Electronic Supplementary Information (ESI)

Controllable synthesis of iridium(III)-based aggregation-induced emission and/or piezochromic luminescence phosphors by simply adjusting the substitutions on ancillary ligands

Guo-Gang Shan, Hai-Bin Li, Hai-Zhu Sun, Dong-Xia Zhu, Hong-Tao Cao and Zhong-Min Su*

Institute of Functional Material Chemistry, faculty of chemistry, Northeast Normal University Jilin 130024, People's Republic of China.
E-mail: zmsu@nenu.edu.cn

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1.Theoretical calculations

Calculation on the ground and excited electronic state of complexes were investigated by preforming DFT and TD-DFT at B3LYP level. The 6-31G* basis sets were employed for optimizing the C, H, N atoms and the LANL2DZ basis sets for Ir atom. An effective core potential (ECP) replaces the inner core electrons of iridium leaving the outer core $(5s)^2(5p)^6$ electrons and the $(5d)^6$ valence electrons of Ir(III). In order to reduce the computational efforts, the molecular structure of complex **3** was simplified by replacing *tert*-butyl moiety with methyl group. All calculations reported here were carried out with the Gaussian 09 software package.[1]

Table S1 HOMO and LUMO orbitals of complexes **1**, **2** and **3**

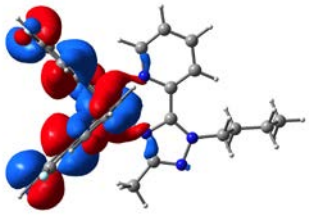
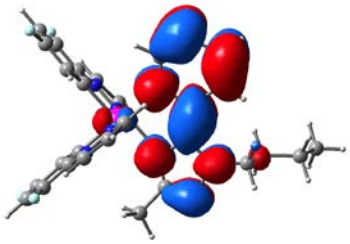
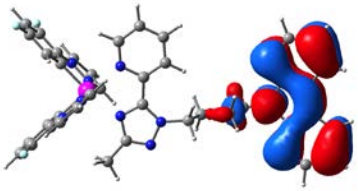
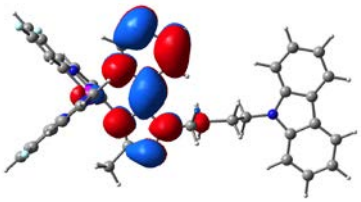
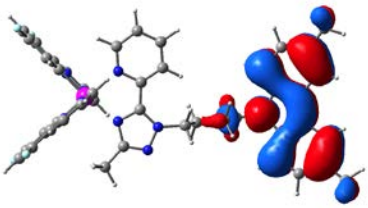
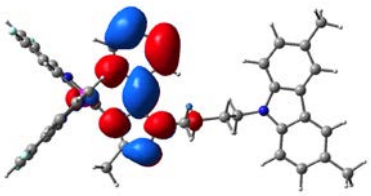
	HOMO	LUMO
complex **1**		
complex **2**		
complex **3**		

Table S2 The calculated energy levels of the lower-lying transitions of complexes **1**, **2** and **3**

Complex	States	Assignment	eV	*f*	Nature
1	T_1	H→L (97%)	2.90	0	^{3}MLCT/^{3}LLCT
2	T_1	H→L (100%)	2.63	0	^{3}ILCT
3	T_1	H→L (100%)	2.45	0	^{3}ILCT

Table S3 Crystal data and summary of data collection and refinement for complex **1**.

	1
Formula	$C_{30}H_{26}F_{10}IrN_8P$
*M*r	911.76
Crystal system	Triclinic
Space group	P-1
a /Å	9.795(5)
b /Å	9.798(5)
c /Å	19.810 (5)
α/°	95.148(5)
β/°	97.711(5)
γ/°	118.407(5)
V/Å^3	1631.2(12)
Z	2
ρ_{calc} (g/cm3)	1.856
temp (K)	293(2)
μ/mm^{-1}	4.235
R_{int}	0.0282
Goodness-of-fit on F^2	1.086
R_1[a], wR_2[b] [I > 2σ(I)]	0.0993, 0.2611
R_1, wR_2 (all data)	0.1082, 0.2662

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

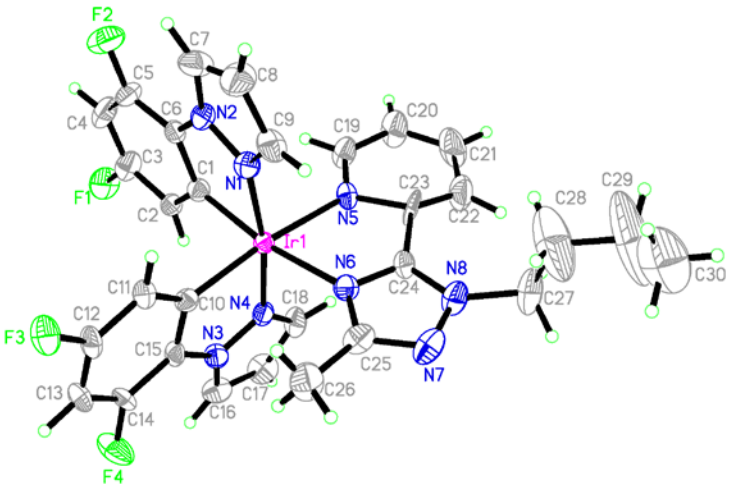


Fig. S1 Crystal structure of complex **1** with thermal ellipsoids drawn at the 30% probability level. The PF_6 counter anions are omitted for clarity.

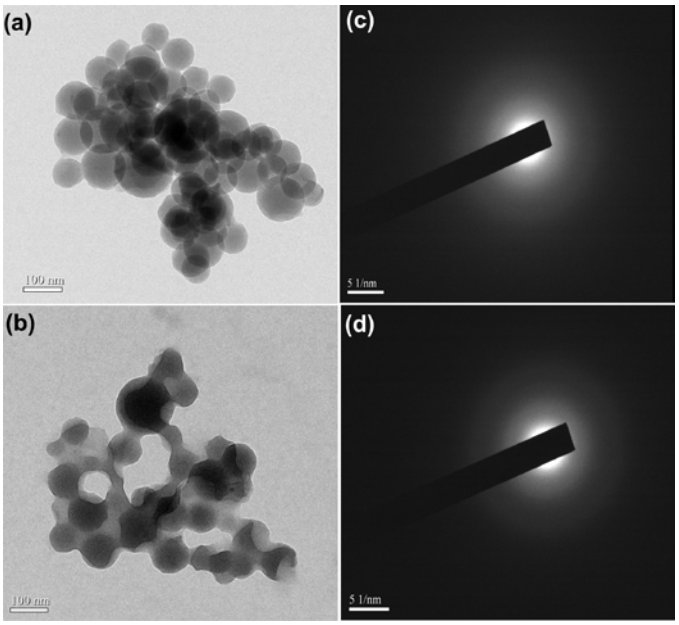


Fig. S2 TEM images of aggregates of complexes **2**(a) and **3** (b) and ED patterns (**2** for c and **3** for d) formed in water/acetone mixtures with water content of 90%, respectively.

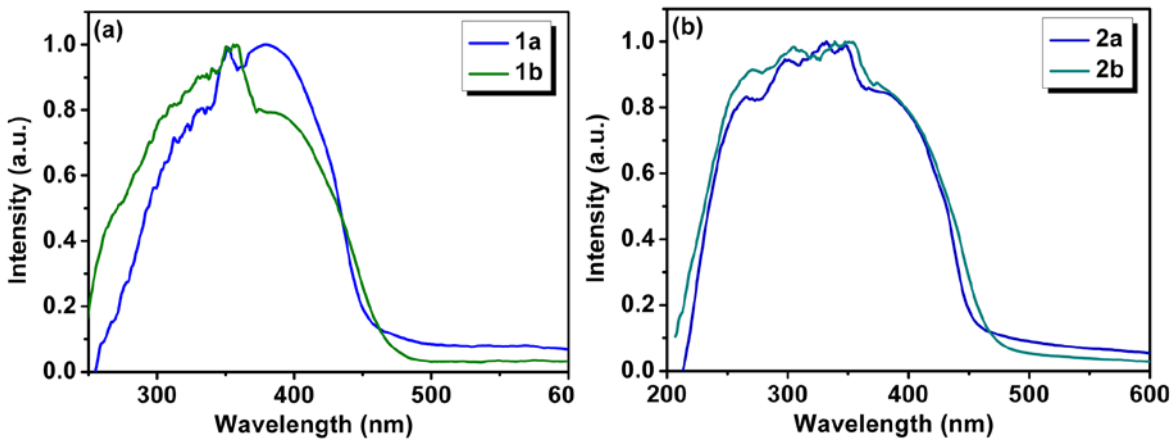


Fig. S3 Solid-state absorption spectra of complexes **1** and **2** before (**1a** and **2a**) and after (**1b** and **2b**) grinding.

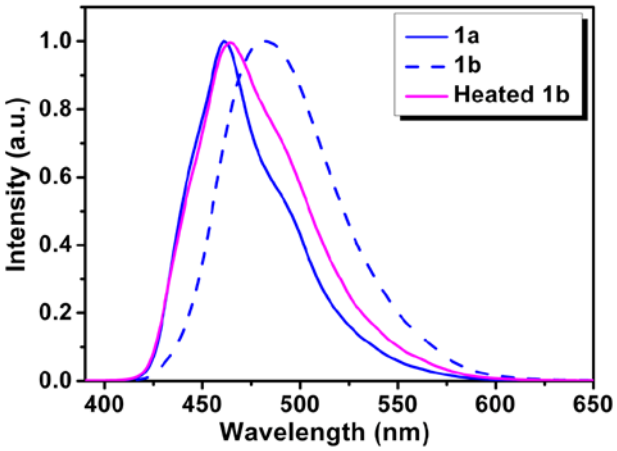


Fig. S4 Emission spectra of **1** in different states at room temperature.

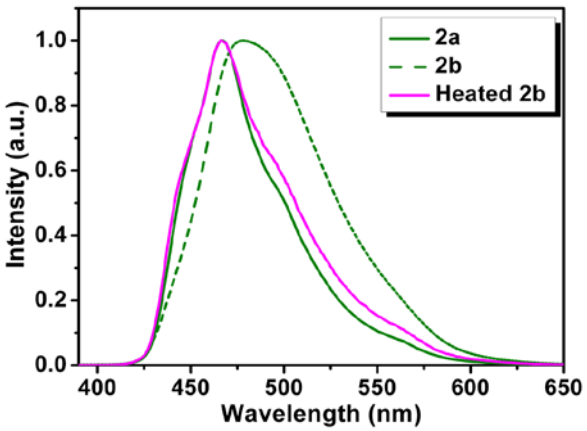


Fig. S5 Emission spectra of **2** in different states at room temperature.

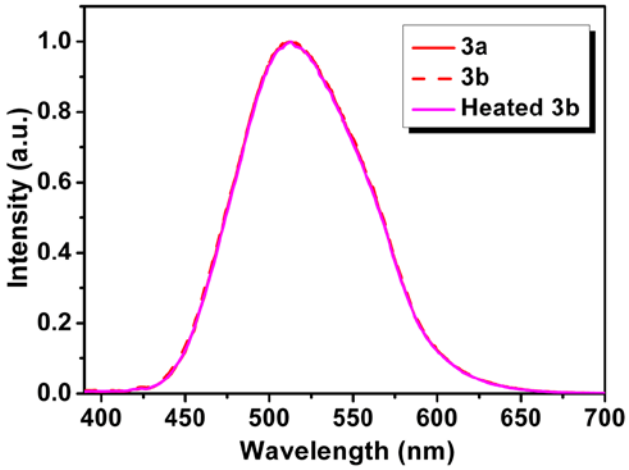


Fig. S6 Emission spectra of **3** in different states at room temperature.

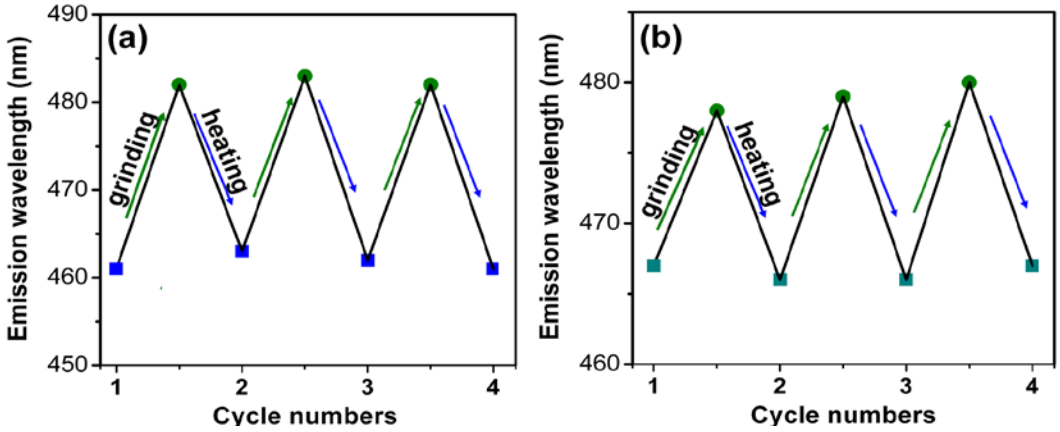


Fig. S7 Reversible switching of emission of **1** (a) and **2** (b) by repeated grinding-heating cycle.

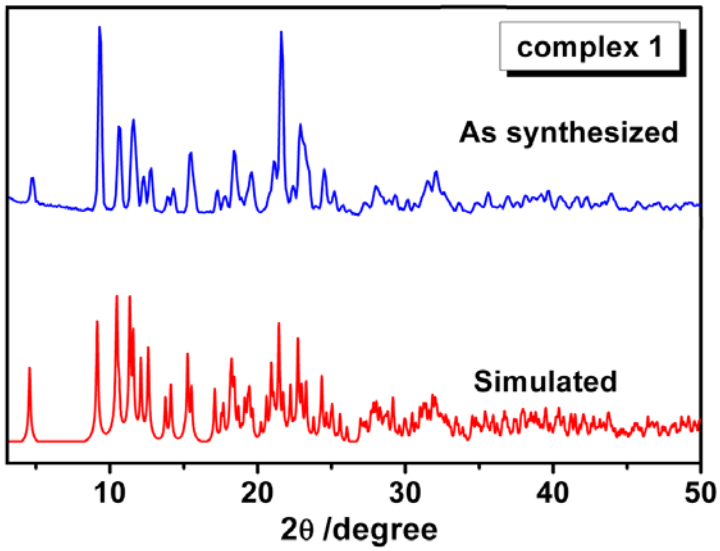


Fig. S8 Experimental and simulated Powder X-ray diffraction patterns.

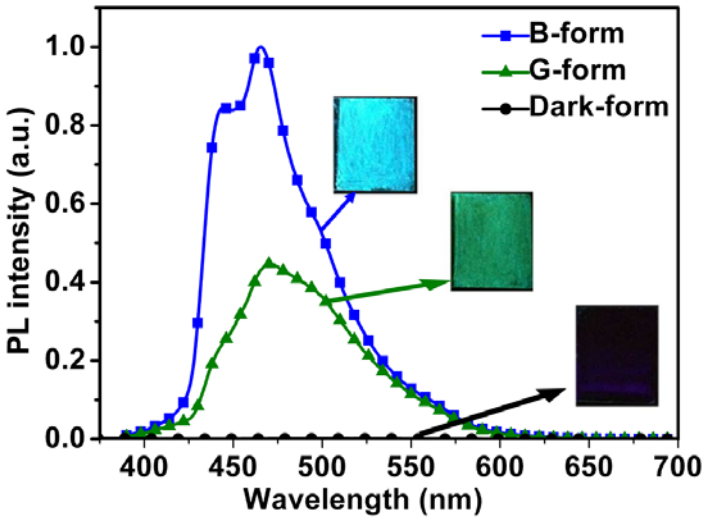


Fig. S9 Emission spectra of B-form, G-form and dark-form at room temperature.

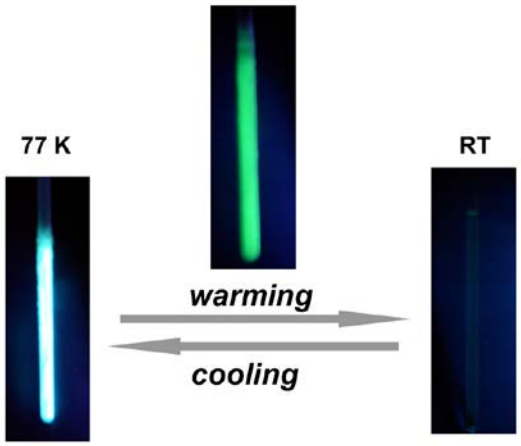


Fig. S10 Luminescence images of CH_3CN solution of complex **2** in a quartz tube at different temperature. RT = room temperature

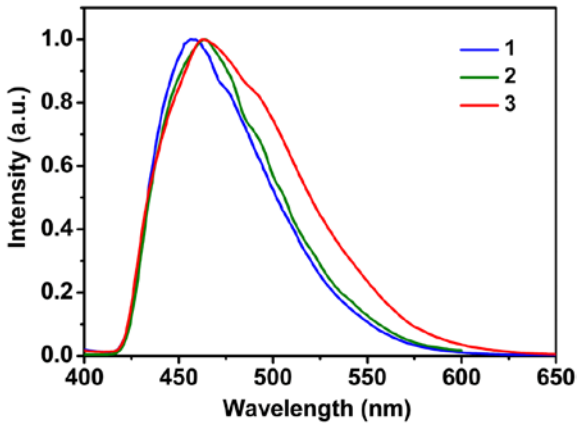


Fig. S11 Emission spectra of complex **1**, **2** and **3** in CH3CN solutions with concentration of 1×10^{-5} M at 77 K.

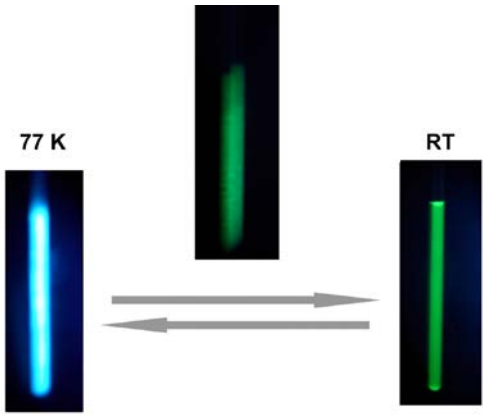


Fig. S12 Photographic images of complex **1** in different temperature with concentration of 1×10^{-5} M.

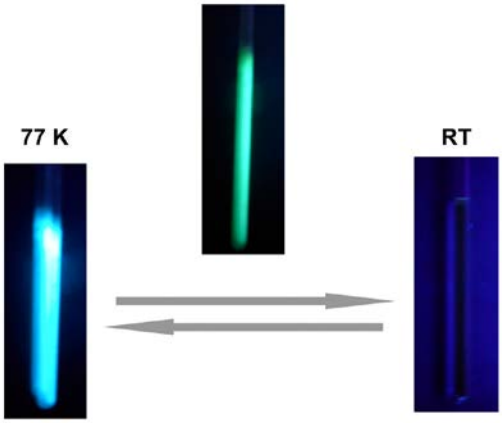


Fig. S13 Photographic images of complex **3** in different temperature with concentration of 1×10^{-5} M.

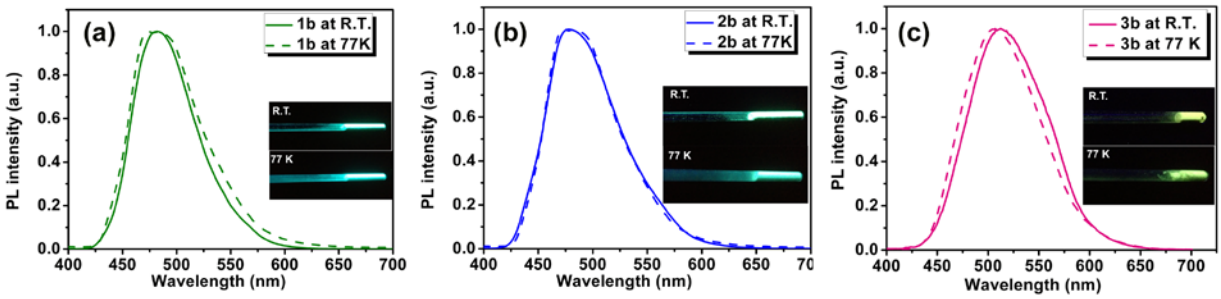


Fig. S14 Emission spectra and photographic images of ground samples **1b**, **2b** and **3b** at room temperature and 77 K.

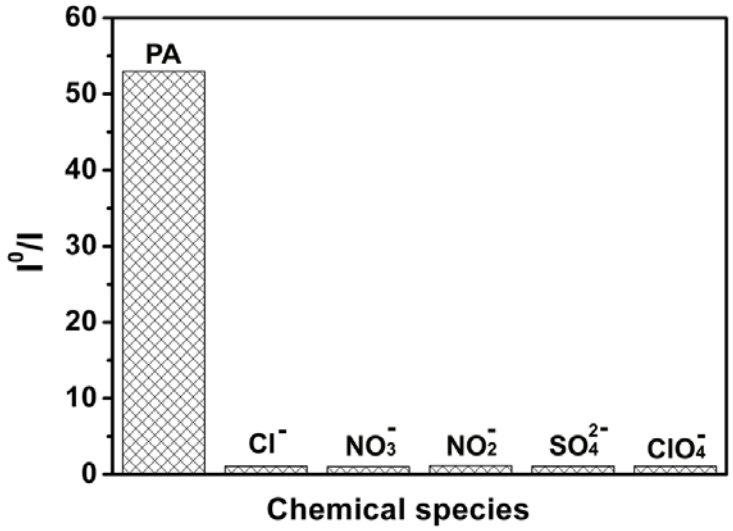


Fig. S15 Luminescent responses of complex **2** in acetone/water (v:v=1:9) mixture to different chemical species with concentration of 10 ppm. Bars represent the ratio of I_0/I of luminescent intensity at 483 nm. Herein, I_0=PL intensity without chemical species.

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.