

Electronic Supplementary Information

Understanding Mechanochromic Luminescence on Account of Molecular Level Based on Phosphorescent Iridium(III) Complex Isomers

Guangfu Li,[†] Tianzhi Yang,[†] Kuizhan Shao,[†] Ying Gao,[‡] Guogang Shan,^{*,†} Zhongmin Su,[†] Xinlong Wang,^{*,†} and Dongxia Zhu^{*,†}

^aKey Laboratory of Nanobiosensing and Nanobioanalysis at Universities of Jilin Province, Department of Chemistry, North-east Normal University, 5268 Renmin Street, Changchun, Jilin Province 130024, P. R. China; Fax: +86-0431-85684009

Tel.: +86-431-85099108, E-mail: shangg187@nenu.edu.cn; zhudx047@nenu.edu.cn; wangxl824@nenu.edu.cn

^b Institute for Interdisciplinary Biomass Functional Materials Studies, Jilin Engineering Normal University, Changchun 130052, P. R. China

Table of Contents

1. Reference Samples
2. ¹³C NMR Spectra
3. Photophysical Properties
4. TEM and ED Experiments
5. TGA and DSC Curves
6. X-ray Crystallographic Data
7. TD-DFT Calculations

1. Reference Samples

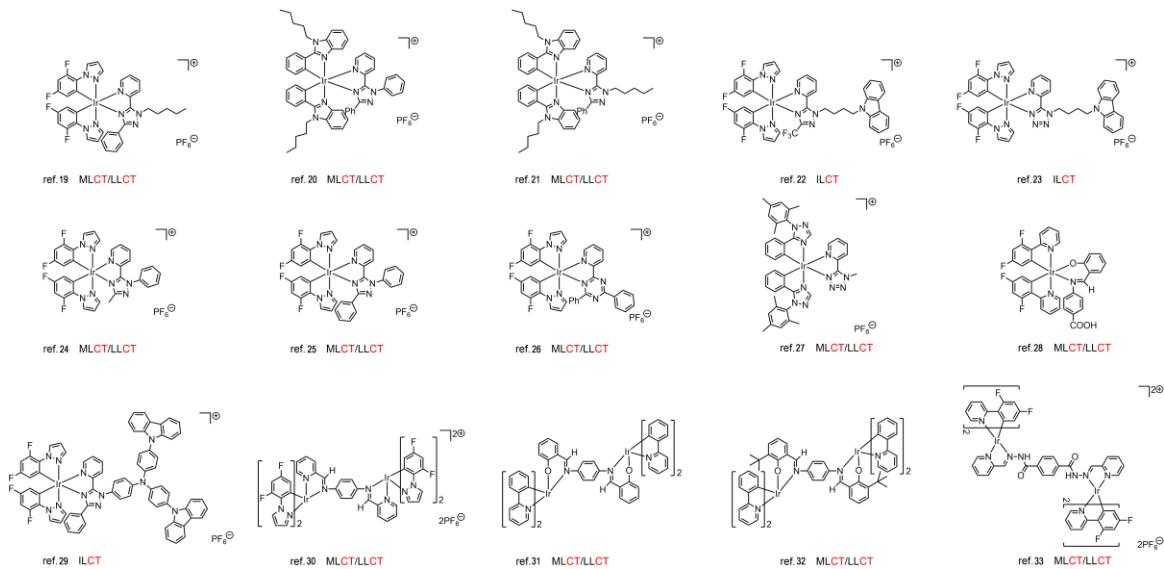


Figure S1. The representative MCL-active iridium(III) complexes previously reported.

2. ^{13}C NMR Spectra

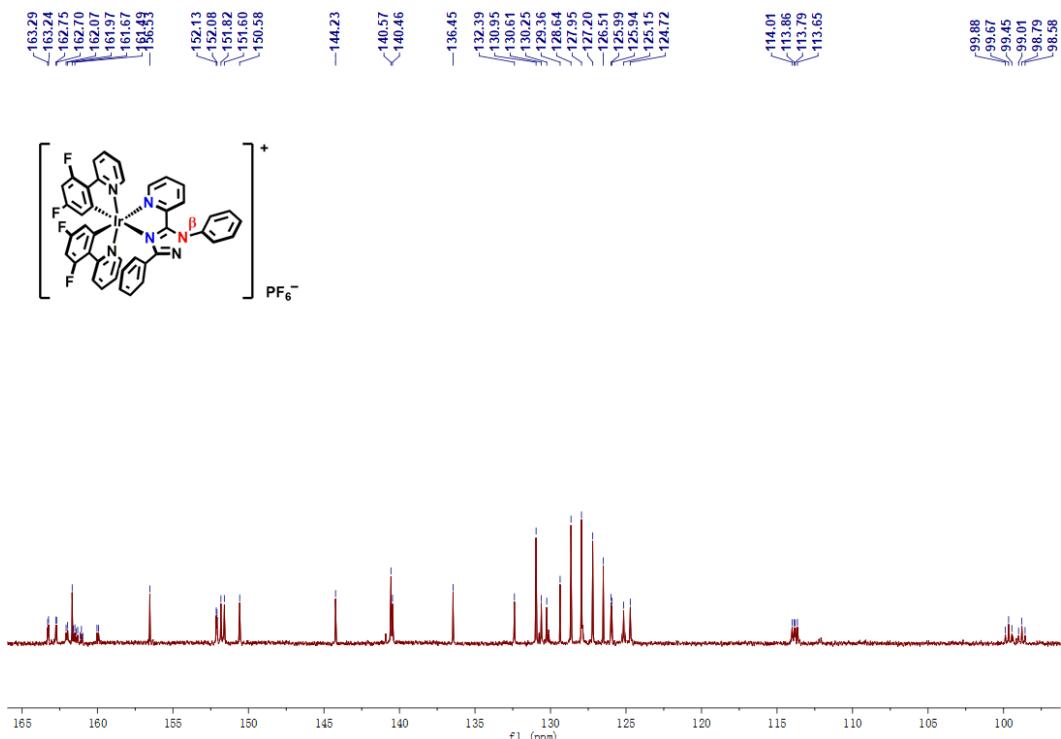


Figure S2. The ^{13}C NMR spectrum of complex **1** in $\text{DMSO}-d_6$.

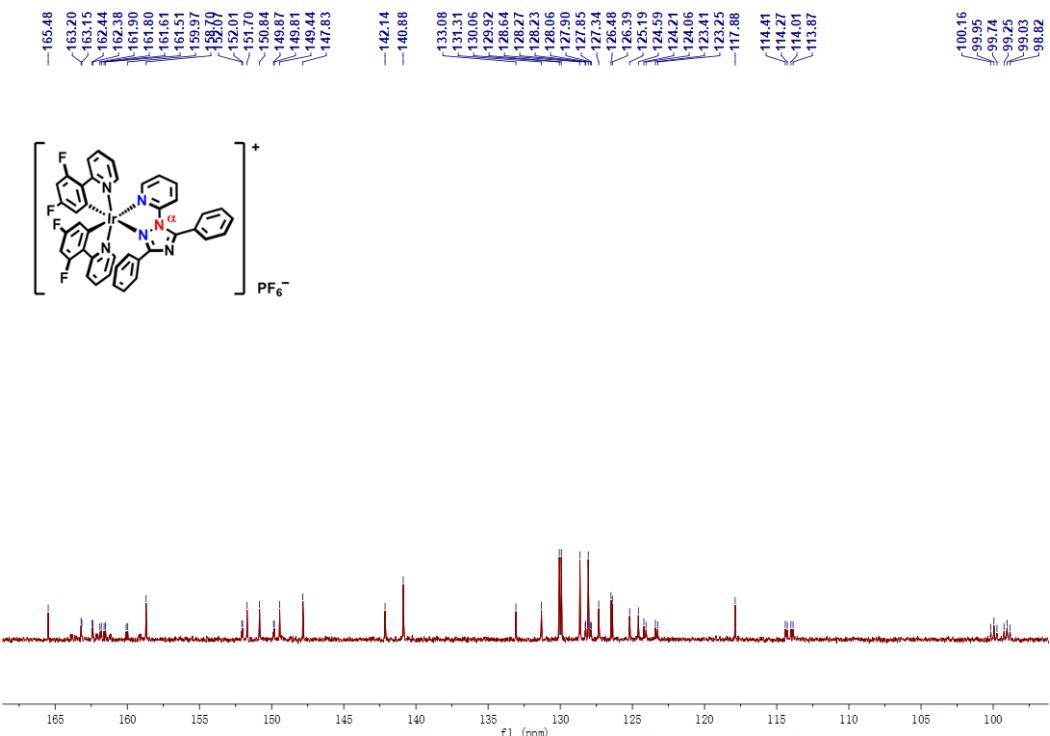


Figure S3. The ^{13}C NMR spectrum of complex 2 in $\text{DMSO}-d_6$.

8. Photophysical Properties

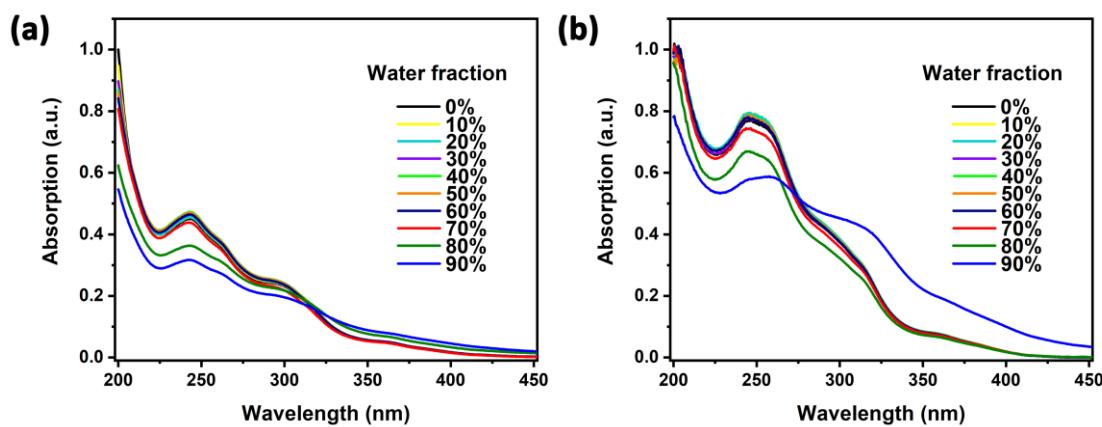


Figure S4. UV-Vis absorption spectra of isomers 1 (a) and 2 (b) in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ mixtures with different water fractions (0–90%).

4. TEM and ED Experiments

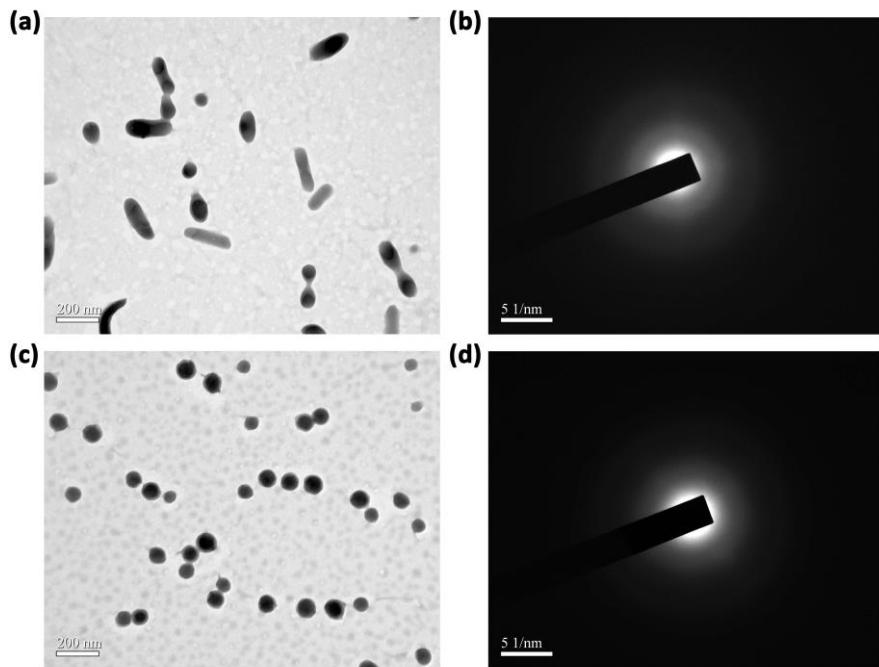


Figure S5. TEM images of nanoaggregates of isomers **1** (a) and **2** (c) formed in $\text{CH}_3\text{CN}-\text{H}_2\text{O}$ mixtures with 90% water fraction. And corresponding electron diffraction pattern of the nanoaggregates of isomers **1** (b) and **2** (d).

5. TGA and DSC Curves

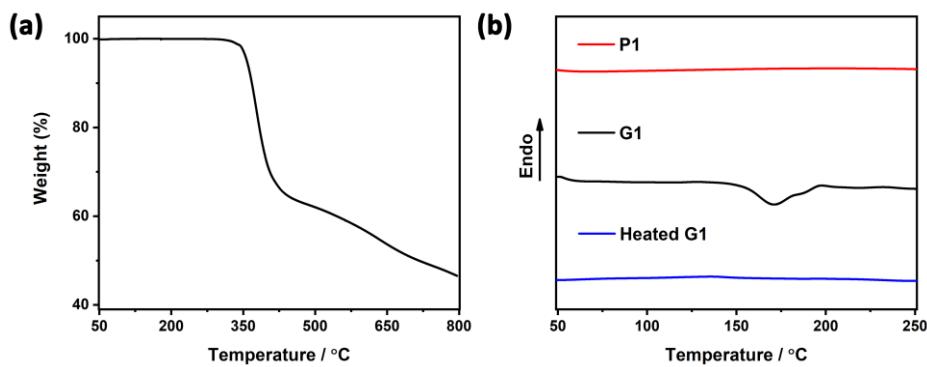


Figure S6. (a) TGA curve of **P1**. (b) DSC curves of **P1**, **G1** and **Heated G1**.

6. X-ray crystallographic data

The molecular structures of iridium(III) complex isomers **1** and **2** were confirmed by X-ray crystallographic analysis of single crystals. The crystals for both isomers were obtained by the solvent diffusion method (from n-pentane to dichloromethane). Diffraction data were collected on a Bruker SMART Apex CCD diffractometer using $\text{k}(\text{Mo-K})$ radiation ($\text{k} = 0.71069 \text{ \AA}$). Cell refinement and data reduction were made by the SAINT program. The structure was determined using the SHELXTL/PC program. The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre with CCDC deposition numbers 2002958 (isomer **1**) and 2002959 (isomer **2**). These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Table S1. Crystal Data and Structure Refinement for Isomers **1** and **2**

	isomer 1	isomer 2
Empirical formula	$\text{C}_{41}\text{H}_{26}\text{F}_4\text{IrN}_6\cdot\text{PF}_6\cdot\text{CH}_2\text{Cl}_2$	$\text{C}_{41}\text{H}_{26}\text{F}_4\text{IrN}_6\cdot\text{PF}_6\cdot\text{CH}_2\text{Cl}_2$
Formula weight	1100.77	1100.77
Temperature (K)	293	173
Crystal system	Triclinic	Triclinic
space group	P-1	P-1
a / \AA	9.238(5)	9.0411(7)
b / \AA	13.659(5)	13.7317(10)
c / \AA	17.037(5)	16.8868(12)
α /°	81.925(5)	82.003(3)
β /°	80.063(5)	80.642(3)
γ /°	84.616(5)	84.524(3)
$V/\text{\AA}^3$	2091.2(15)	2042.8(3)
Z	2	2
ρ_{calc} (g/cm ³)	1.748	1.790
μ/mm^{-1}	3.443	8.672

R _{int}	0.0777	0.0472
Goodness-of-fit on F ²	1.092	1.074
R ₁ ^a , wR ₂ ^b [I>2σ(I)]	0.0373, 0.0843	0.0321, 0.0807
R ₁ , wR ₂ (all data)	0.0528, 0.0911	0.0340, 0.0828

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

7. TD-DFT Calculations

The calculations reported here were carried out by using the Gaussian 09 software package.¹ The geometrical structures of the ground state and the lowest triplet state for iridium(III) complexes were fully optimized with C1 symmetry constraints by using the restricted closed-shell and openshell B3LYP methods with the LANL2DZ basis set for the Ir atom and 6-31G* for the rest of the atoms.² The effective core potential on Ir replaced the inner-core electrons, leaving the outer core (5s)2(5p)6 electrons and the (5d)6 valence electrons of iridium(III). On the basis of the optimized structures, the time-dependent DFT (TD-DFT) calculations were performed in order to study the excited state property. The solvent effect was also considered with the polarized continuum model.

Table S2. Excited State Transition Components of Isomers **1** and **2** Calculated by TD-DFT Method

Transition					
States	E (eV)	f	dipole moment (Debye)	Assignment ^a	Nature
1 T ₁	2.19	0	0.266	H→L (61%)	³ MLCT/ ³ LLCT
				H-3→L (17%)	³ MLCT/ ³ LLCT/ ³ LC
2 T ₁	1.89	0	0.0454	H→L (10%)	³ MLCT/ ³ LLCT
				H-1→L (71%)	³ MLCT/ ³ LC

^a H and L represent HOMO and LUMO, respectively.

- (1) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Keith, T.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Revision A.01; Gaussian, Inc.: Wallingford, CT, 2009.
- (2) Franc1, M. M.; Pietro, W. J.; Hehre, W. J.; Binkley, J. S.; Gordon, M. S.; Defrees, D. J.; Pople, J. A. Self-Consistent Molecular Orbital Methods. XXIII. A Polarization-Type Basis Set for Second-row Elements. *J. Chem. Phys.* 1982, 77, 3654–3665.