Supporting Information for

Piezochromic luminescent (PCL) behavior and aggregation-induced emission (AIE) property of a new cationic iridium(III) complex

Guo-Gang Shan,[a] Hai-Bin Li,[a] Jun-Sheng Qin,[a] Dong-Xia Zhu,[a] Yi Liao*[b] and Zhong-Min Su*[a]

[a]*Institute of Functional Material Chemistry, Faculty of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China;* Fax: +86-431-85684009 Tel.: +86-431-85099108, E-mail: zmsu@nenu.edu.cn

[b]*Department of Chemistry, Capital Normal University, Beijing, People's Republic of China. E-mail:* liaoy271@nenu.edu.cn

Table of Contents

1. Theoretical calculations 2
2. Experimental section 3–8
3. X-ray crystallography data 9–10
4. Photophysical property 11–13
5. Confocal luminescence images of complex **1** 14
6. References 15

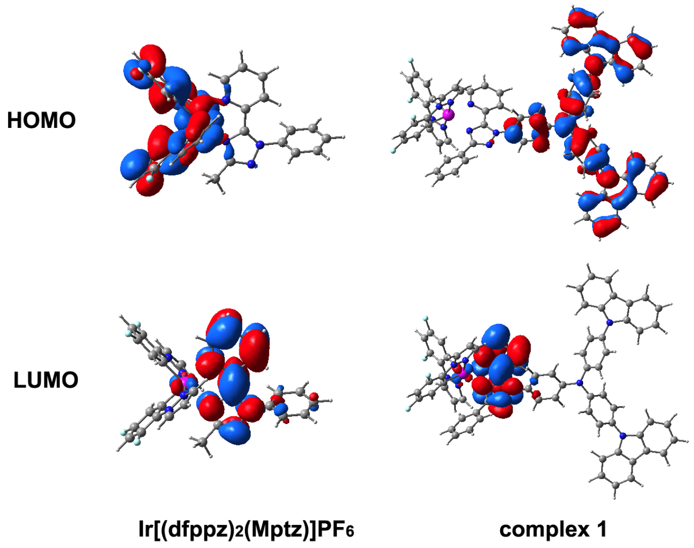
1.Theoretical calculations

Calculations on the ground and excited electronic states of the complexes were investigated by performing DFT and TD-DFT calculations at B3LYP level. The 6-31G* basis set was employed for optimizing the C, H, N atoms and the LANL2DZ basis set for Ir atom. An effective core potential (ECP) replaces the inner core electrons of Ir leaving the outer core $(5s)^2(5p)^6$ electrons and the $(5d)^6$ valence electrons of Ir(III). All calculations were performed with the Gaussian 09 software package.[1]

Table S1 Calculated triplet states for the cationic Ir(III) complexes **1** and Ir[$(dfppz)_2(Mptz)$]PF_6[a] by a TDDFT approach.

Complex	States	Assignment	eV	*f*	Nature
1	T_1	H→L (97%)	2.40	0	^{3}ILCT
Ir[$(dfppz)_2(Mptz)$]PF_6	T_1	H→L (94%)	2.87	0	^{3}MLCT/^{3}LLCT

[a]Ref. *Chem. Commun.,* 2012, **48**, 2000.



Ir[$(dfppz)_2(Mptz)$]PF_6 complex 1

Fig. S1 HOMO and LUMO orbitals for complexes **1** and Ir[$(dfppz)_2(Mptz)$]PF_6.

2. Experimental section

2.1 Materials and instruments

All materials and solvents were commercially available and used as received without further purification. All manipulations were performed under a dry nitrogen atmosphere using standard techniques. Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TG-7 analyzer under nitrogen atmosphere with a heating rate of 10 °C min^{-1}. Differential scanning calorimetry (DSC) curves were obtained with a Perkin-Elmer thermal analysis DSC-7 under nitrogen with a heating rate 10 °C min^{-1}. Powder X-ray diffraction (XRD) patterns of the samples were collected on a Rigaku Dmax 2000. ^{1}H NMR spectra were recorded using a Bruker AV 500 MHz with tetramethylsilane (TMS) as the internal standard. ^{13}C CP/MAS spectra were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 7 mm standard bore CP MAS probehead whose X channel was tuned to 100.62 MHz for ^{13}C and the other channel was tuned to 400.18 MHz for broad band 1H decoupling, using a magnetic field of 9.39 T at 297 K. The dried powdered samples were packed in the ZrO_2 rotor closed with Kel-F caps which were spun at 5 kHz rate. The experiments were conducted at a contact time of 2 ms. A total of 10000 scans was recorded with 5 s recycle delay for each sample. All ^{13}C CPMAS chemical shifts are referenced to the resonances of adamantane ($C_{10}H_{16}$) standard (δCH_2=38.5). The molecular weights of the complexes were tested by using matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectrometry. Emission spectra were recorded using the F-7000 FL spectrophotometer. Emission spectra were measured at their maximal excitation wavelengths. Absolute photoluminescence quantum yields were determined in Edinburgh FLS900 with an integrating sphere system. Transmission electron microscopy (TEM) and electron diffraction pattern of the sample were performed using a TECNAI F20 microscope. The samples were prepared by placing microdrops of the solution on a holey carbon copper grid.

For crystal structure of complex **1**, the data collection was performed on a Bruker Smart Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ

= 0.71069 Å) at room temperature. All absorption corrections were performed by using the SADABS program. The crystal structure was solved by direct methods of SHELXTL-97[2] and refined by full-matrix least-squares techniques using SHELXTL-97 within WINGX.[3] All hydrogen atoms of aromatic rings were included in the structure factor calculation at idealized positions by using a riding model. The detailed crystallographic data and structure refinement parameters are summarized in **Table S2**. Further details of the crystal structure determination have been deposited to the Cambridge Crystallographic Data Centre as supplementary publication. CCDC 870135 (**1**) contains the supplementary crystallographic data for this paper.

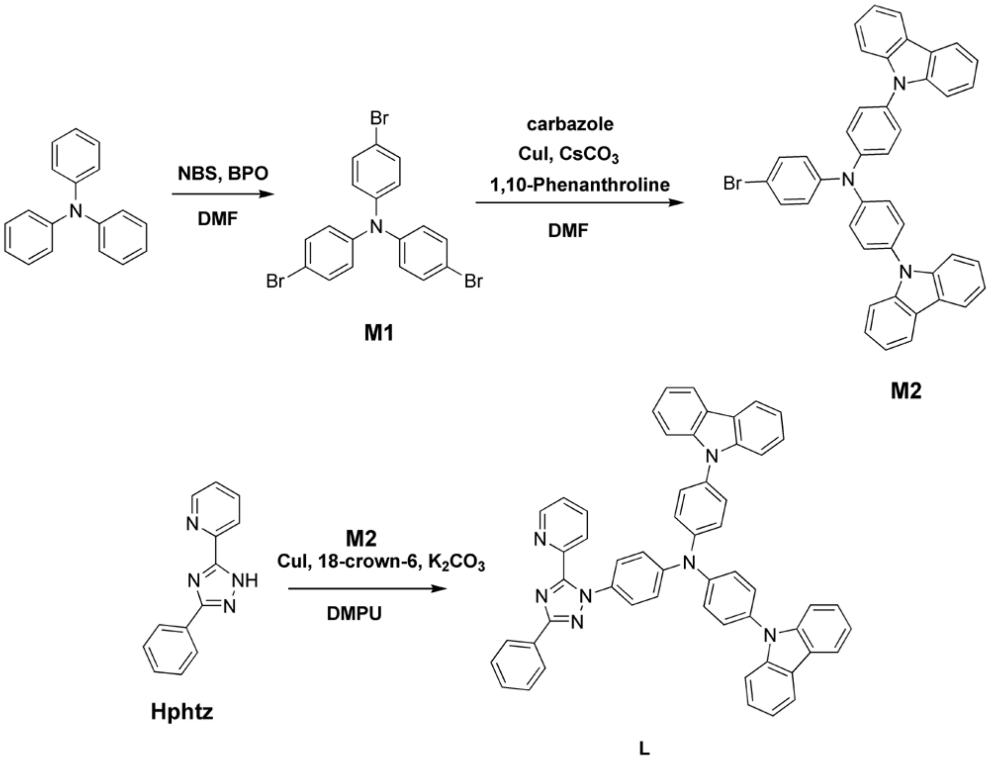
Table S2 Crystal data and summary of data collection and refinement of complex **1**.

	1
Formula	$C_{73}H_{47}F_{10}IrN_{11}PO_4$
Mr	931.75
Crystal system	Triclinic
Space group	P-1
a /Å	13.080(5)
b /Å	13.594(5)
c /Å	23.084 (5)
α/°	77.078(5)
β/°	80.701(5)
γ/°	61.405(5)
V/Å^3	3505(2)
Z	2
ρ_{calc} (g/cm3)	1.474
temp (K)	293(2)
μ/mm^{-1}	2.011
R_{int}	0.0282
Goodness-of-fit on F^2	1.064
R_1[a], wR_2[b] [I > 2σ (I)]	0.0596, 0.1657
R_1, wR_2 (all	0.0927,

data)	0.1841

^{a} $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo|$. ^{b} $wR_2 = \{\Sigma[w(Fo^2 - Fc^2)^2]/\Sigma[w(Fo^2)^2]\}^{1/2}$

2.2. Synthesis and characterization of the ancillary ligand L



Scheme S1. Synthetic routes of the ancillary ligand **L**.

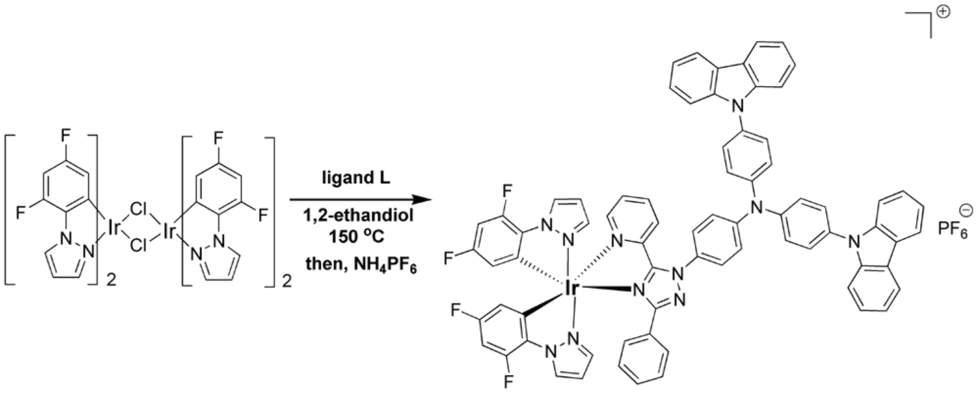
2.2.1 Synthesis of N-(4-(9*H*-carbazol-9-yl)phenyl)-N-(4-bromophenyl)-4-(9*H*-carbazol-9-yl)-benzenamine (M2)

The intermediate tris(4-bromophenyl)amine (**M1**) was synthesized according to the literature method.[4] Intermediate **M1** (0.48 g, 1.0 mmol), carbazole (0.42 g, 2.5 mmol), 1,10-phenanthroline (0.24 g, 1.3 mmol), copper(I) iodide (0.12 g, 0.63 mmol), and cesium carbonate (0.98 g, 3.0 mmol) were dissolved in 30 mL dimethylformamide (DMF). The mixture was stirred vigorously for 10 min at room temperature (RT) and subsequently refluxed under an argon atmosphere for another 18 h. After cooling to RT, the solvent was removed under vacuum and the residue was extracted with CH_2Cl_2 (200 mL). The product was then obtained by column chromatography on silica gel with dichloromethane/petrol ether (2:3) as the eluent to yield a white solid (51%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.15 (d, J = 7.5 Hz, 4H), 7.41–7.50 (m, 14H), 7.36–7.38 (m, 4H), 7.28–7.31 (m, 4H), 7.18–7.20 (m, 2H).

2.2.2 Synthesis and characterization of the ancillary ligand L

A mixture of **M2** (0.65 g, 1.0 mmol), **Hphtz** (0.25g, 1.1 mmol),[5] copper(I) iodide (19 mg, 0.10 mmol), 18-crown-6 (26 mg, 0.10 mmol), K_2CO_3 (0.21 g, 1.5 mmol), and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU, 3 mL) was heated to 190 °C for 24 h under argon atmosphere. After cooling to RT, the reaction was quenched with 2N hydrochloric acid and then the reaction mixture was extracted with CH_2Cl_2. After washing with $NH_3 \cdot H_2O$ and water, drying over anhydrous Na_2SO_4, and evaporating the solvents, we purified the residue by column chromatography on silica gel using dichloromethane as eluent to give a white solid (**L**). Yield: 56%. ^{1}H NMR (500 MHz, d_6–DMSO, ppm): δ 8.55 (d, *J* = 4 Hz, 1H), 8.25 (d, *J* = 7.5 Hz, 4H), 8.14 (d, *J* = 8 Hz, 2H), 8.10 (d, *J* = 7.5 Hz, 1H), 8.01–8.02 (m, 1H), 7.63–7.65 (m, 4H), 7.45–7.55 (m, 18H), 7.27–7.33 (m, 6H). ^{13}C NMR (126 MHz, $CDCl_3$):161.75, 153.22, 149.32, 147.58, 147.46, 146.05, 140.84, 136.83, 133.829, 132.91, 130. 514, 129.49, 128.58, 128.14, 126.78, 126.60, 125.91, 125.45, 124.48, 124.44, 123.88, 123.29, 120.33, 119.92, 109.73.

2.3 Synthesis and characterization of complex 1



Complex 1

Scheme S2. Synthetic routes of complex **1**.

The dichloro-bridged diiridium complex $[Ir(dfppz)_2Cl]_2$ (1.2 g, 1.0 mmol) and ligand **L** (0.50 g, 2.1 mmol) were dissolved in 1,2-ethandiol (30 mL). The mixtures was heated at 150 ^{o}C for 15 h under an argon atmosphere in dark and then cooled to room temperature. To the reaction mixture was added 20 mL methanol. Then, the aqueous solution of NH_4PF_6 (2.0g in 100 mL of deionized water) was slowly added into the reaction mixture under stirring. The obtained yellow suspension was filtrated, and washed with water and methanol. The crude product was purified by silica gel column chromatography using dichloromethane/ethyl acetate (6:1, v/v) as the eluent. The product was then recrystallized from dichloromethane and petrol ether mixture, yielding a yellow solid (62%). ^{1}H NMR (500 MHz, d_6–DMSO, ppm): δ 8.67 (d, *J* = 2.5 Hz, 1H), 8.55 (d, *J* = 2 Hz, 1H), 8.25–8.28 (m, 5H), 8.06 (d, *J* = 2 Hz, 1H), 8.03 (d, *J* = 5 Hz, 1H), 7.83–7.84 (m, 2H), 7.69–7.75 (m, 4H), 7.64–7.66 (m, 5H), 7.46–7.56 (m, 12H), 7.28–7.33 (m, 5H), 7.09–7.14 (m, 5H), 6.90 (t, *J* = 2.5 Hz, 1H), 6.85 (t, *J* = 2.5 Hz, 1H), 6.69–6.73 (m, 1H), 5.55–5.57 (m, 1H), 5.13–5.15 (m, 1H). ^{13}C NMR (126 MHz, d_6-DMSO):161.75, 158.79, 158.70, 158.33, 158.26, 156.92, 152.27, 150.28, 149.92, 149.81,149.25, 149.15, 147.90, 147.79, 147.24, 147.14, 145.69, 141.10, 140.92, 140.65, 140.30, 135.69, 134.93, 133.52, 133.09, 132.98, 132.64, 132.53, 130.65, 129.96, 129.85, 128.85, 128.79, 128.69, 128.04, 127.46, 127.14, 126.98, 126.76, 125.78, 125.23, 123. 15, 120.63, 115.45, 115.30, 115.06, 114.90, 110.25, 110.02, 100.52, 100.33, 99.26, 99.03. ^{19}F NMR (470 MHz, d_6-DMSO) -66.56 (d, *J* = 711.6 Hz, 6F), -109.47 (t, *J* = 6.6 Hz, 1F), -111.11 (t, *J* = 6.6 Hz, 1F), -119.75(d, *J* = 6.6 Hz, 1F), -121.62 (d, *J* = 6.6 Hz, 6F). (MALDI-TOF): m/z 1346.3 (M–PF6).

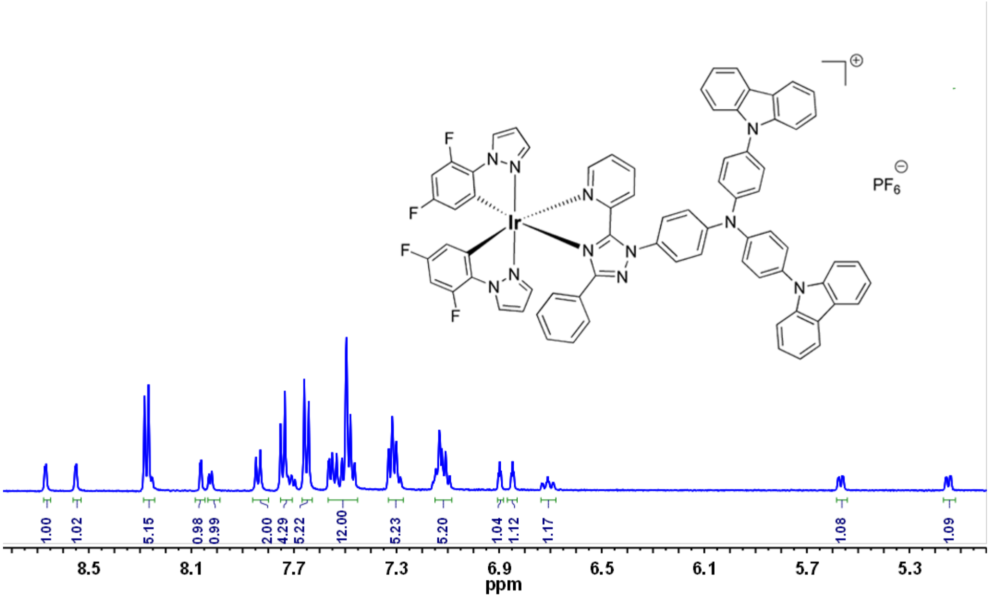


Fig. S2. ^{1}H NMR spectrum of complex **1** in d_6-DMSO.

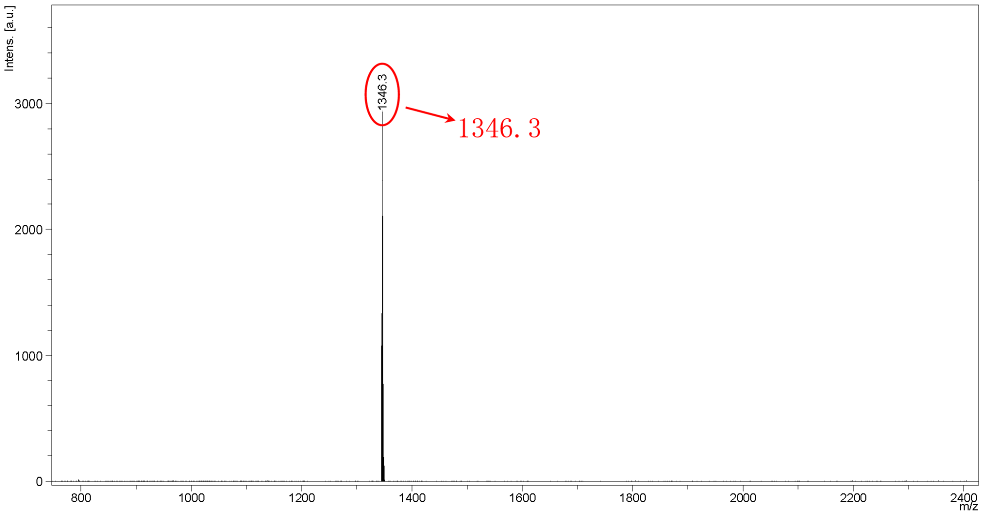


Fig. S3. MALDI-TOF MS spectrum of complex **1** (positive mode).

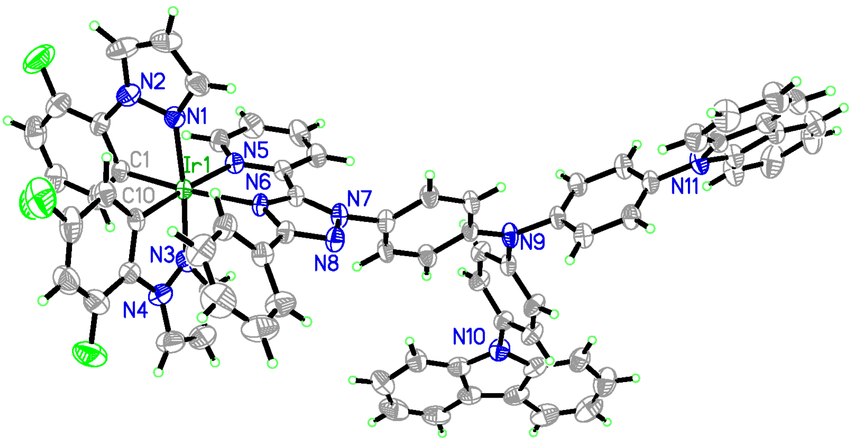


Fig. S4. X-ray crystal structure of complex **1** with thermal ellipsoids drawn at the 30% probability level. The PF_6 counter anion and hydrogen atoms are omitted for clarity.

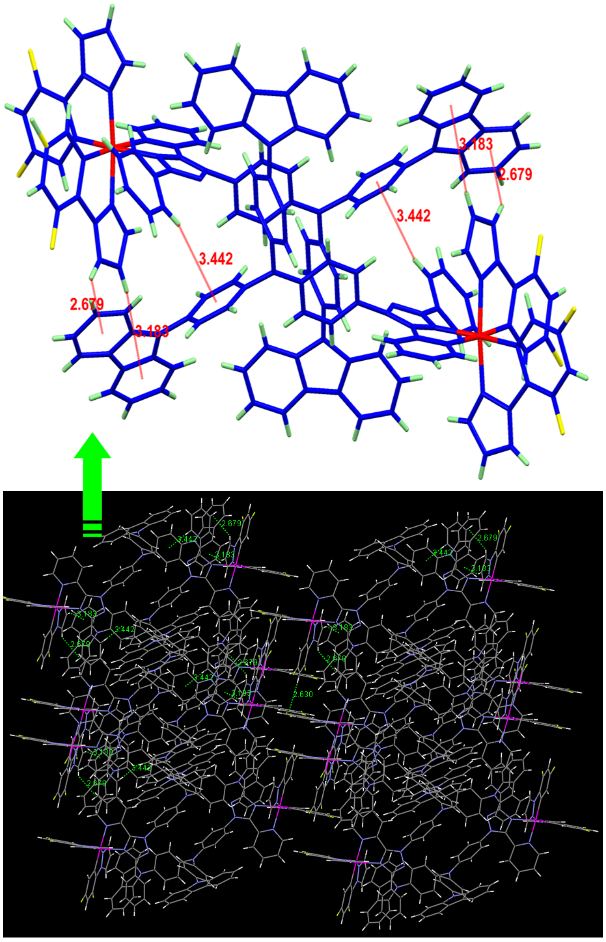


Fig. S5. Perspective view of packing arrangements in crystal of complex **1**. The red lines (up) and green lines (bottom) represent C-H···π intermolecular interactions, respectively. The counter anion and water molecules are omitted for clarity.

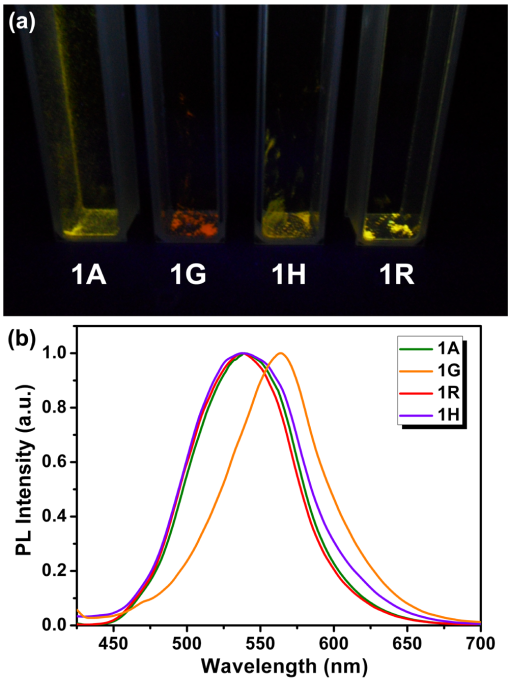


Fig. S6. (a) Photographic images (excited at 365 nm using a UV lamp) and (b) emission spectra of complex **1** in the solid states at room temperature.

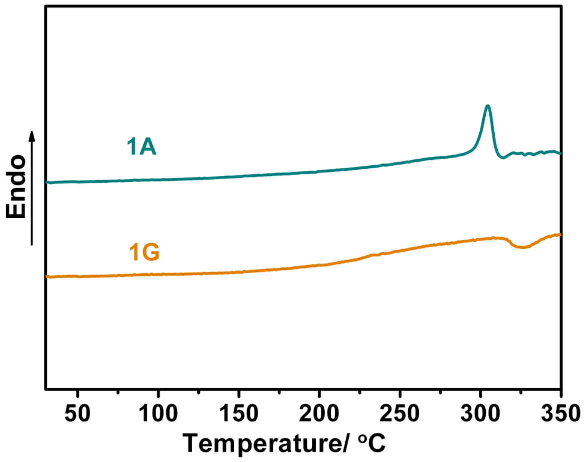


Fig. S7. DSC curves of the samples **1A** and **1G**.

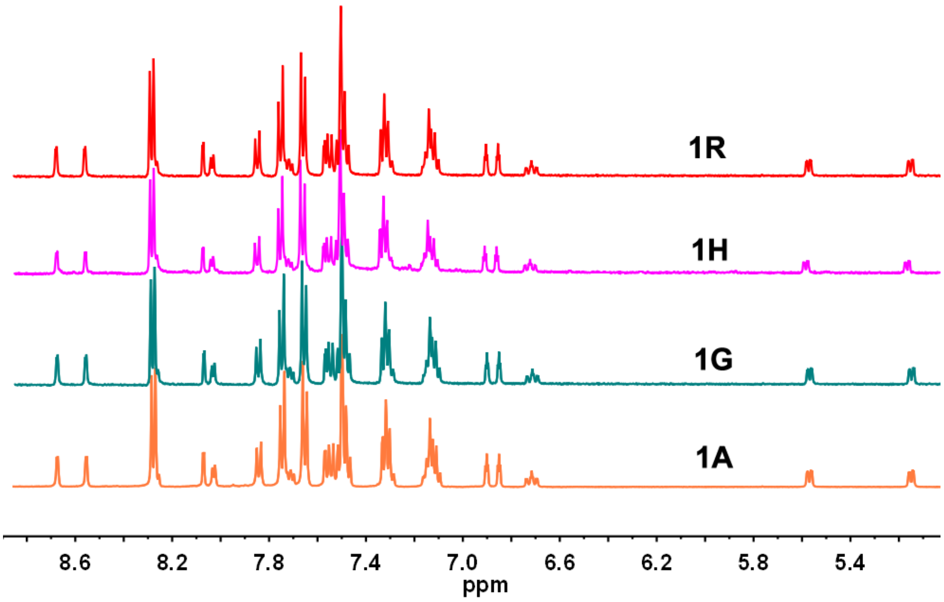


Fig. S8. ^{1}H NMR spectra of complex **1** in d_6-DMSO solution.

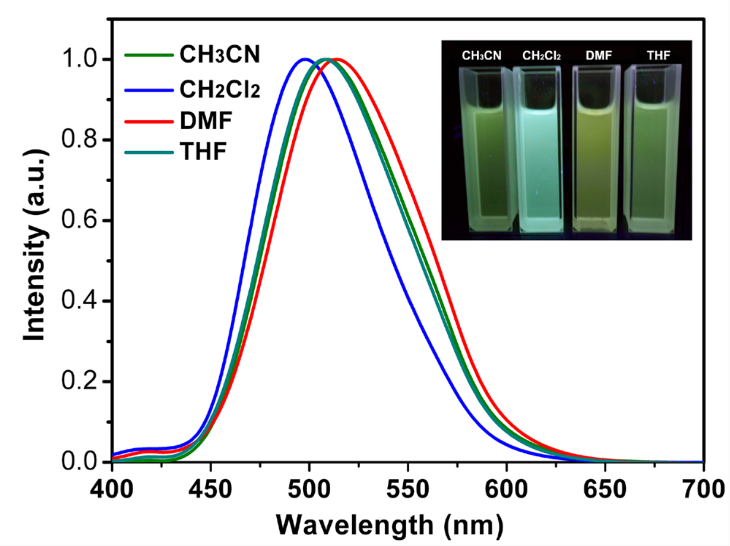


Fig. S9. Emission spectra of Ir[(dfppz)$_2$(Mptz)]PF$_6$ in CH_3CN, CH_2Cl_2, DMF and THF solutions with a concentration of 1×10^{-4} M

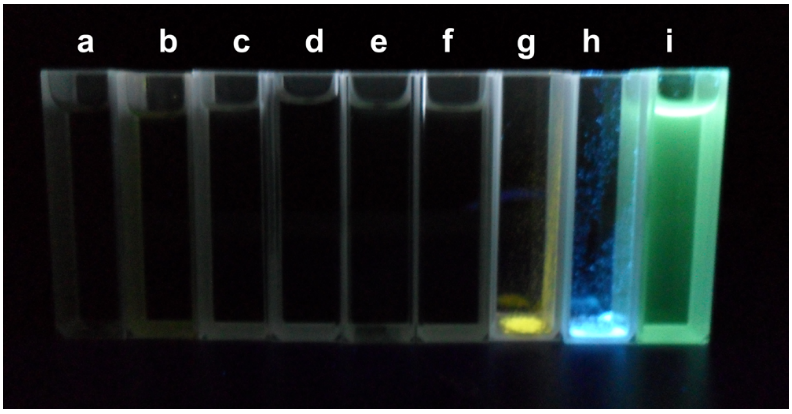


Fig. S10. Photographic images of complex **1** in various solutions with a concentration of 1×10^{-4} M: (a) CH_3CN; (b) CH_2Cl_2; (c) $CHCl_3$; (d) DMF; (e) THF; (f) acetone, and in the solid state (g). Photographic images of Ir[(dfppz)$_2$(Mptz)]PF_6 (**Ref. 6**) in the solid state (h) and in CH_2Cl_2 solutions (i). All photographs were taken under UV-light (λ_{max}=365 nm).

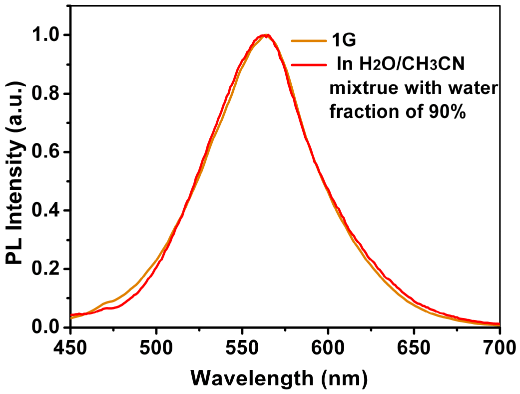


Fig. S11. Emission spectra of complex **1** in CH_3CN/H_2O mixtures with water fraction of 90% and in the ground state.

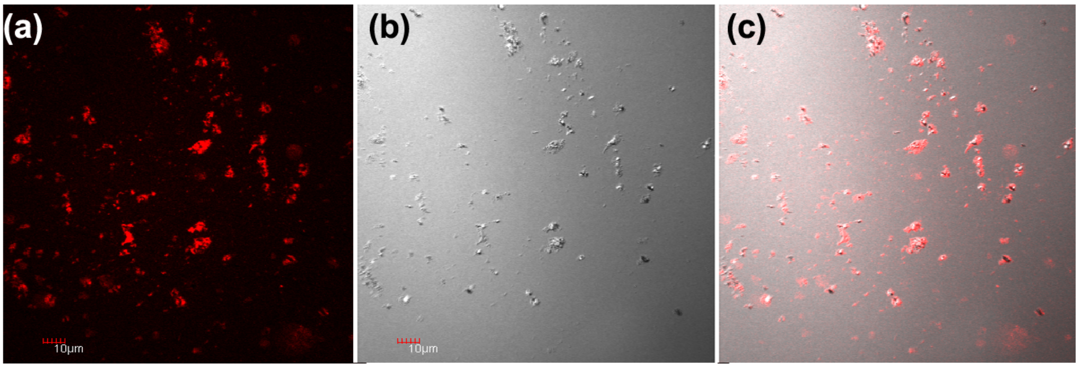


Fig. S12. (a) Confocal luminescence and (b) brightfield images of complex **1** in CH_3CN/H_2O mixtures with water fraction of 90%. (c) The overlay image of (a) and (b).

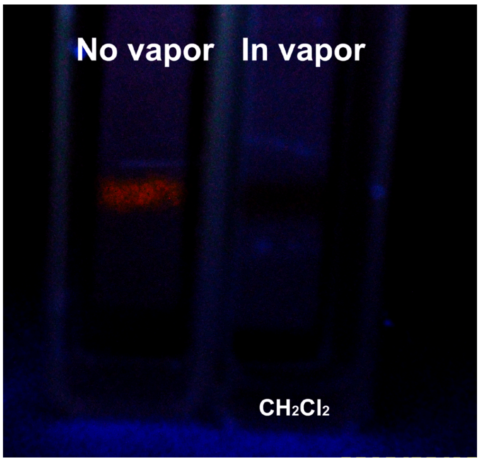


Fig. S13. On/off switching of complex **1** on TLC plates without vapor (left) and in CH_2Cl_2 vapor (right) under UV light (λ_{max}=365 nm) illumination at room temperature.

References

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, Gaussian 09W, Revision A.02; Gaussian, Inc., Wallingford CT, 2009.
2. G. M. Sheldrick, SHELXL-97, *Program for Crystal Structure Refinement*, University of Göttingen, 1997.
3. L. J. Farrugia, WINGX, *A Windows Program for Crystal Structure Analysis;* University of Glasgow; Glasgow, UK, 1988.
4. C. C. Lee, K. M. Yeh and Y. Chen, *Polymer*, 2009, **50**, 410.
5. E. Orselli, G. S. Kottas, A. E. Konradsson, P. Coppo, R. Fröhlich, L. De Cola, A. van Dijken, M. Büchel and H. Börner, *Inorg. Chem.*, 2007, **46**, 11082.
6. G. G. Shan, H. B. Li, H. T. Cao, D. X. Zhu, P. Li, Z. M. Su and Y. Liao, *Chem. Commun.*, 2012, **48**, 2000.