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Supporting Information

Light-emitting electrochemical cells based on a supramolecularly-caged phenantroline-based iridium complex

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Materials and Methods

The solvents (puriss grade) were purchased from Fluka. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 500 MHz spectrometer; chemical shifts are defined with TMS = 0 ppm for ^{1}H and ^{13}C spectra and are measured relative to residual solvent. Electrospray ionization (ESI) mass spectra were recorded on a Bruker Esquire 3000^{plus} mass spectrometer. UV-vis spectra were recorded in a 1 cm path length quartz cell on a 845x UV-visible Agilent spectrophotometer, operating with UV-visible ChemStation Software. Steady-state luminescence spectra were measured on a Photon Technology spectrofluorometer, equipped with a lamp power supply (LPS-220B), working at room temperature. The excited-state lifetimes were measured from fresh solutions, which were degassed by N_2 bubbling for 30 min. They were deduced from time-resolved absorption spectroscopy utilizing a laser flash photolysis system based on a pulsed Nd:YAG laser, using 355 nm as exciting wavelength. The single pulses were approximately 10 ns duration and the energy was approximately 15 mJ/pulse. A Lo255 Oriel xenon lamp was employed as the detecting light source. The laser flash photolysis apparatus consisted of the pulsed laser, the Xe lamp, a 77200 Oriel monochromator, and

an Oriel photomultiplier (PMT) system made up of a 77348 PMT power supply. The oscilloscope was a TDS-640A Tektronix. The quantum yield measurements were performed in a de-aerated acetonitrile solution at an excitation wavelength of 355 nm using the quantum yield measurement system from Hamamatsu, model C9920-01.

Synthesis and Characterisation

[Ir(ppy)$_2$(pphen)][PF$_6$]

An orange suspension of [Ir(ppy)$_2$(μ-Cl)]$_2$[1] (350 mg, 0.326 mmol) and 2-phenyl-1,10-phenanthroline (pphen) (167 mg, 0.653 mmol) in MeOH (30 cm^3) was heated at reflux under N_2 in the dark for 12 h. The organe solution was then cooled to room temperature and solid NH_4PF_6 (532 mg, 3.27 mmol) was added. The mixture was stirred for 2 h at room temperature and solvent was then removed in vacuo. The crude product was purified twice by column chromatography (Merck Alox 90; CH_2Cl_2 changing to CH_2Cl_2/MeOH 100:1 by vol.). The isolated product was dissolved in CH_2Cl_2, precipitated with hexanes, and washed with hexanes, ethyl acetate and toluene. After further column chromatography (Merck Alox 90; CH_2Cl_2 changing to CH_2Cl_2/MeOH 100:2 by vol.), [Ir(ppy)$_2$(pphen)][PF$_6$] was isolated as an orange solid (470 mg, 0.53 mmol, 80 %). ^{1}H NMR (500 MHz, CD_2Cl_2) δ / ppm 8.73 (d, *J* 8.3 Hz, 1H), 8.64 (dd, *J* 8.2, 1.2 Hz, 1H), 8.31 (d, *J* 8.8 Hz, 1H), 8.26 (d, *J* 8.8 Hz, 1H), 8.21 (dd, *J* 5.1, 1.3 Hz, 1H), 7.93 (d, *J* 8.0 Hz, 1H), 7.36 (d, *J* 7.7 Hz, 1H), 7.05 (d, *J* 7.6 Hz, 1H), 7.02 (d, *J* 7.6 Hz, 1H), 6.98-6.89 (m, 3H), 6.85 (s br, 2H), 6.69 (t, *J* 7.5 Hz, 1H), 6.45 (td, *J* 7.5, 1.1 Hz, 1H), 6.10 (d, *J* 7.6 Hz, 1H), 5.66 (d, *J* 7.5 Hz, 1H). ^{13}C NMR (126 MHz, CD_2Cl_2) δ / ppm 169.2, 167.5, 166.8, 151.3, 149.3, 147.7, 147.4, 147.0, 143.3, 143.3, 139.3, 138.7, 138.45, 138.4, 137.9, 132.2, 132.0, 131.2, 130.9, 130.7, 130.2, 129.7, 129.5, 129.0, 128.5, 128.2, 127.7, 126.5, 125.0, 124.8, 123.7, 123.3, 122.7, 121.3, 120.25, 120.2. ESI-

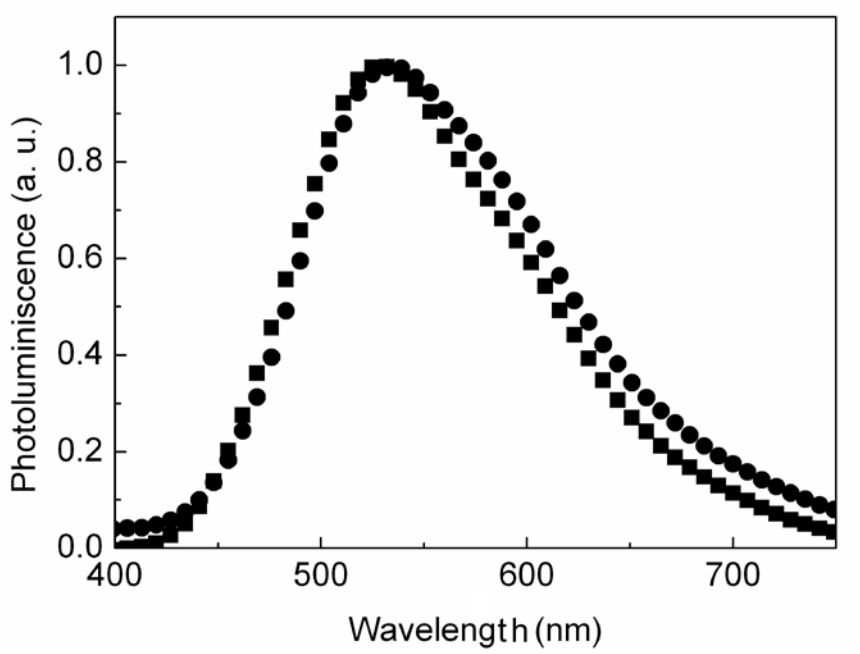
MS *m/z* 757.1 $[M - PF_6]^+$ (calc. 757.2). UV/VIS (CH_2Cl_2, 4.05×10^{-4} mol dm^{-3}) λ_{max}/nm 232 (ε/dm^3 mol^{-1} cm^{-1} 53000), 269 (57000), 343 (sh 11000), 383 (6700), 412 (sh 3700), 471 (840). Found: C 52.10, H 3.23, N 5.85; $C_{40}H_{28}F_6IrN_4P{\cdot}H_2O$ requires C 52.23, H 3.29, N 6.09 %.

Crystallography: $[Ir(ppy)_2(pphen)][PF_6]{\cdot}2H_2O$

Data were collected on a Bruker-Nonius Kappa CCD diffractometer; data reduction, solution and refinement used the programs COLLECT,[2] SIR92,[3] DENZO/SCALEPACK[4] and CRYSTALS.[5] $C_{40}H_{28}F_6IrN_4O_2P$, M = 933.87, yellow needle, monoclinic, space group $C2/m$, a = 19.0044(4), b = 25.7833(6), c = 16.0565(3) Å, β = 96.2600(10)^o, U = 7820.7(3) Å^3, Z = 8, D_c = 1.586 Mg m^{-3}, μ(Mo-K$_\alpha$) = 3.523 mm^{-1}, T = 123 K. Total 88828 reflections, 17233 unique, R_{int} = 0.034. Refinement of 12062 reflections (545 parameters) with $I > 3\sigma(I)$ converged at final $R1$ = 0.0254 ($R1$ all data = 0.0415), $wR2$ = 0.0292 ($wR2$ all data = 0.0387), gof = 1.0214.

Photophysical Characterization

The photoluminescence spectra shown in Figure S1 were taken in acetonitrile at room temperature using an excitation wavelength of 355 nm. The $[Ir(ppy)_2(pphen)][PF_6]$ complex shows a strong emission with a maximum at 530 nm. The unstructured and broad emission band is typical of complexes containing a combination of orthometallating and neutral ligands.[6–8] Figure S1 also includes the electroluminescence (EL) spectrum recorded for an ITO/PEDOT:PSS/$[Ir(ppy)_2(pphen)][PF_6]$:IL(1:1)/Al device. The EL spectrum shows the same shape that the photoluminescence spectrum with maximum emission at 578 nm.



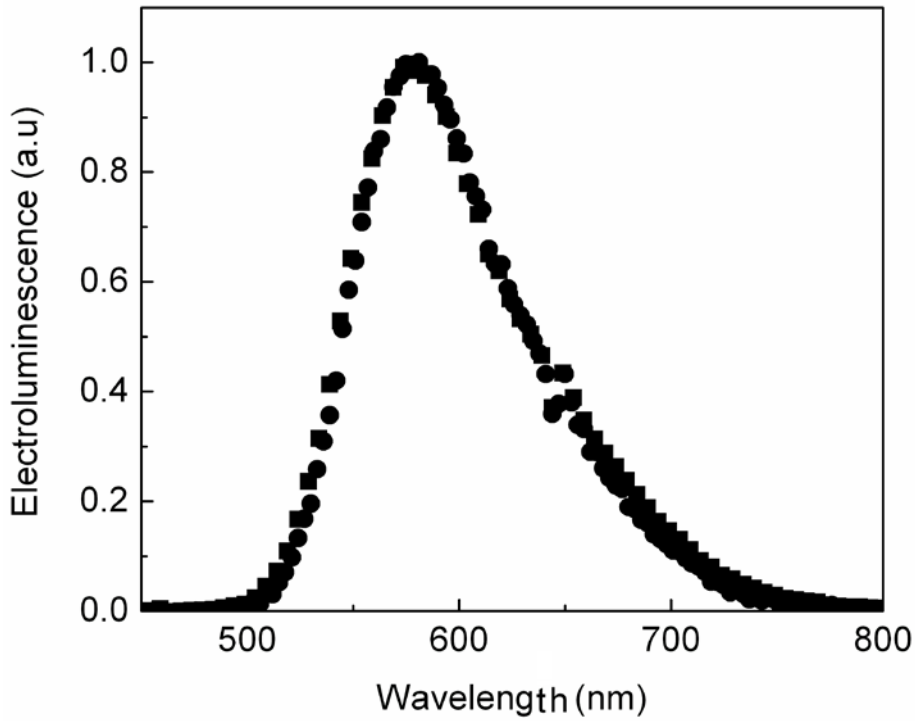


Figure S1. Top: Photoluminescence spectra of complexes $[Ir(ppy)_2(phen)][PF_6]$ (circles) and $[Ir(ppy)_2(pphen)][PF_6]$ (squares) in acetonitrile solution. Bottom: Electroluminescence spectra of an ITO/PEDOT:PSS/iTMC:IL(1:1)/Al device at an applied bias of 3 V for complexes $[Ir(ppy)_2(phen)][PF_6]$ (circles) and $[Ir(ppy)_2(pphen)][PF_6]$ (squares).

Table S1. Photophysical data

Complex	Emission[a] (298 K)		
	λ (nm)	ϕ_{sol}[b]	τ[b] (μs)
$[Ir(ppy)_2(pphen)][PF_6]$ (**1**)	530	0.13	1.11
$[Ir(ppy)_2(phen)][PF_6]$ (**2**)	530	0.17	1.29

[a] λ_{exc} = 355 nm; de-aerated CH_3CN solution (10^{-4} M). [b] Emission lifetime (τ) and photoluminiscence quantum yield (ϕ_{sol}) ± 10 %.

Device Preparation and Characterization

Poly(3,4-ethylenedioxythiophene):poly-styrenesulfonate (PEDOT:PSS) was purchased from HC-Starck and solvents used were obtained from Aldrich. Indium tin oxide (ITO)-coated glass plates (15 Ω □$^{-1}$) were patterned using conventional photolithography (obtained from Naranjosubstrates, www.naranjosubstrates.com). The substrates were extensively cleaned using sonification in subsequently water-soap, water and 2-propanol baths. After drying, the substrates were placed in a UV-ozone cleaner (Jelight 42-220) for 20 minutes.

The electroluminescent devices were prepared as follows. Transparent thin films of complex **1** containing different amount of ionic liquid (1-butyl-3-methylimidazolium hexafluorophosphate) were obtained by spinning from acetonitrile solutions using concentrations of 20 mg/mL at 2000 rpm for 40 seconds. The resulting films had a thickness of 90 nm. Prior to the deposition of the emitting layer, a 100 nm layer of PEDOT:PSS was deposited to increase the device preparation yield. The thickness of the films was determined using an Ambios XP1 profilometer. After spinning the organic layers, the samples were transferred to an inert atmosphere glovebox (< 0.1 ppm O_2 and H_2O, MBraun) and dried on a hot plate at 80 °C for 1 hour. Aluminium metal electrodes (80 nm) were thermally evaporated using a shadow mask under a vacuum (< 1×10^{-6}

mbar) using an Edwards Auto500 evaporator integrated into an inert atmosphere glovebox.

Current density and luminance versus voltage were measured using a Keithley 2400 source meter and a photodiode coupled to a Keithley 6485 pico-amperometer using a Minolta LS100 to calibrate the photocurrent. An Avantes luminance spectrometer was used to measure the EL spectrum. Lifetime data were obtained by applying a constant voltage over the device and monitoring the current flow and simultaneously the current generated by a Si-photodiode (Hamamatsu S1336-8BK) calibrated using a Minolta LS100 luminance meter. A custom-made equipment consisting of a multi-channel rack, muetta consult, 16 boards with power source and DAQ (data acquisition)-12 bits ADC (analogue to digital converter) was used to measure the luminance and current density over the time. A custom-designed labview program was used to control the equipment and gather the data on a personal computer. Both the multi-channel rack and the PC are connected via an autonomic power supply unit (SALICRU SLC cube).

Theoretical Calculations

Density functional calculations (DFT) were carried out with the D.02 revision of the Gaussian 03 program package[9] using Becke's three-parameter B3LYP exchange-correlation functional[10-12] together with the 6-31G** basis set for C, H, and N,[13] and the "double-ζ" quality LANL2DZ basis set for the Ir element.[14] The geometries of the singlet ground state (S_0), the lowest triplet state (T_1) and the metal-centred triplet state (^{3}MC) were fully optimised. The geometry of the $[Ir(ppy)_2(pphen)]^+$ cation in S_0 shows a near-octahedral coordination of the Ir(III) core. The Ir–C_{ppy} (2.028 and 2.014 Å), Ir–N_{ppy} (2.078 and 2.083 Å) and Ir-N_{pphen} (2.365 and 2.216 Å) bond distances compare

well with X-ray values. The HOMO is composed of a mixture of Ir d_π orbitals and phenyl π orbitals distributed among the two ppy ligands, and the LUMO resides on the N^N ligand showing no overlap with the HOMO. The geometries of the T_1 and ^{3}MC states were calculated at the spin-unrestricted UB3LYP level with a spin multiplicity of 3. The T_1 state mainly results from the HOMO LUMO monoexcitation and is computed to lie 2.32 eV above S_0 (adiabatic energy difference). Excitation to the T_1 state implies an electron transfer from the Ir-ppy environment to the pphen ligand. This electron transfer is confirmed by the unpaired-electron spin density distribution calculated for T_1 (Ir: 0.49, ppys: 0.46, pphen: 1.04). The spin-density distribution computed for the ^{3}MC state indicates that the metal supports 1.46 unpaired electrons which corroborates the metal-centred nature of this excited state.

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