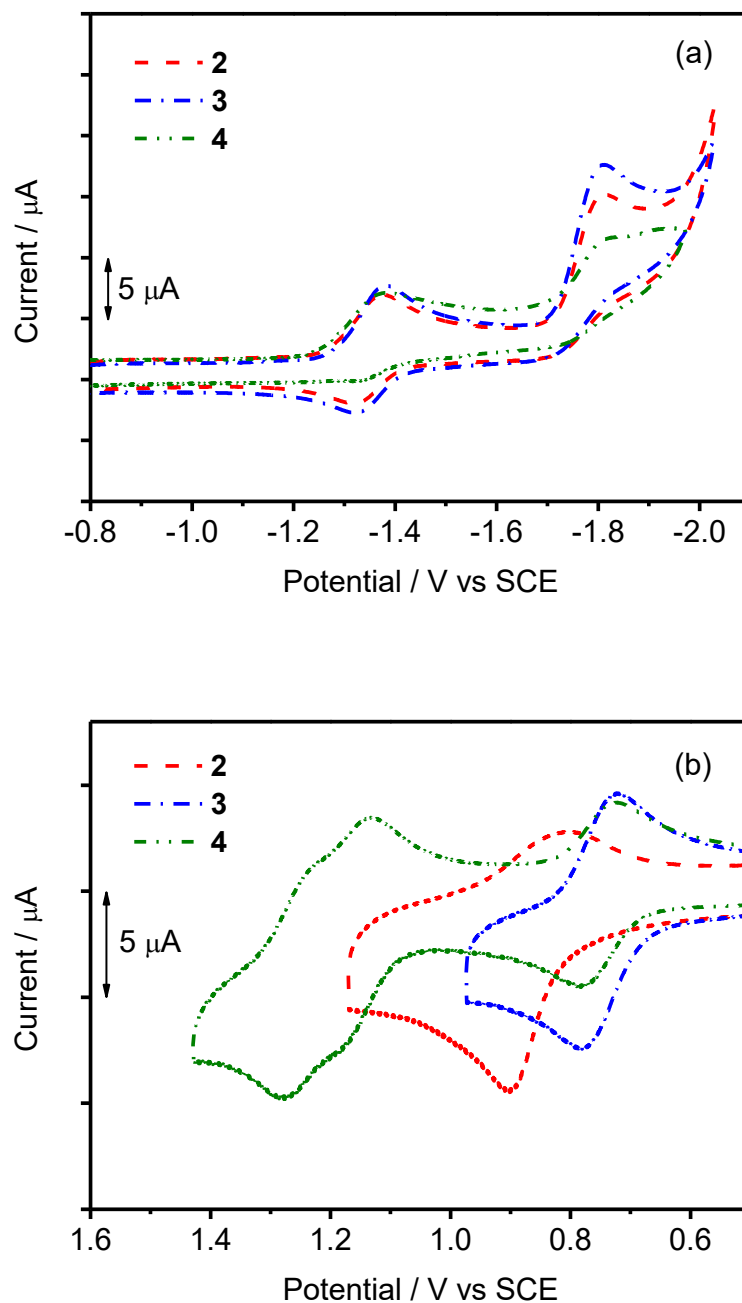


Figure S8. Cyclic voltamograms for the (a) reduction scan and (b) oxidation scan of complexes 2–4 in dichloromethane (0.1 M $n\text{BuN}_4\text{PF}_6$).

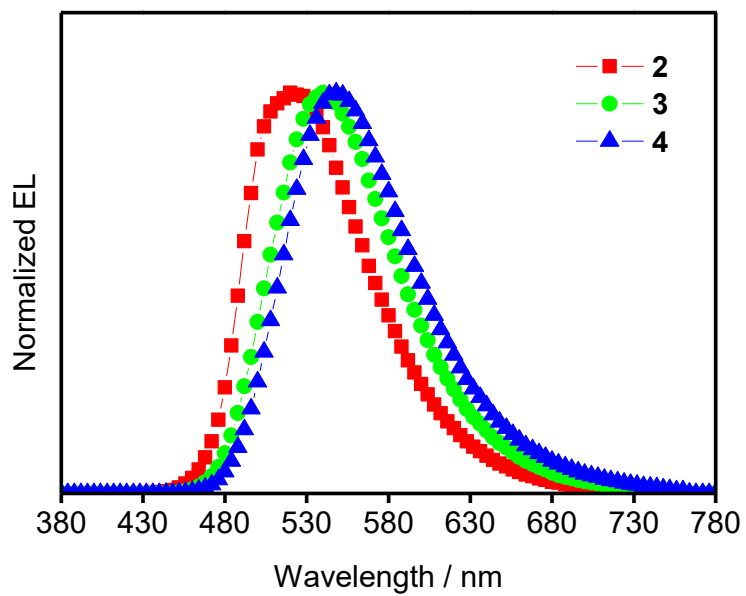


Figure S9. Normalized EL spectra of devices doped with 20 wt% complexes **2–4**.

Table S1. Photophysical properties of complexes **1–5**

Complex	Absorption $\lambda_{\max} / \text{nm}$ ($\epsilon_{\max} / \text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	Medium (Temperature / K)	Emission $\lambda_{\max} / \text{nm}$ ($\tau_0 / \mu\text{s}$) [τ_0 / ns]	Φ_{PL} (soln) ^a	Φ_{PL} (film) ^b
1	277 (67105), 297 (63370), 404 (5130), 425 (5800)	CH ₂ Cl ₂ (298)	Non-emissive	--	--
		Glass (77) ^{c,d} Solid (298) Solid (77)	491, 515, 553, 602 sh (230) Non-emissive 517, 554, 601 sh (15)		
2	296 (76550), 320 sh (55220), 403 (12970), 422 (12175) 328 sh (23180), 400 (5620), 424 (5620)	CH ₂ Cl ₂ (298)	692 (< 0.1)	1 × 10 ⁻³	
		Toluene (298)	580 (< 0.1)	0.22	
		<i>p</i> -Xylene (298)	569 [198]	0.20	
		Chlorobenzene (298)	644 [22]	0.03	
		<i>o</i> -Dichlorobenzene (298)	675 (< 0.1)	0.01	
		1,2,4-Trichlorobenzene (298)	607 [55]	0.06	
		Chlorocyclohexane (298)	651 (< 0.1)	0.01	
		Bromobenzene (298)	638 [23]	0.03	
		Iodobenzene (298)	628 [39]	0.04	
		Glass (77) ^{c-e}	489, 510, 546, 599 sh (62, 144)		
		Solid (298)	595 (0.1)		
		Solid (77)	574 (2.6)		
		Thin Film (298)			0.60
		5 % in MCP:TCTA ^f	525 (9.9)		0.62
10 % in MCP:TCTA ^f	532 (7.2)		0.60		
20 % in MCP:TCTA ^f	542 (3.9)		0.46		
50 % in MCP:TCTA ^f	563 (0.7)				

3	278 (67870), 292 (66500), 363 (55660), 424 (12260) 362 (47730), 426 (8780), 460 sh (5270)	CH ₂ Cl ₂ (298)	720 (< 0.1)	6×10 ⁻²
		Toluene (298)	580 (< 0.1)	0.37
		Glass (77) ^{d,e}	552 (87, 382)	
		Solid (298)	599 (0.1)	
		Solid (77)	586 (1.3)	
		Thin Film (298)		
		5 % in MCP:TCTA ^f	537 (5.7)	0.65
		10 % in MCP:TCTA ^f	545 (2.2)	0.74
		20 % in MCP:TCTA ^f	558 (0.9)	0.63
4	297 (105310), 376 (79060), 426 sh (13080) 375 (73340), 428 (11240), 461 sh (6230)	50 % in MCP:TCTA ^f	579 (0.4)	0.55
		CH ₂ Cl ₂ (298)	Non-emissive	
		Toluene (298)	566 (< 0.1)	0.48
		Glass (77) ^{d,e}	556 (60, 283)	
		Solid (298)	601 (0.2)	
		Solid (77)	591 (2.7)	
		Thin Film (298)		
		5 % in MCP:TCTA ^f	533 (3.9)	0.68
		10 % in MCP:TCTA ^f	542 (3.0)	0.70
20 % in MCP:TCTA ^f	550 (1.4)	0.72		
50 % in MCP:TCTA ^f	566 (0.5)	0.60		

^a Relative luminescence quantum yield, measured at room temperature using degassed acetonitrile solution of [Ru(bpy)₃]Cl₂ as reference (excitation wavelength = 436 nm, Φ_{lum} = 0.06).

^b Absolute luminescence quantum yield of thin films was measured with 350 nm excitation.

^c Vibronic-structured emission band.

^d Measured in EtOH-MeOH-CH₂Cl₂ (40:10:1, v/v).

^e Double-exponential decay.

^f In MCP:TCTA (3:1, w/w).

Table S2. Electrochemical data for **2–4**^a

Compound	Oxidation $E_{1/2}$ / V vs SCE ^b (ΔE_p / mV)	Reduction $E_{1/2}$ / V vs SCE ^b [E_{pc} / V vs SCE ^c] (ΔE_p / mV)	E_{HOMO} / eV ^d	E_{LUMO} / eV ^d
2	+0.92 (87)	-1.35 (60), [-1.81]	-5.72	-3.45
3	+0.75 (63)	-1.35 (66), [-1.81]	-5.55	-3.45
4	+0.75 (61), +1.15 (63), +1.25 (61)	-1.35 (67), [-1.81]	-5.55	-3.45

^a Working electrode: glassy carbon, scan rate = 100 mV s⁻¹

^b $E_{1/2} = (E_{pa} + E_{pc})/2$; E_{pa} and E_{pc} are the peak anodic and peak cathodic potentials respectively.

$$\Delta E_p = (E_{pa} - E_{pc}).$$

^c E_{pc} refers to the cathodic peak potential for irreversible reductions.

^d E_{HOMO} and E_{LUMO} were calculated from electrochemical potentials with the formula,

$$E_{\text{HOMO}} = -e(4.8 \text{ V} + E_{1/2}^{\text{ox}}); E_{\text{LUMO}} = -e(4.8 \text{ V} + E_{1/2}^{\text{red}}).$$

Table S3. Key parameters of devices based on **2–4** doped in MCP:TCTA (w/w = 3:1) at different concentrations

Complex	Dopant concentration / wt%	Max. current efficiency / cd A^{-1}	Max. power efficiency / lm W^{-1}	Max. EQE / %	$\lambda_{\text{max}} / \text{nm}^a$
2	5	33.5	19.1	10.2	520 (0.30, 0.58)
	10	36.5	22.9	11.1	521 (0.31, 0.58)
	20	51.6	35.9	15.3	540 (0.37, 0.58)
	50	23.6	16.1	7.6	558 (0.44, 0.54)
3	5	49.2	39.0	14.3	541 (0.37, 0.58)
	10	37.0	28.1	11.1	556 (0.40, 0.56)
	20	33.6	25.5	10.6	563 (0.43, 0.55)
	50	27.3	23.1	9.9	577 (0.49, 0.50)
4	5	21.0	14.4	6.2	547 (0.38, 0.56)
	10	24.7	20.4	7.5	553 (0.39, 0.56)
	20	32.0	27.5	9.8	557 (0.40, 0.56)
	50	23.6	21.0	7.8	568 (0.46, 0.53)

^a CIE coordinates in parentheses, measured at 100 cd m^{-2} .

References

1. F. Kröhnke, *Synthesis*, 1976, **1976**, 1.
2. C.-H. Lee, M.-C. Tang, Y.-C. Wong, M.-Y. Chan and V. W.-W. Yam, *J. Am. Chem. Soc.*, 2017, **139**, 10539.
3. G. A. Crosby and J. N. Demas, *J. Phys. Chem.*, 1971, **75**, 991.
4. (a) K. M.-C. Wong, X. Zhu, L.-L. Hung, N. Zhu, V. W.-W. Yam and H.-S. Kwok, *Chem. Commun.*, 2005, 2906; (b) K. M.-C. Wong, L.-L. Hung, W. H. Lam, N. Zhu and V. W.-W. Yam, *J. Am. Chem. Soc.*, 2007, **129**, 4350; (c) K.-H. Wong, K.-K. Cheung, M. C.-W. Chan and C.-M. Che, *Organometallics*, 1998, **17**, 3505.