Supporting Information

Aggregation-Induced Phosphorescent Emission (AIPE) of Iridium(III) Complexes

Qiang Zhao, Lei Li, Fuyou Li*, Mengxiao Yu, Zhipan Liu*, Tao Yi, Chunhui Huang*

Department of Chemistry & Lab of Advanced Materials, Fudan University, Shanghai, 200433, P. R. China.

Email: **fyli@fudan.edu.cn;**

Experimental Section

General Experiments. ^{1}H NMR spectra were recorded with Varian spectrometer at 400 MHz. Mass spectra were obtained on a SHIMADZU matrix-assisted laser desorption/ionization time-of-flight mass spectrometer (MALDI-TOF-MASS). Elemental analyses were carried out with VarioEL III O-Element Analyzer system. The UV-visible spectra were recorded on Shimadzu UV-2550 spectrometer. Steady-state emission experiments were measured on an Edinburgh instrument Xe-900 spectrometer at room temperature. Lifetime studies were performed with an Edinburgh FL-920 photo-counting system with a hydrogen-filled as the excitation source. The data were analyzed by iterative convolution of the luminescence decay profile with the instrument response function using software package provided by Edinburgh Instruments. Measurement of the absolute photoluminescence (PL) efficiency was performed on LabsphereIS-080(8”), which contained an integrating sphere coated on the inside with a reflecting material barium sulfate, and the diameter of the integrating sphere was 8 inch. The wavelength range studied was from 400-700 nm.

Confocal fluorescence imaging was performed with an OLYMPUS ZX81 laser scanning microscopy and a 60x oil-immersion objective lens. Excitation at 405 nm was carried out with a semiconductor laser. Emission was collected from 550 to 650 nm. For spectral measurements, stepsize was 10 nm and bandwidth was 10 nm.

Materials. Commercially available chemical reagents were used without further purification. 2-Phenylpyridine and dibenzoylmethane (HDBM) were obtained from Acros and used without further purification. 2-((Naphthalen-1-ylimino)methyl)phenol (SB) was prepared by the previous literature.[1] The Gd(III) complexes Gd(DBM)$_3$(H$_2$O)$_2$ and Gd(SB)$_3$(H$_2$O)$_2$ were synthesized according to the method reported previously.[2]

Synthesis of Iridium Complexes. The complex Ir(ppy)$_2$(DBM) was synthesized according to the previous literature.[3] A mixture of 2-ethoxyethanol and water (3:1, v/v) was added to a flask containing $IrCl_3 \cdot 3H_2O$ (1 mmol) and 2-phenylpyridine (2.5 mmol). The mixture was refluxed for 24 h. After cooling, the yellow solid precipitate was filtered to give crude cyclometalated Ir(III) chlorobridged dimer. The crude chlorobridged dimer (0.2 mmol) was mixed with Na_2CO_3 (1.4 mmol). 2-Ethoxyethanol and DBM (0.5 mmol) were added and then the mixture was refluxed for 12 h. After cooling to room temperature, yellow precipitate was collected by filtration and chromatographed using CH_2Cl_2/petroleum ether (1:1, v/v) to afford the complex Ir(ppy)$_2$(DBM). Ir(ppy)$_2$(DBM). ^{1}H NMR: (400 MHz, CDCl$_3$), δ (ppm): 8.59 (d, 2H), 7.86 (d, 2H), 7.80 (d, 4H), 7.67-7.70 (t, 2H), 7.60 (d, 2H), 7.35-7.41 (t, 2H), 7.30 (d, 4H), 7.01-7.06 (t, 2H), 6.84-6.87 (t, 2H), 6.72-6.75 (t, 2H), 6.57 (s, 1H), 6.37 (d, 2H). Anal. Calcd. for $IrC_{37}H_{27}N_2O_2$: C, 61.39; H, 3.76; N, 3.87. Found: C, 61.63; H, 3.53; N, 3.57. MS (LDI-TOF): m/e 724.

The other cyclometalated Ir(III) complex Ir(ppy)$_2$(SB) was prepared by the similar procedure. Ir(ppy)$_2$(SB). ^{1}H NMR: (400 M Hz, CDCl$_3$), δ (ppm): 9.08 (d, 1H), 9.02 (d, 1H), 8.94 (t, 1H), 8.20 (d, 1H), 7.89 (d, 1H), 7.72 (t, 1H), 7.59-7.55 (m, 2H), 7.359 (t, 1H), 7.31-7.28 (m, 1H), 7.19 (t, 1H), 7.12-7.07 (m, 3H), 6.92 (d, 1H), 6.87-6.80 (m, 4H), 6.75 (d, 1H), 6.68 (t, 2H), 6.60 (d, 1H), 6.45-6.41 (m, 2H), 6.39 (d, 1H), 6.17 (d, 1H) 6.01 (d, 1H). Anal. Calcd. for $IrC_{39}H_{28}N_3O$: C, 61.72; H, 3.78; N, 5.63. Found: C, 61.95; H, 3.55; N, 5.41. MS (LDI-TOF): m/e 747.

X-ray Crystallography Analysis. The single crystals of Ir(ppy)$_2$(DBM) and Ir(ppy)$_2$(SB) were mounted on glass fiber and transferred to a Bruker SMART CCD area detector. Crystallographic measurement was carried out using a Bruker SMART CCD diffractometer, σ scans, graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) under room temperature. The crystal structures were solved by direct method and refined by full-matrix least-squares on F^2 values using the program SHELXS-97.[4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated in ideal geometries. For the full-matrix least-squares refinements [$I > 2\sigma(I)$], the unweighted and weighted agreement factors of $R1 = \Sigma(F_o-F_c)/ \Sigma F_o$ and $wR2 = [\Sigma_w(F_o^2-F_c^2)^2/\Sigma_w F_o^4]^{1/2}$ were used. CCDC reference number 610633 and 611152 for $Ir(ppy)_2(DBM)$ and $Ir(ppy)_2(SB)$, respectively.

Theoretical Calculations. All periodic DFT calculations were performed using SIESTA code[5] with numerical-orbital basis sets. The exchange-correlation functional used is the generalized-gradient-approximation method, known as GGA-PBE. A double zeta plus polarization basis set was employed. The orbital-confining cutoff radii were determined from an energy shift of 0.01 eV. The energy cutoff for the real space grid used to represent the density was set as 150 Ry. To further speed up calculations, Kohn-Sham equation was solved by an iterative parallel diagonalization method that utilizes the ScaLAPACK subroutine pdsygvx with two-dimensional block cyclicly distributed matrix. The accuracy of the SIESTA method was carefully benchmarked with the plane-wave code previously.[6]

Measurement of phosphorescence spectra of $Gd(DBM)_3(H_2O)_2$ and $Gd(SB)_3(H_2O)_2$. The triplet energy levels of the ligands DBM, SB and acac were estimated by referring to their lower wavelength emission edges of the corresponding phosphorescence spectra. The triplet energy level of the ligand should not be affected significantly by the lanthanide ion, and the lowest lying excited level ($^6P_{7/2} \rightarrow {}^8S_{7/2}$) of Gd(III) is located at 32150 cm^{-1}.[7] On this basis, the phosphorescence spectra of $Gd(DBM)_3(H_2O)_2$, $Gd(SB)_3(H_2O)_2$ and $Gd(acac)_3(H_2O)_2$ allow one to evaluate the $^3\pi\pi^*$ energy levels corresponding ligand anions DBM, SB and acac.

According to previous report,[8] the phosphorescence spectra of $Gd(DBM)_3(H_2O)_2$ and $Gd(SB)_3(H_2O)_2$ were measured and are shown in Figure S4. The phosphorescence spectra of $Gd(DBM)_3(H_2O)_2$, $Gd(SB)_3(H_2O)_2$ and $Gd(acac)_3(H_2O)_2$ at 77 K present their bands with maxima at ca. 550, 542 and 483 nm, respectively, and their energies of zero-phonon transition of the triplet states ($^3\pi\pi^*$)[9] at about 18750 cm^{-1} (533 nm), 19048 cm^{-1} (525 nm) and 21460 cm^{-1} (466 nm) for ancillary ligands DBM, SB and acac, respectively (see Figure S4).

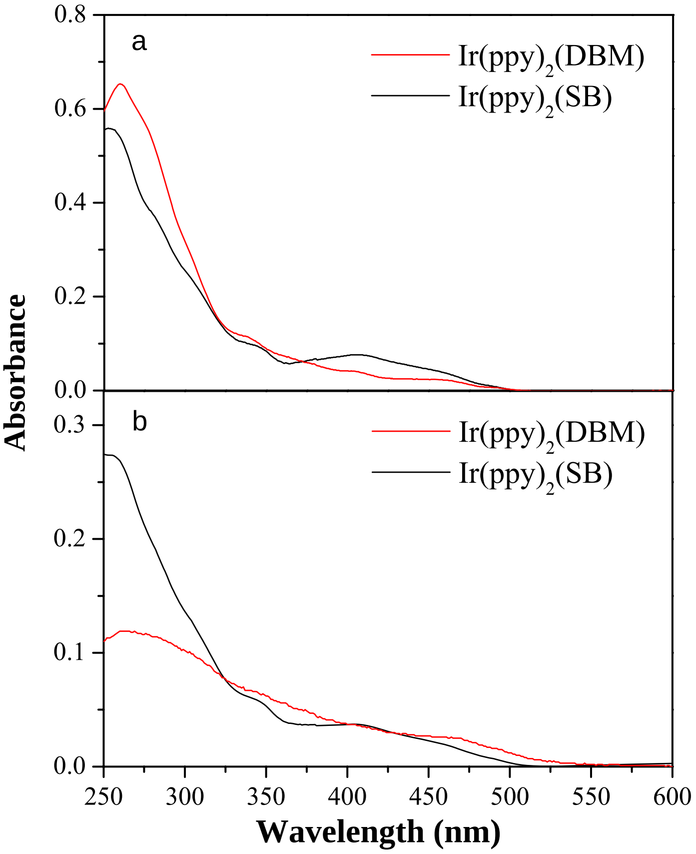

Figure S1. Absorption spectra of iridium (III) complexes in solution (a) and solid state (b).

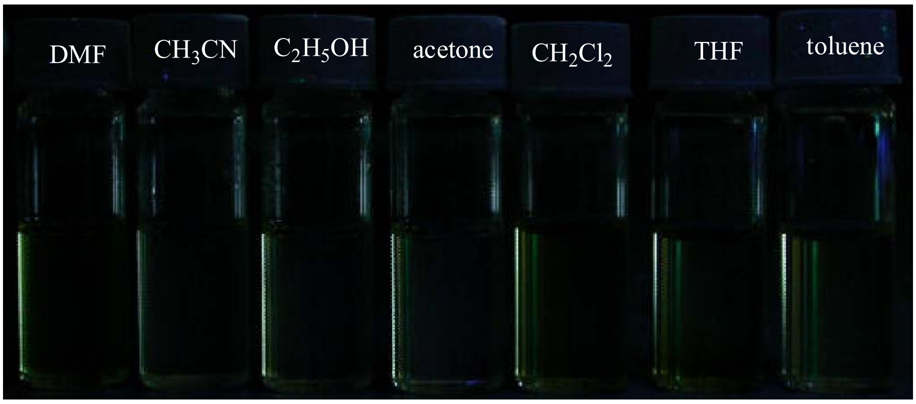

Figure S2. Luminescent photographs of $Ir(ppy)_2(SB)$ (as an example) in various solvents with different dielectric constants (ε) at a concentration of 2×10^{-5} mol·L^{-1}: DMF (ε=38.3), CH_3CN (ε=36.6), C_2H_5OH (ε=24.3), acetone(ε=20.7), CH_2Cl_2 (ε=8.9), THF (ε=7.52), and toluene (ε=2.37).

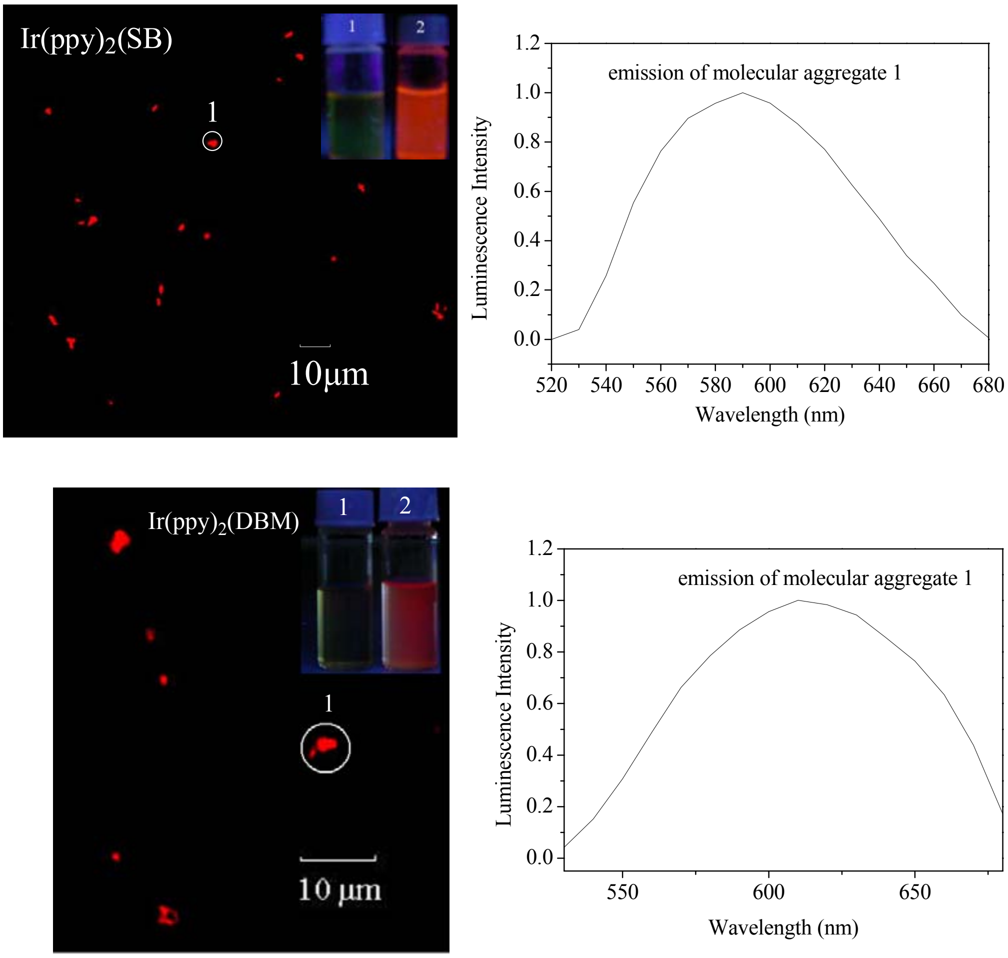

Figure S3. Left: Confocal fluorescence microscope images of Ir(ppy)$_2$(SB) and Ir(ppy)$_2$(DBM) and in water-CH$_3$CN mixtures with the water content of 80% and luminescent photographs (inset) of three complexes in water-CH$_3$CN mixtures with the water content of 0% (1) and 80% (2) at a concentration of 2×10^{-5} mol·L^{-1} at 298 K. Right: Photoluminescent spectra of molecular aggregate domain ***1*** of three complexes were measured by laser scanning microscopy.

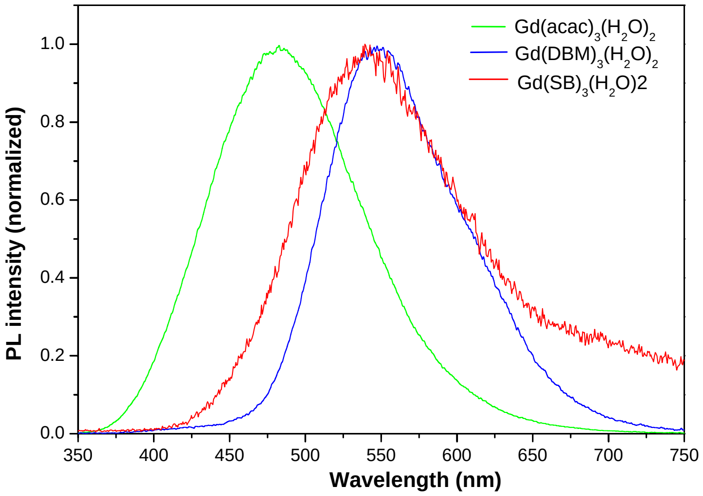

Figure S4. Phosphorescent spectra of Gd(acac)$_3$(H$_2$O)$_2$, Gd(DBM)$_3$(H$_2$O)$_2$, and Gd(SB)$_3$(H$_2$O)$_2$ at 77 K.

Table S1. Bond lengths of Ir(ppy)$_2$(DBM) in different conditions.

Model	d_{Py-Py}[a] (Å)	Ir-O (Å)	Ir-C (Å)	Ir-N (Å)
State I	20.4	2.170	2.003	2.054
State II	3.4	2.164	2.000	2.050
Single crystal	3.36	2.152	1.973	2.043

[a]: the distance of adjacent pyridyl groups.

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