Luminescent Cyclometalated Platinum(II) Complex and its Green Organic Light Emitting Device with High Device Performance

Anthony Yiu-Yan Tam, Daniel Ping-Kuen Tsang, Mei-Yee Chan*, Nianyong Zhu and Vivian Wing-Wah Yam*

Electronic Supplementary Information

Experimental:

Synthesis of 1,3-bis(*N*-butyl-benzimidazol-2-yl)benzene (L1)

To a solution of 2,6-bis(benzimidazol-2'-yl)benzene (1 g, 3.22 mmol) and sodium hydride (oil dispersion, 60 %, 0.31 g, 12.89 mmol) in DMF was added 1-bromobutane (1.4 ml, 12.89 mmol). The resultant mixture was stirred at 100 °C for overnight under an inert atmosphere of nitrogen. After solvent removal *in vacuo*, the residue was redissolved in $CHCl_3$, washed with water (3 × 30 ml), and then dried over anhydrous Na_2SO_4. After filtration and removal of the solvent, the residue was purified by column chromatography on silica gel using $CHCl_3$ as the eluent to give the pure product as a yellow oil. Yield: 1.1 g (80 %). ^1H NMR (400 MHz, $CDCl_3$): δ 0.85 (t, J = 7.33 Hz, 6H, $-CH_3$), 1.26 (m, 4H, $-CH_2-$), 1.80 (m, 6H, $-CH_2-$), 4.29 (t, J = 7.33 Hz, 6H, $-NCH_2-$), 7.34 (m, 4H, benzimidazolyl H), 7.44 (m, 2H, benzimidazolyl H), 7.71 (t, J = 7.72 Hz, 1H, $-C_6H_4-$), 7.84 (m, 2H, benzimidazolyl H), 7.88 (dd, J = 1.58, 7.72 Hz, 2H, $-C_6H_4-$), 8.06 (t, J = 1.58 Hz, 1H, $-C_6H_4-$). Positive FAB–MS: m/z 423 $[M + H]^+$.

Synthesis of Complex 1

To a solution of **L1** (1.65 g, 2.53 mmol) in glacial acetic acid (10 ml) was added K_2PtCl_4 (0.7 g, 1.69 mmol) in deionized water (3 ml). The resultant red suspension was heated under reflux for 3 days. Upon cooling, the greenish yellow suspension was filtered and the solid was washed with deionized water, methanol, and diethyl ether to yield a greenish yellow solid. Yellow single crystals suitable for X-ray crystallography were obtained by layering of *n*-hexane onto a dichloromethane solution of the complex. Yield: 0.68 g (62 %). ^1H NMR (400 MHz, $CDCl_3$): δ 0.97 (t, J = 7.30 Hz, 6H, $-CH_3$), 1.44 (m, 4H, $-CH_2-$), 1.90 (m, 4H, $-CH_2-$), 4.49 (t, J = 7.30 Hz, 4H, $-CH_2-$), 7.21 (m, 4H, benzimidazolyl H), 7.35 (m, 6H, benzimidazolyl and $-C_6H_3-$), 9.00 (d, *J* = 7.86 Hz, 2H, benzimidazolyl H). Positive FAB–MS: m/z 616 $[M - Cl]^+$. Anal. Calcd for $C_{28}H_{29}N_4ClPt\cdot 0.5CH_2Cl_2$: C, 49.76; H, 4.41; N, 7.88. Found: C, 49.28; H, 4.35; N, 8.07.

Crystal Structure Determination for $\mathbf{1\cdot 0.5CH_2Cl_2}$: Single crystals of complex **1** suitable for X-ray diffraction studies were grown by layering of *n*-hexane onto a dichloromethane solution of the complex. The X-ray diffraction data were collected on a MAR diffractometer using graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å). Raw frame data were integrated with SAINT[1] program. Semi-empirical absorption correction with SADABS[2] was applied.

The structure was solved by direct methods employing SHELXS-97 program[3] on PC. Pt, Cl and many non-H atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using program SHELXL-97[4] on PC. There were two formula units in the asymmetric unit. One dichloromethane solvent molecule was located with disorderness, which is in the mode of rotation along C atom.

According to the SHELXL-97 program,[4] all 10207 independent reflections (R_{int}[5] equal to 0.0273, 8324 reflections larger than $4\sigma(F_o)$) from a total 31836 reflections were participated in the full-matrix least-square refinement against F^2. These reflections were in the range $-14 \le h \le 16$, $-20 \le k \le 20$, $-29 \le l \le 29$ with $2\theta_{\max}$ equal to 51.36°.

One crystallographic asymmetric unit consists of two formula units. In the final stage of least-squares refinement, all non-H atoms were refined anisotropically. H atoms were generated by program SHELXL-97.[4] The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final *R*-indices.[6]

Convergence ($(\Delta/\sigma)_{max}$ = 0.001, av. 0.001) for 658 variable parameters by full-matrix least-squares refinement on F^2 reaches to R_1 = 0.0264 and wR_2 = 0.0641 with a goodness-of-fit of 1.034, the parameters a and b for weighting scheme are 0.0418 and 0.4442. The final difference Fourier map shows maximum rest peaks and holes of 2.103 (near Pt atom) and –0.749 eÅ^{-3} respectively.

Crystal data for **1·0.5CH_2Cl_2**: $C_{28}H_{29}ClN_4Pt\cdot 0.5CH_2Cl_2$, M_r = 694.55, crystal dimensions 0.43 mm × 0.19 mm × 0.14 mm, monoclinic, space group $P2_1/c$, a = 13.3920(13) Å, b = 16.6100(17) Å, c = 24.535(2) Å, β = 98.78(1)°, V = 5393.6(9) Å^3, Z = 8, density = 1.711 g cm^{-3}, μ(Mo-K$_\alpha$) = 5.426 mm^{-1}, $F(000)$ = 2728, T = 301 K. Final R = 0.0264, wR = 0.0641 with $I > 2\sigma(I)$; R_2 = 0.0390, wR_2 = 0.0706 for all data; GOF = 1.034 for 658 variable parameters and a total of 31836 reflections, of which 10207 reflections were independent (R_{int} = 0.0273) and 8324 reflections were larger than $4\sigma(F_o)$. θ range for data collection of 1.97° to 51.36°. CCDC-767389 (**1·0.5CH_2Cl_2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Physical Measurements and Instrumentation

^{1}H NMR spectra were recorded on a Bruker AVANCE 400 (400 MHz) Fourier-transform NMR spectrometer with chemical shifts reported relative to tetramethylsilane, $(CH_3)_4Si$. Positive ion FAB mass spectra were recorded on a Finnigan MAT95 mass spectrometer. IR spectra were obtained as Nujol mulls on KBr disks on a Bio-Rad FTS-7 Fourier transform infrared spectrophotometer (4000–400 cm^{-1}). Elemental analyses of the newly synthesized complex were preformed on a Flash EA 1112 elemental analyzer at the Institute of Chemistry, Chinese Academy of

Sciences in Beijing.

The electronic absorption spectra were obtained using a Hewlett-Packard 8452A diode array spectrophotometer. The concentrations of solution samples for electronic absorption measurements were typically in the range of 2×10^{-4} to 2×10^{-5} mol dm^{-3}. Steady state excitation and emission spectra at room temperature were recorded on a Spex Fluorolog-2 Model F111 fluorescence spectrofluorometer. All solutions for photophysical studies were degassed on a high-vacuum line in a two-compartment cell consisting of a 10-ml Pyrex bulb and a 1-cm path length quartz cuvette and sealed from the atmosphere by a Bibby Rotaflo HP6 Teflon stopper. The solutions were rigorously degassed with at least four successive freeze-pump-thaw cycles. Emission lifetime measurements were performed using a conventional laser system. The excitation source used was a 355-nm output (third harmonic) of a Spectra-Physics Quanta-Ray Q-switched GCR-150-10 pulsed Nd-YAG laser. Luminescence decay signals were detected by a Hamamatsu R928 PMT and recorded on a Tektronix Model TDS-620A (500 MHz, 2 GS/s) digital oscilloscope and analyzed using a program for exponential fits. Luminescence quantum yields were measured by the optical dilute method reported by Demas and Crosby.[7] An aqueous solution of quinine sulphate in 1.0 N H_2SO_4 ($\phi = 0.55$, excitation wavelength at 365 nm) was used as the reference.[8] The photoluminescence quantum yield of the thin film was measured on a Hamamatsu C9920-03 Absolute PL Quantum Yield Measurement System,[9] in which the thin film was prepared by spin-coating the solution of **1** (6 wt%) doped into poly(methyl methacrylate).

Cyclic voltammetric measurements were performed by using a CH Instruments, Inc. model CHI 620A electrochemical analyzer. Electrochemical measurements were performed in dichloromethane solution with 0.1 mol dm^{-3} $^{n}Bu_4NPF_6$ (TBAH) as supporting electrolyte at room temperature. The reference electrode was a Ag/$AgNO_3$

(0.1 mol dm^{-3} in acetonitrile) electrode and the working electrode was a glassy carbon electrode (CH Instruments, Inc.) with a platinum wire as the counter electrode. The working electrode surface was first polished with 1 μm alumina slurry (Linde) on a microcloth (Buehler Co.) and then with 0.3 μm alumina slurry. It was then rinsed with ultra-pure deionized water and sonicated in a beaker containing ultra-pure water for five minutes. The polishing and sonicating steps were repeated twice and then the working electrode was finally rinsed under a stream of ultra-pure deionized water. The ferrocenium/ferrocene couple ($FeCp_2^{+/0}$) was used as the internal reference.[10] All solutions for electrochemical studies were deaerated with pre-purified argon gas prior to measurements.

OLED Fabrication and Characterization

Patterned indium-tin-oxide (ITO)-coated glass substrates (30 Ω/□) were cleaned with Decon 90, rinsed in deionized water, then dried in an oven, and finally treated in an ultraviolet-ozone chamber. PHOLEDs were fabricated with a hole-transporting NPB layer, a carrier confinement TCTA layer, and an electron-transporting BAlq layer; while complex **1** was doped into CBP layer as EML. All organic materials were used as purchased and all the films were sequentially deposited by thermal evaporation in a Trovato high vacuum deposition chamber without vacuum break. A shadow mask was used to define the cathode and to make four 0.1 cm^2 devices on each substrate. Deposition rates were controlled by a quartz oscillating thickness monitor to be 1–2 Å/s for the organic materials and metals. The current density–voltage–luminance (J–V–L) characteristics and EL spectra were measured simultaneously with a programmable Keithley model 2420 power source and a Photoresearch PR655 colorimeter. All measurements were carried out in air at room temperature.

Ultraviolet Photoelectron Spectroscopy

For the UPS study, the specimen was analyzed in a VG ESCALAB 220i-XL surface analysis system which had a base pressure of 5×10^{-10} mbar, in which the UPS spectrum was recorded with a sample bias of –4.0 V to allow the observation of the inelastic electron cut-off.

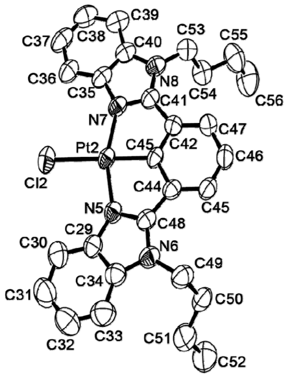


Figure S1 Perspective drawing of one of the two independent molecules of complex **1** with atomic numbering. Hydrogen atom and solvent molecules are omitted for clarity. Thermal ellipsoids were shown at 40 % probability level.

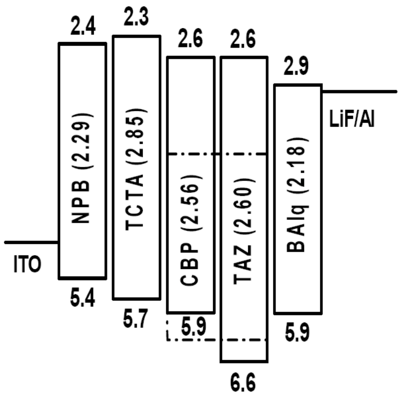
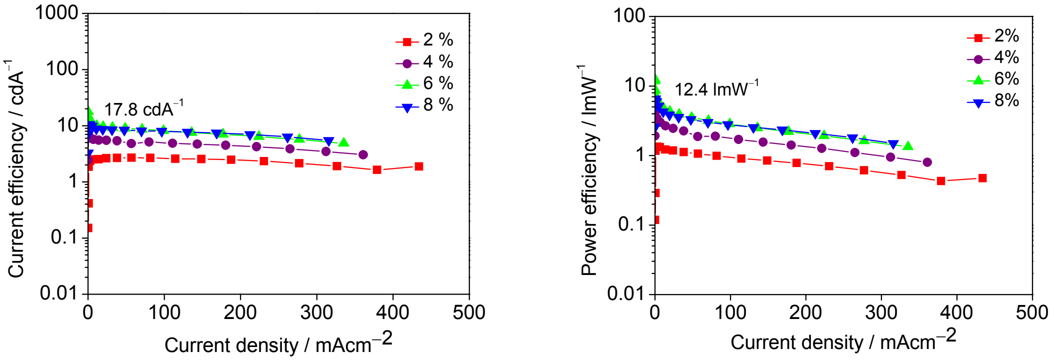
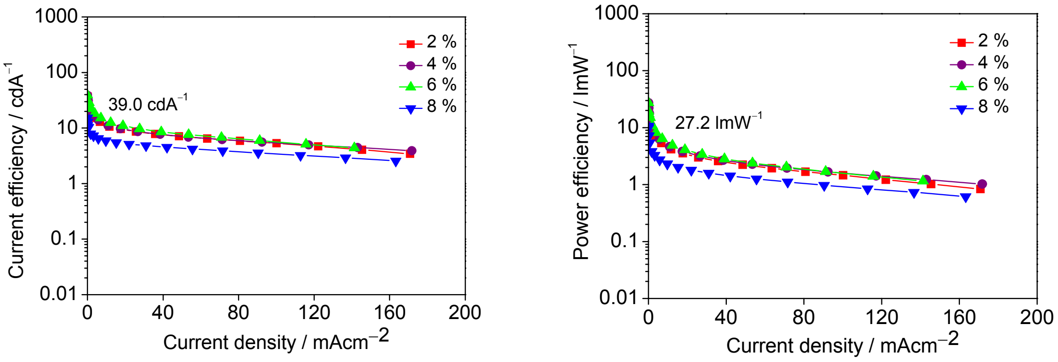


Figure S2 Proposed energy level diagram of the OLED. Numbers indicate the respective HOMO and LUMO energies relative to the vacuum level as well as the triplet energy levels (in parentheses) in eV. HOMO and LUMO energies of **1** are indicated with dotted lines.



(a) (b)

Figure S3 (a) Current efficiency and (b) power efficiency of the devices with the configuration of ITO/NPB (70 nm)/TCTA (5 nm)/**1**:CBP (30 nm)/BAlq (30 nm)/LiF (0.8 nm)/Al (200 nm) with different concentrations of **1** (2, 4, 6 and 8 %) as phosphorescent guest doped into CBP layer.



(a) (b)

Figure S4 (a) Current efficiency and (b) power efficiency of the devices with the configuration of ITO/NPB (70 nm)/TCTA (5 nm)/6 % **1**:CBP (30 nm)/**1**:TAZ (10 nm)/BAlq (30 nm)/LiF (0.8 nm)/Al (200 nm) with different concentrations of **1** (2, 4, 6 and 8 %) as phosphorescent guest doped into TAZ layer.

References:

1 SAINT+. SAX area detector integration program. Version 7.34A. Bruker AXS, Inc. Madison, WI.

2 G. M. Sheldrick, SADABS, Empirical Absorption Correction Program. University of Göttingen: Göttingen, Germany, 2004.

3 SHELXS97, Sheldrick, G. M. (1997). SHELX97. Programs for Crystal Structure Analysis (Release 97-2). University of Goetingen, Germany.

4 SHELXL97, Sheldrick, G. M. (1997). SHELX97. Programs for Crystal Structure Analysis (Release 97-2). University of Goetingen, Germany.

5 $R_{\mathrm{int}} = \Sigma\ |F_o^2 - F_o^2(\mathrm{mean})|\ /\ \Sigma\ [\ F_o^2]$.

6 Since the structure refinements are against F^2, R-indices based on F^2 are larger than (more than double) those based on F. For comparison with older refinements based on F and an *OMIT* threshold, a conventional index R_1 based on observed F values larger than $4\sigma(F_o)$ is also given (corresponding to Intensity $\geq 2\sigma(I)$). $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]\ /\ \Sigma[w(F_o^2)^2]\}^{1/2}$, $R_1 = \Sigma||F_o| - |F_c||\ /\ \Sigma|F_o|$. The Goodness of Fit is always based on F^2: $GOF = S = \{\Sigma[w(F_o^2 - F_c^2)^2]\ /\ (n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined. The weighting scheme is $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP\ ]$, where P is $[2F_c^2 + \mathrm{Max}(F_o^2,0)]/3$.

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