Electronic Supplementary Information (ESI)

Intramolecular π-stacking in cationic iridium(III) complexes with triazole-pyridine type ancillary ligand: synthesis, photophysics, electrochemistry properties and piezochromic behavior

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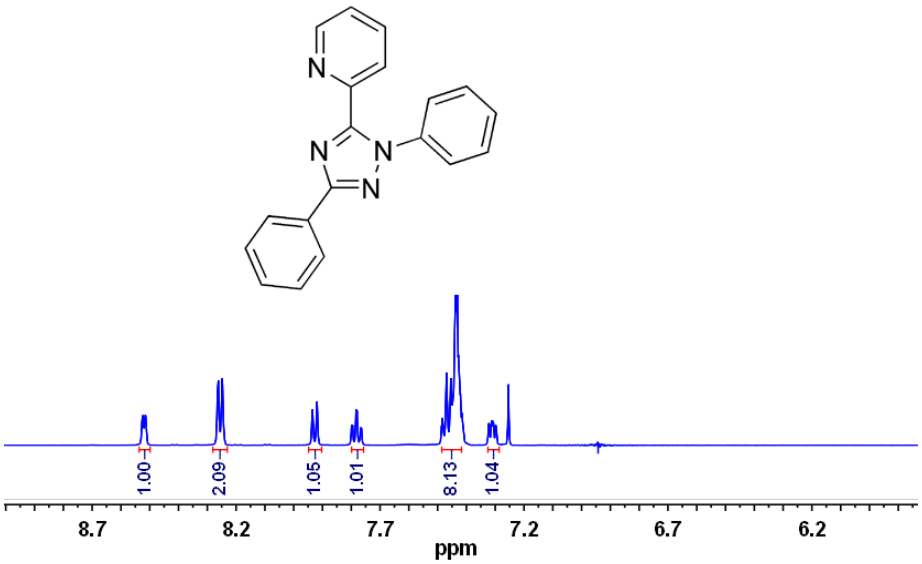

Fig. S1 ^{1}H NMR spectrum of ligand **Phtz** in $CDCl_3$.

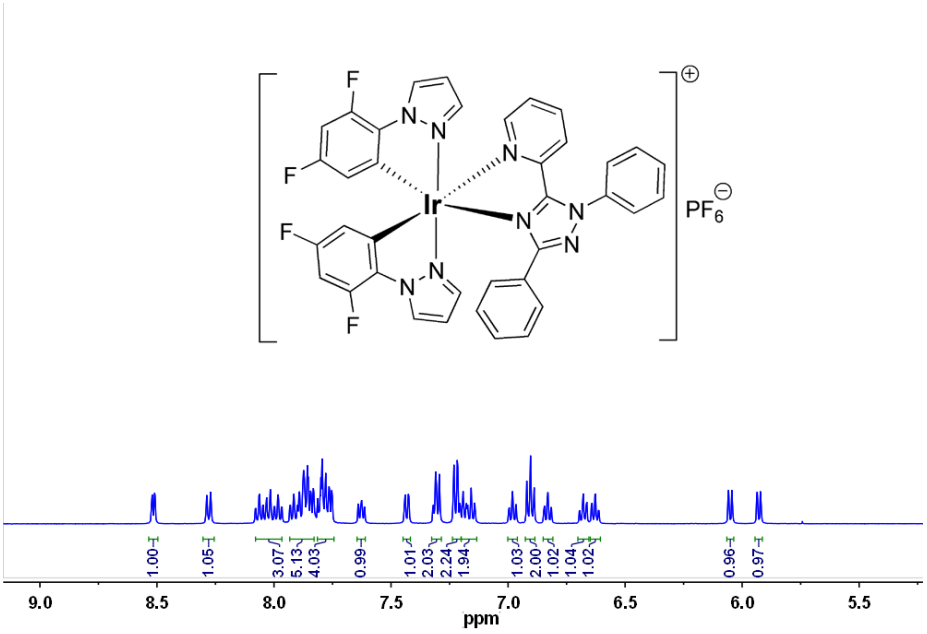

Fig. S2 ^{1}H NMR spectrum of **1** in d_6-DMSO.

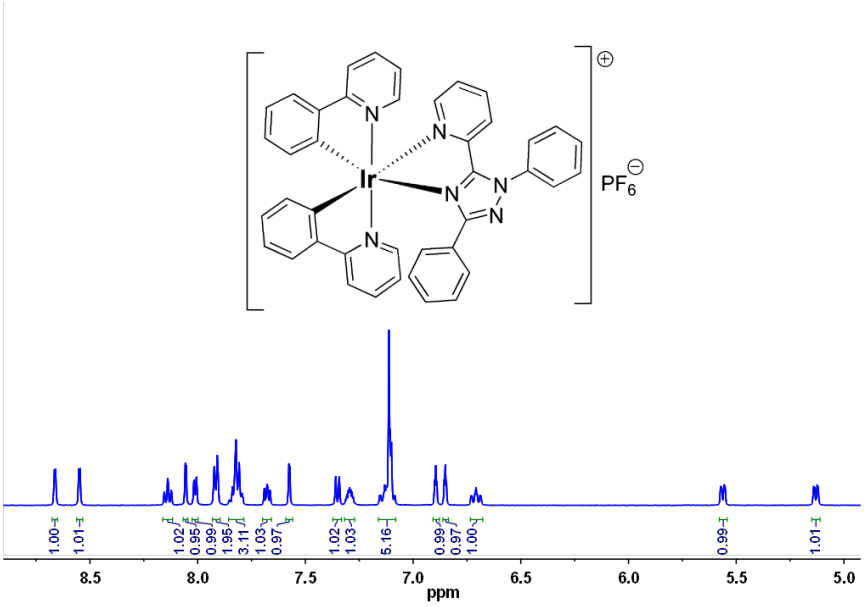

Fig. S3 ^{1}H NMR spectrum of **2** in d_6-DMSO.

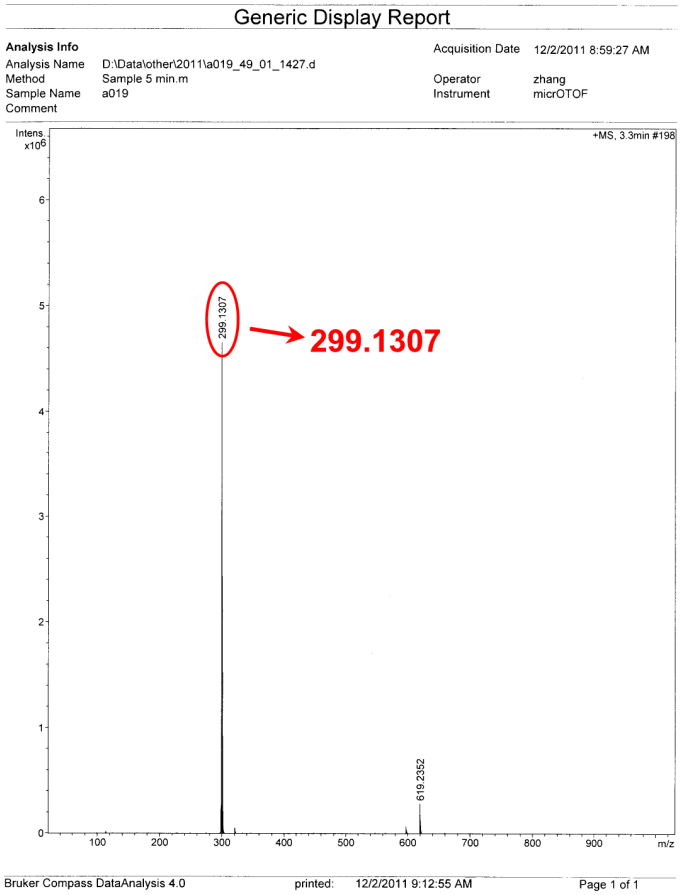

Fig. S4 Copy of High resolution mass spectrum for **Phtz** ligand.

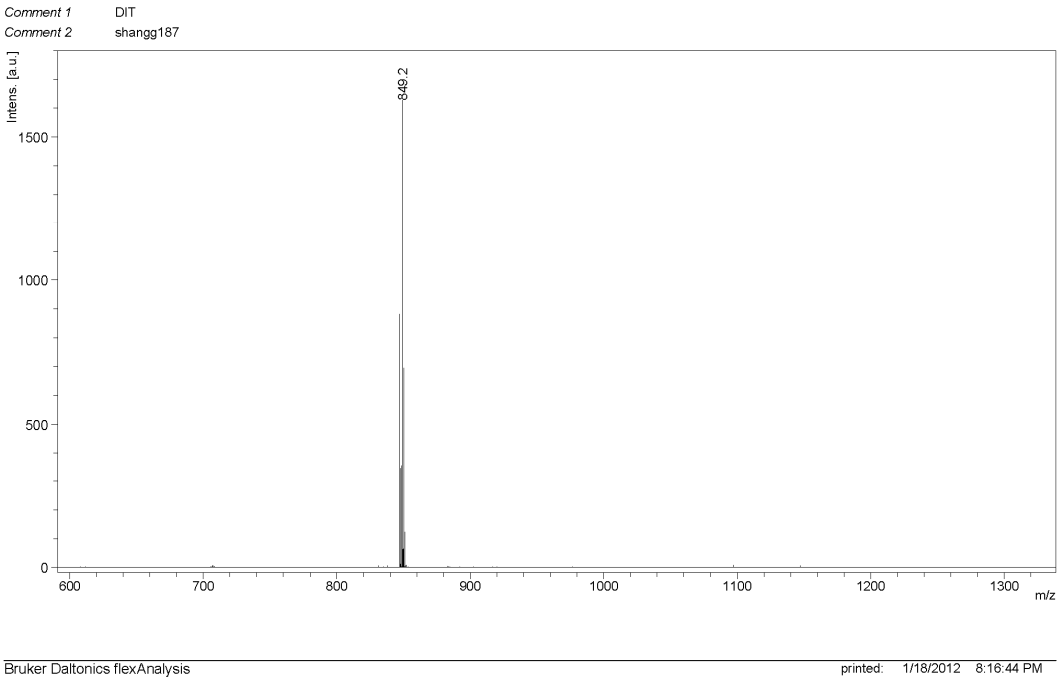

Fig. S5 Copy of the MALDI-TOF MS spectrum for **1** (positive mode)

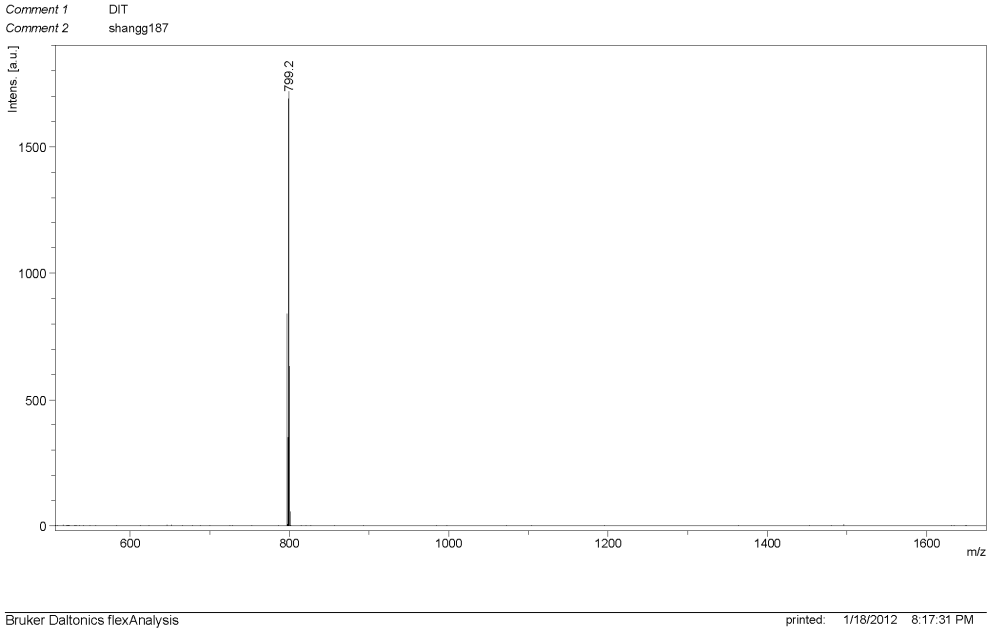

Fig. S6 Copy of the MALDI-TOF MS spectrum for **2** (positive mode).

Table S1 Crystal data and summary of data collection and refinement for complexes **1** and **2**

	1	**2**
Formula	$C_{37}H_{24}F_{10}IrN_8P$	$C_{82}H_{60}F_{12}Ir_2N_{12}P_2$
*M*r	993.81	1887.76
Crystal system	Monoclinic	Triclinic
Space group	P2(1)/c	P-1
a /Å	10.089(5)	14.469(5)
b /Å	22.846(5)	15.705(5)
c /Å	16.127(5)	17.649(5)
α/°	90	109.763(5)
β/°	100.922(5)	90.435(5)
γ/°	90	91.581(5)
V/Å^3	3650(2)	3694(2)
Z	4	2
ρ_{calc} (g/cm^3)	1.809	1.697
temp (K)	293(2)	293(2)
μ/mm^{-1}	3.794	3.728
R_{int}	0.0626	0.0364
Goodness-of-fit on F^2	0.986	1.008
R_1[a], wR_2[b] [I > 2σ(I)]	0.0408, 0.0484	0.0565, 0.1232
R_1, wR_2 (all data)	0.0920, 0.0568	0.1134, 0.1565

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

Table S2 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

Complex **1**			
Ir1–N2	2.028(4)	Ir1–N4	2.018(4)
Ir1–C10	2.004(5)	Ir1–C1	2.005(5)
Ir1–N5	2.161(3)	Ir1–N6	2.145(4)
C1–Ir1–N2	80.02(19)	N5–Ir1–N6	75.98(14)
C10–Ir1–N4	80.26(19)		
Complex **2**			
Ir1–N1	2.010(8)	Ir2–N7	2.032(8)
Ir1–N2	2.043(8)	Ir2–N8	2.069(8)
Ir1–C1	1.999(10)	Ir2–C42	1.994(10)
Ir1–C12	1.998(8)	Ir2–C58	2.005(9)
Ir1–N3	2.158(7)	Ir2–N9	2.174(8)
Ir1–N4	2.187(8)	Ir2–N10	2.221(8)
C1–Ir1–N1	80.3(3)	C42–Ir2–N7	81.4(4)
C12–Ir1–N2	79.6(3)	C58–Ir2–N8	79.3(4)
N3–Ir1–N4	76.0(3)	N9–Ir2–N10	75.5(3)

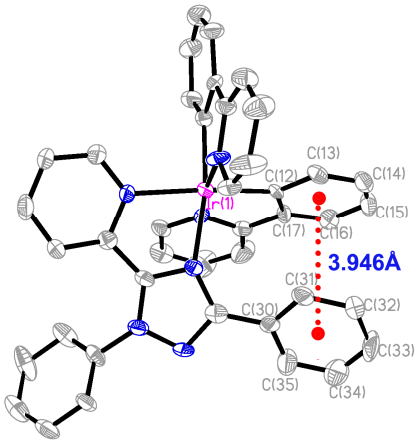

Fig. S7 The intramolecular π-π interaction in complex **2.**

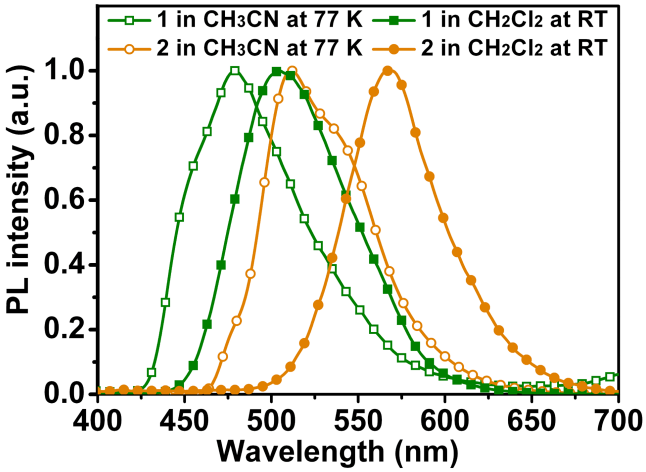

Fig. S8 The emission spectra of complexes **1** and **2** in CH_2Cl_2 at room temperature and CH_3CN at 77 K.

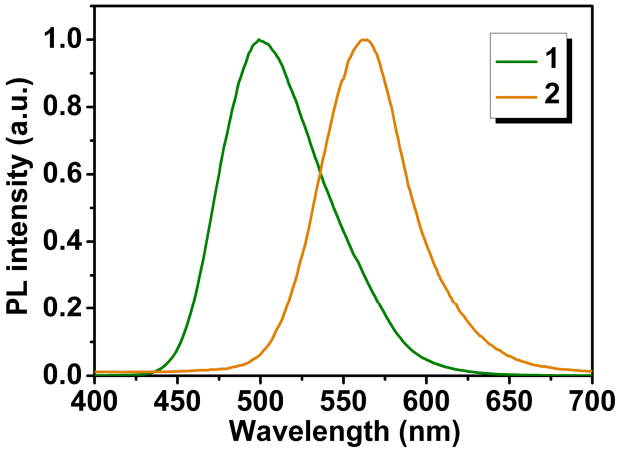

Fig. S9 The emission spectra of complexes **1** and **2** in neat film.

Table S3 The calculated energy levels of the lower-lying transitions of complexes **1** and **2**.

Complex	States	Assignment	eV	*f*	Nature
1	T_1	H→L (91%)	2.86	0	^{3}MLCT/^{3}LLCT
2	T_1	H→L (95%)	2.53	0	^{3}MLCT/^{3}LLCT

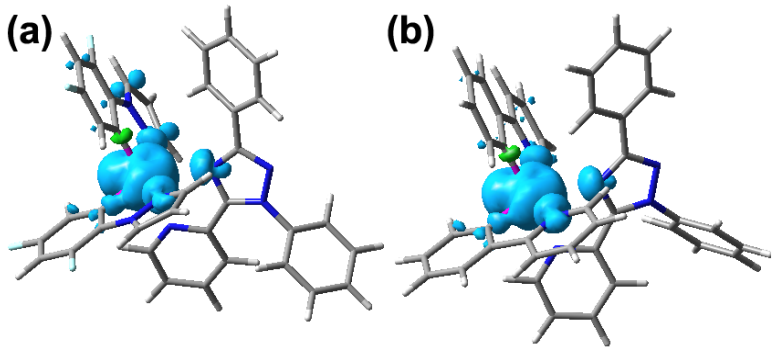

Fig. S10 Spin-density distributions of complexes **1** and **2**.

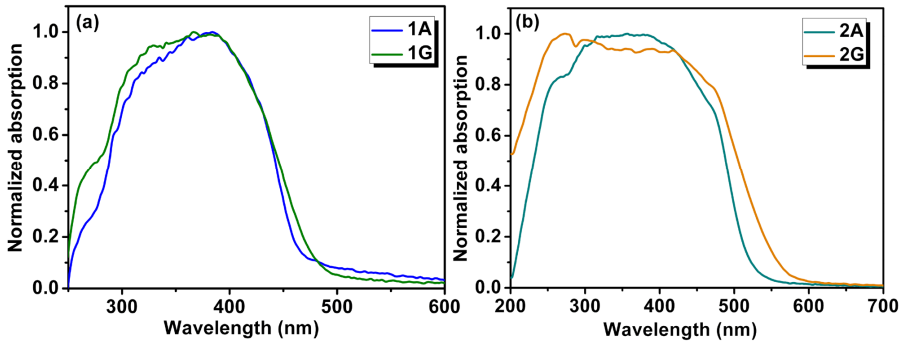

Fig. S11 Solid-state absorption spectra of complexes **1** and **2** before (**1A** and **2A**) and after (**1G** and **2G**) grinding.

Table S4 Solid-state photophysical data and of DSC results of complexes **1** and **2** before (**1A** and **2A**) and after (**1G** and **2G**) grinding.

compound	emission λ_{max} [nm]	lifetime [μs]	T_{cry}[°C][a] (ΔH [J/g])
1A	471	0.94	–
1G	499	1.0	192 (15.7)
2A	542	0.70	–
2G	563	0.50	217 (15.5)

[a] Crystallization temperature.

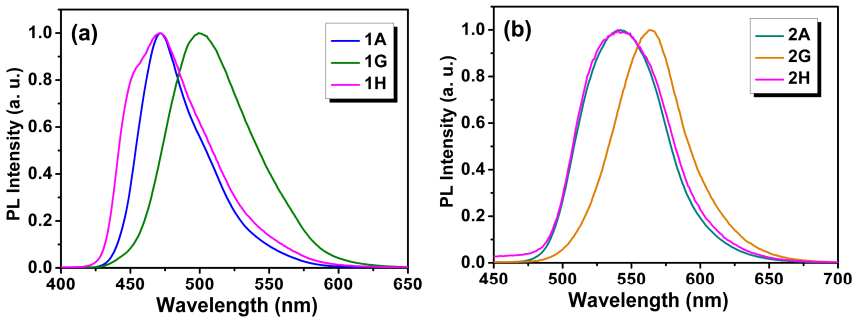

Fig. S12 Emission spectra of **1A** (a) and **2A** (b) in different states at room temperature.

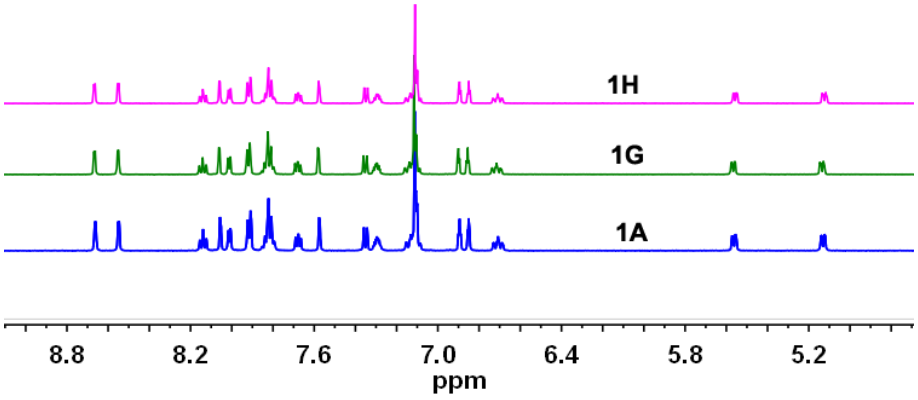

Fig. S13 ^{1}H NMR spectra of **1A** in different states.

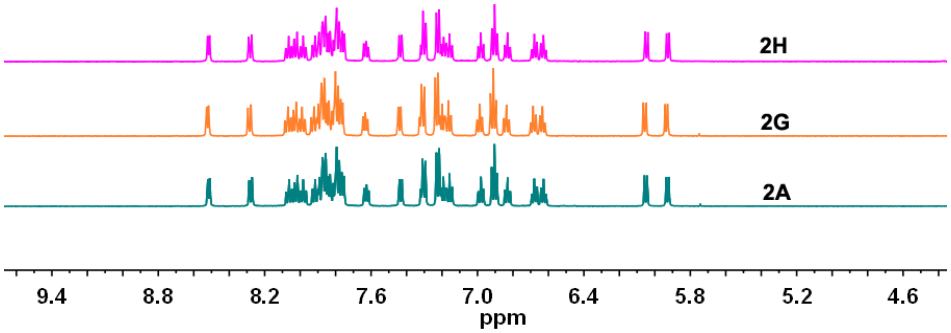

Fig. S14 ^{1}H NMR spectra of **2A** in different states.

Fig. S15 The samples **1A** (up) and **2A** (down) were cast on the filter paper and the letters "IFMC" were written with a spatula under UV-light at room temperature.

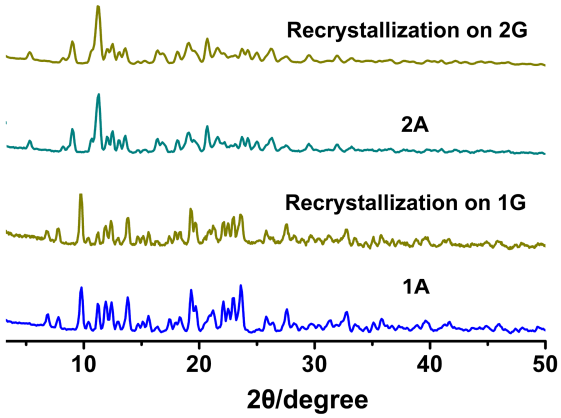

Fig. S16 The Power X-ray diffraction patterns of the recrystallization on ground samples.

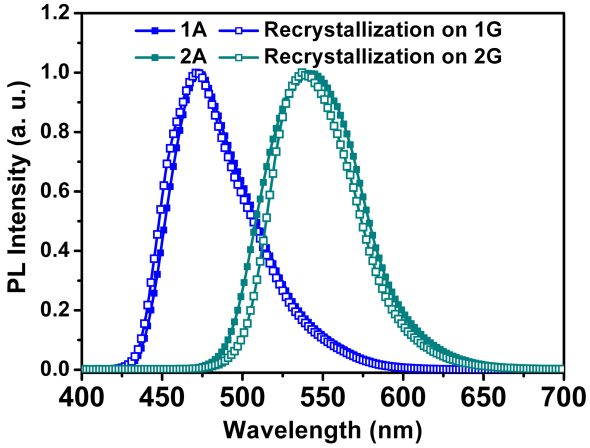

Fig. S17 The emission spectra of the recrystallization on ground samples.