Supporting Information for

Reversible piezochromic behavior of two new cationic iridium(III) complexes

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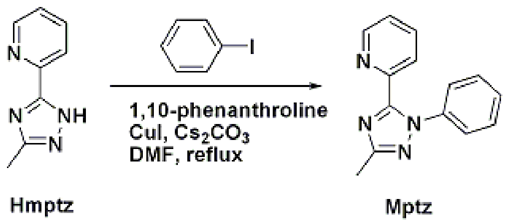
1. Experimental general information

All reagents and solvents employed were commercially available and used as received without further purification. The solvents for syntheses were freshly distilled over appropriate drying reagents. All experiments were performed under a nitrogen atmosphere by using standard Schlenk techniques. All reactions were monitored using precoated TLC plates (0.20 mm with fluorescent indicator UV_{254}). Elemental analyses (C, H, and N) were performed on a Perkin-Elmer 240C elemental analyzer. TG analyses were performed on a Perkin-Elmer TG-7 analyzer heated from room temperature to 700 °C in flowing of nitrogen. Thermal transitions were investigated by a Perkin-Elmer Thermal Analysis DSC-7 under nitrogen at a heating rate 10 °C min^{-1}. Powder X-ray diffraction (XRD) patterns of the samples were collected on a Rigaku Dmax 2000. Solvent ^1H NMR spectra were measured on Bruker Avance 500 MHz with tetramethylsilane as the internal standard. While, The ^{13}C CP/MAS spectra were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a7 mm standard bore CPMAS 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 and finely powdered samples were packed in the ZrO_2 rotor closed with Kel-F cap which were spun at 5 kHz rate. The experiments were conducted at a contact time of 2 ms. A total of 10000 scans were 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 ^{15}N CP MAS spectra of **B1** and **G1** were recorded on a Bruker AVANCE III 400 WB spectrometer equipped with a 4 mm standard bore CP MAS probehead whose X channel was tuned to 40.55 MHz for ^{15}N and the other channel was tuned to 400.18 MHz for broad band ^1H decoupling, using a magnetic field of 9.39T at 297 K. The dried and finely powdered samples were packed in the ZrO_2 rotor closed with Kel-F cap which were spun at 12 kHz rate. The experiments were conducted at a contact time of 2 ms. A total of 20000 scans were recorded with 6 s recycle delay for each sample. All ^{15}N CP MAS chemical shifts are referenced to the resonances of aglycine ($C_2H_2NO_2$) standard (δ=31.0). The molecular weights of complexes were also tested by using matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectrometry. The emission spectra were recorded using the F-7000 FL spectrophotometer. The emission spectra were measured at their maximal excitation wavelengths. The excited-state lifetimes were measured by exciting the samples with 355 nm light pulses with ~3 ns pulse width from a Quanty-Ray DCR-2 pulsed Nd: YAG laser.

For crystal structure of **B1**, 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[1] and refined by full-matrix least-squares techniques using SHELXTL-97 within WINGX.[2] The 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 S1**. Further details of the crystal structure determination have been deposited to the Cambridge Crystallographic Data Centre as supplementary publication. CCDC 843779 (**B1)** contains the supplementary crystallographic data for this paper.

2. Ancillary ligand synthesis and characterization



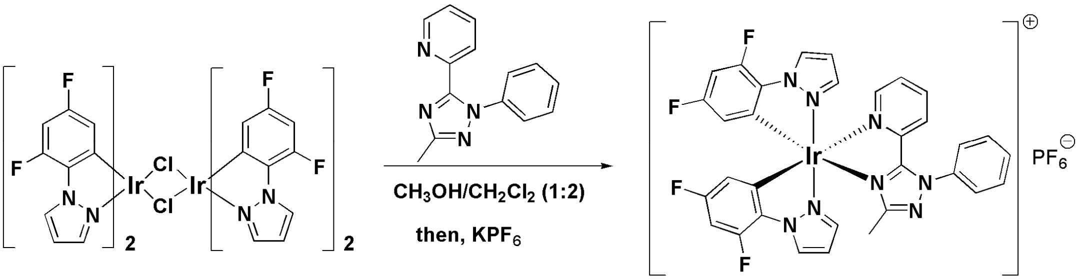
Scheme S1 The synthetic routes of ancillary ligand.

2.1 2-(5-methyl-2-phenyl-2H-1,2,4-triazol-3-yl)pyridine (Mptz)

The precursor 2-(5-methyl-2H-1,2,4-triazol-3-yl)pyridine (Hmptz) was synthesized by a previously reported procedure.[3] Hmptz (1.22g, 7.6 mmol), iodobenzene (2.45g, 12mmol), 1,10-phenanthroline (0.96g, 4.8 mmol), copper(I) iodide (0.48g, 2.5 mmol), and cesium carbonate (3.72g, 11 mmol) were dissolved in DMF (40 mL). The mixture was stirred vigorously for10 min at room temperature (RT) and subsequently refluxed under an argon atmosphere for another 24 h. After cooled to RT, the solvent was removed under vacuum, then the residue was extracted with CH_2Cl_2 (200 mL). The product was then obtained by column chromatography on silica gel with ethyl acetate/ petroleum ether (4:1) as the eluent to yield a white solid (68%). ^{1}H NMR (500 MHz, $CDCl_3$, ppm): δ 8.50 (d, J = 4.5 Hz, 1 H), 7.80–7.81 (m, 1 H), 7.75–7.76 (m, 1 H), 7.35–7.41 (m, 5 H), 7.28–7.30 (m, 1 H), 2.53 (s, 3 H). Anal. Calcd. for $C_{14}H_{12}N_4$: C, 71.17; H, 5.12; N, 23.71. Found: C, 71.18; H, 5.20, N, 23.65. ESI-MS (*m/z*): 237.1135 $[M + H]^+$

Complexes B1 and Y1 synthesis and characterization

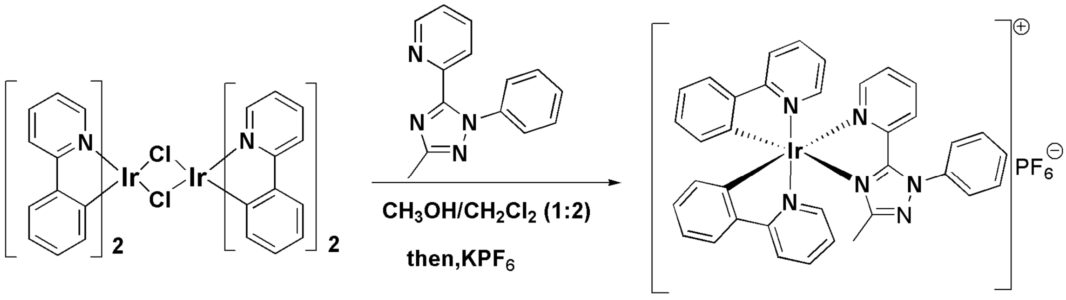
[Ir(dfppz)$_2$(Mptz)](PF$_6$) (B1)



Scheme S2 The synthetic routes of **B1**.

A solution of ligand **Mptz** (0.50 g, 2.1 mmol) and the dichloro-bridged diiridium complex $[Ir(dfppz)Cl]_2$ (1.2 g, 1.0 mmol) in dichloromethane (30 ml) and methanol (15 ml) was refluxed for 24 h in the dark. After cooling to room temperature, the mixture was filtrated, and then an excess of solid KPF_6 was added and stirred for another 0.5 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using ethyl acetate to yiled **B1** as a off-white powder (72%). ^{1}H NMR (500 MHz, d_6–DMSO, ppm): δ 8.65–8.67 (m, 2 H), 8.10 (t, *J* = 8 Hz, 1 H), 8.04 (d, *J* = 4.5 Hz, 1 H), 7.89 (d, *J* = 2 Hz, 1 H), 7.75–7.85 (m, 5 H), 7.65 (t, *J* = 6.5 Hz, 1 H), 7.40 (d, *J* = 2 Hz, 1 H), 7.25 (d, *J* = 8 Hz, 1 H), 7.07–7.16 (m, 2 H), 6.85–6.87 (m, 2 H), 5.64–5.66 (m, 1 H), 5.58–5.60 (m, 1 H), 1.82 (s, 3 H). Anal. Calcd. for $IrC_{32}H_{22}N_8F_{10}P$: C, 41.25; H, 2.38; N, 12.03. Found: C, 41.46; H, 2.43, N, 12.20. MS (MALDI-TOF): m/z 787.2 (M–PF_6).

[Ir(ppy)$_2$(Mptz)](PF_6) (Y1)



Y1

Scheme S3 The synthetic routes of **Y1**.

A solution of ligand **Mptz** (0.50 g, 2.1 mmol) and the dichloro-bridged diiridium complex [Ir(ppy)Cl]$_2$ (1.1 g, 1.0 mmol) in dichloromethane (30 ml) and methanol (15 ml) was refluxed for 24 h in the dark. After cooling to room temperature, the mixture was filtrated, and then an excess of solid KPF_6 was added and stirred for another 0.5 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography using ethyl acetate to yiled **Y1** as a light-yellow powder (65%). ^{1}H NMR (500 MHz, d$_6$–DMSO, ppm): δ 8.25–8.29 (m, 2 H), 8.18 (d, *J* = 5.5 Hz, 1 H), 7.96–8.08 (m, 3 H), 7.90 (d, *J* = 3 Hz, 2 H), 7.74–7.84 (m, 6 H), 7.71 (d, *J* = 6 Hz, 1 H), 7.65 (t, *J* = 7 Hz, 1 H), 7.72–7.29 (m, 3 H), 7.01 (t, *J* = 7.5 Hz, 1 H), 6.97 (t, *J* = 7 Hz, 1 H), 6.89 (t, *J* = 7 Hz, 1 H), 6.85 (t, *J* = 7.5 Hz, 1 H), 6.19 (d, *J* = 7.5 Hz, 1 H), 6.14 (d, *J* = 7.5 Hz, 1 H), 1.67 (s, 3 H). Anal. Calcd. for $IrC_{36}H_{28}N_6F_6P$: C, 49.03; H, 3.20; N, 9.53. Found: C, 49.06; H, 3.40, N, 9.61. MS (MALDI-TOF): m/z 737.2 (M–PF_6).

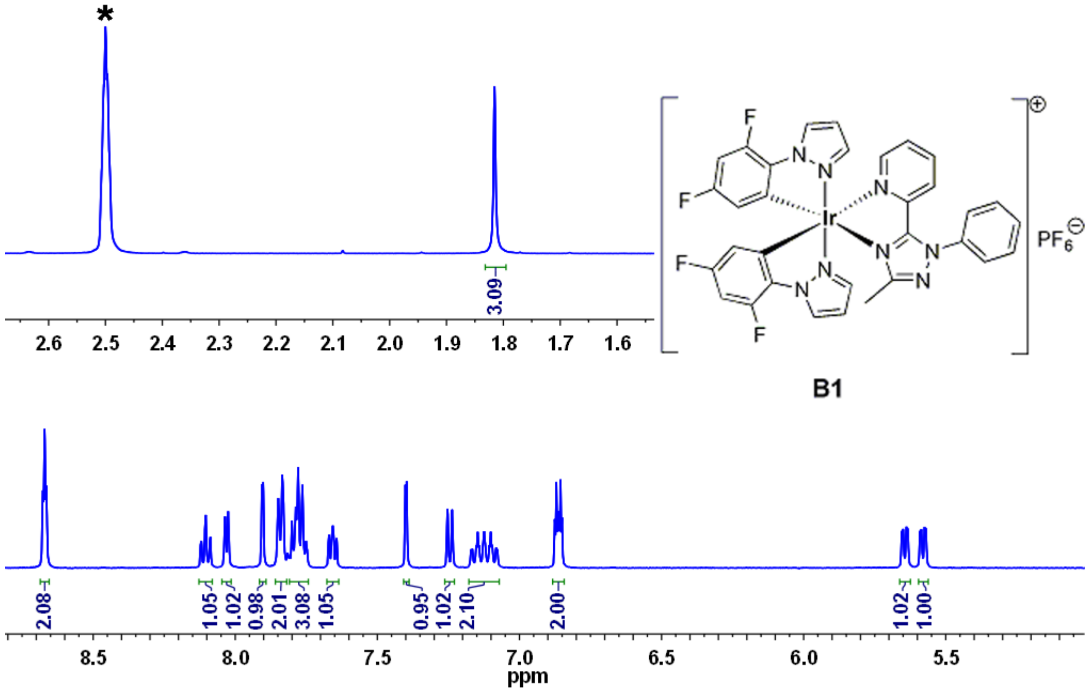


Fig. S1 The spectrum of **B1** in d$_6$-DMSO (* denote the peaks of d$_6$-DMSO).

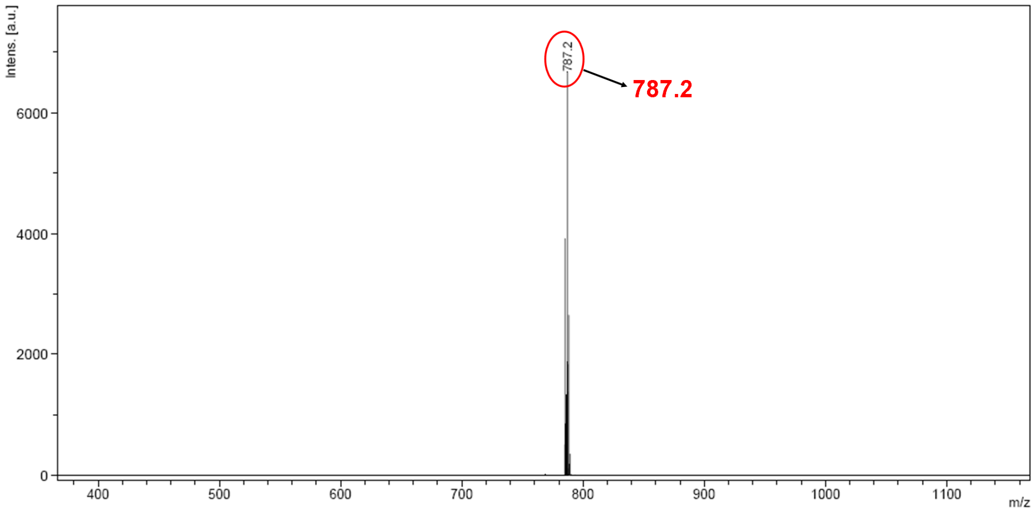


Fig. S2 Copy of the MALDI-TOF MS spectrum for **B1** (positive mode).

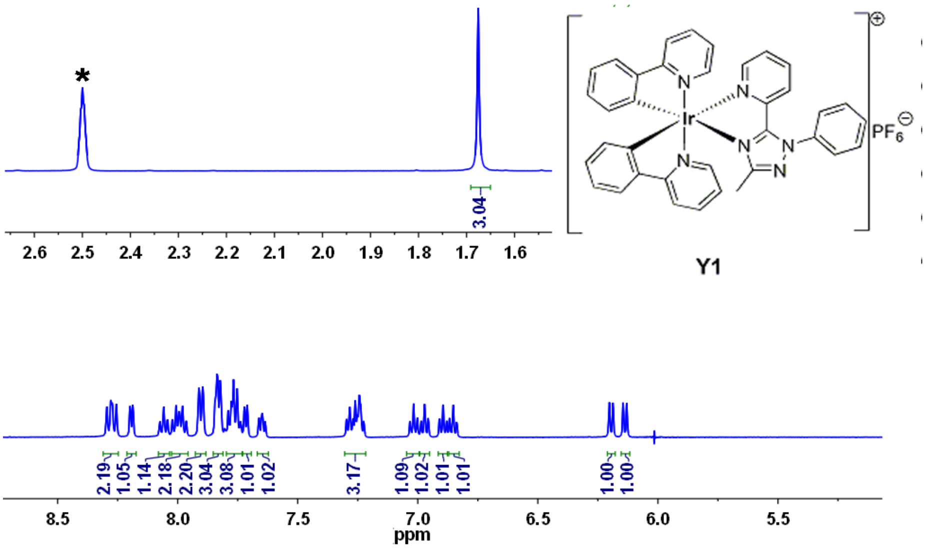


Fig. S3 The spectrum of **Y1** in d_6-DMSO (* denote the peaks of d_6-DMSO).

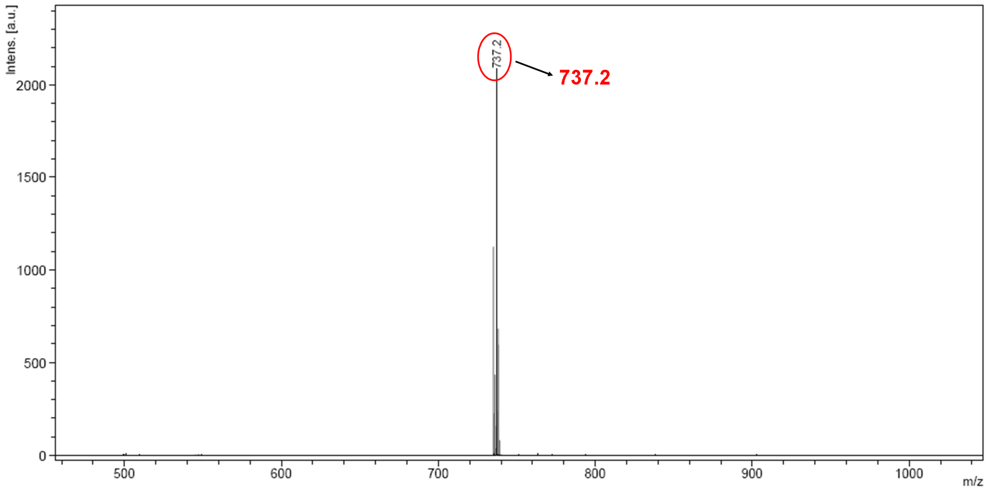


Fig. S4 Copy of the MALDI-TOF MS spectrum for **Y1** (positive mode).

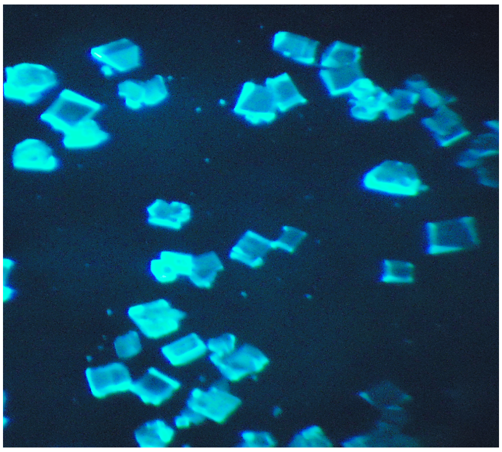


Fig. S5 Crystals of **B1** irradiated with UV-light.

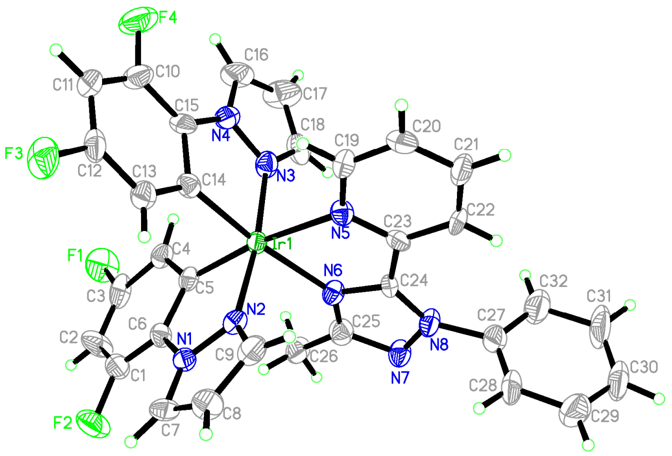


Fig. S6 Crystal structures of **B1**. Thermal ellipsoids are drawn at 30% probability. The PF_6 counter anion and H atoms are omitted for clarity.

Table S1 Crystal data and summary of data collection and refinement for **B1**

	B1
Formula	$C_{32}H_{22}F_{10}$ IrN_8P
*M*r	931.75
Crystal system	Tetragonal
Space group	I4(1)cd
a /Å	18.452(5)
b /Å	18.452(5)
c /Å	41.756(5)
α/°	90.000
β/°	90.000
γ/°	90.000
V/Å^3	14217(6)
Z	16
ρ_{calc} (g/cm3)	1.741
temp (K)	293(2)
μ/mm^{-1}	3.890
R_{int}	0.0881
Goodness-of-fit on F^2	1.034
R_1^a, wR_2^b [I >	0.0471,

2σ(I)]	0.1063
R_1, wR_2 (all data)	0.0735, 0.1179

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

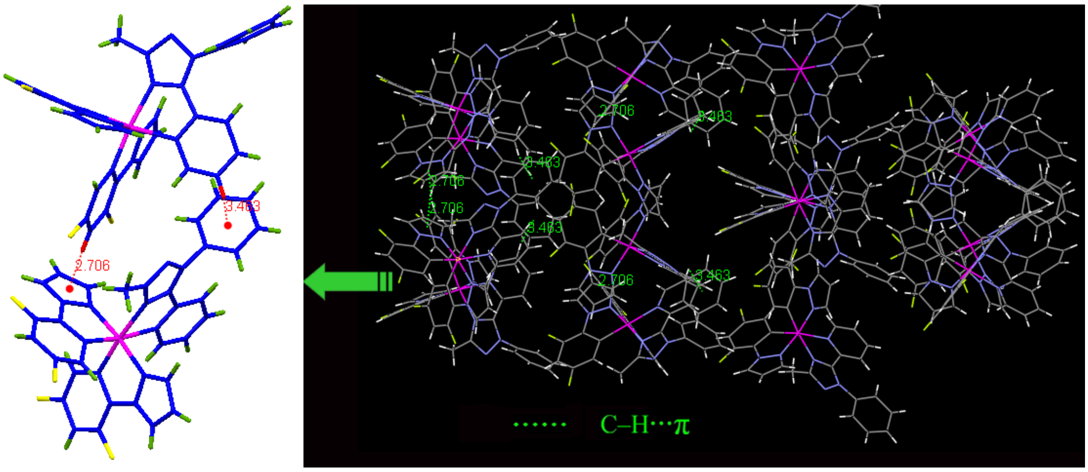


Fig. S7 Packing diagram of the crystal structure of **B1**.

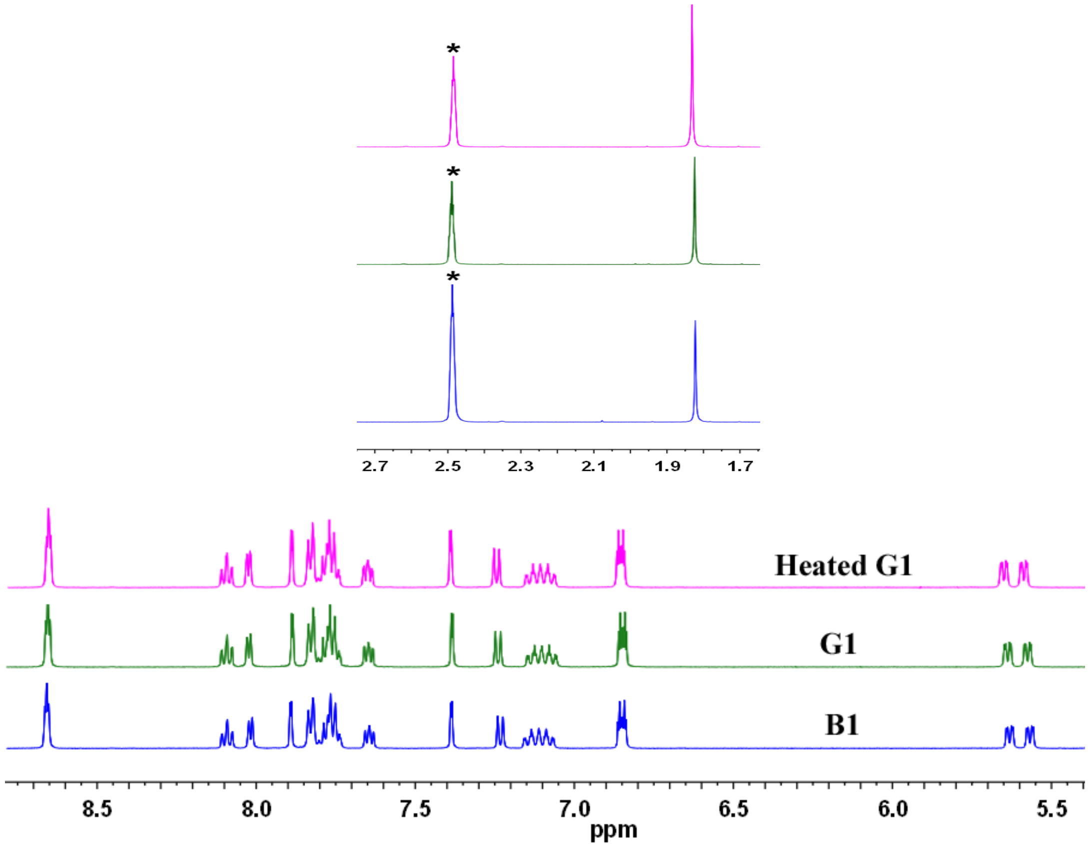


Fig. S8 ^{1}H NMR spectra of **B1** in different states.

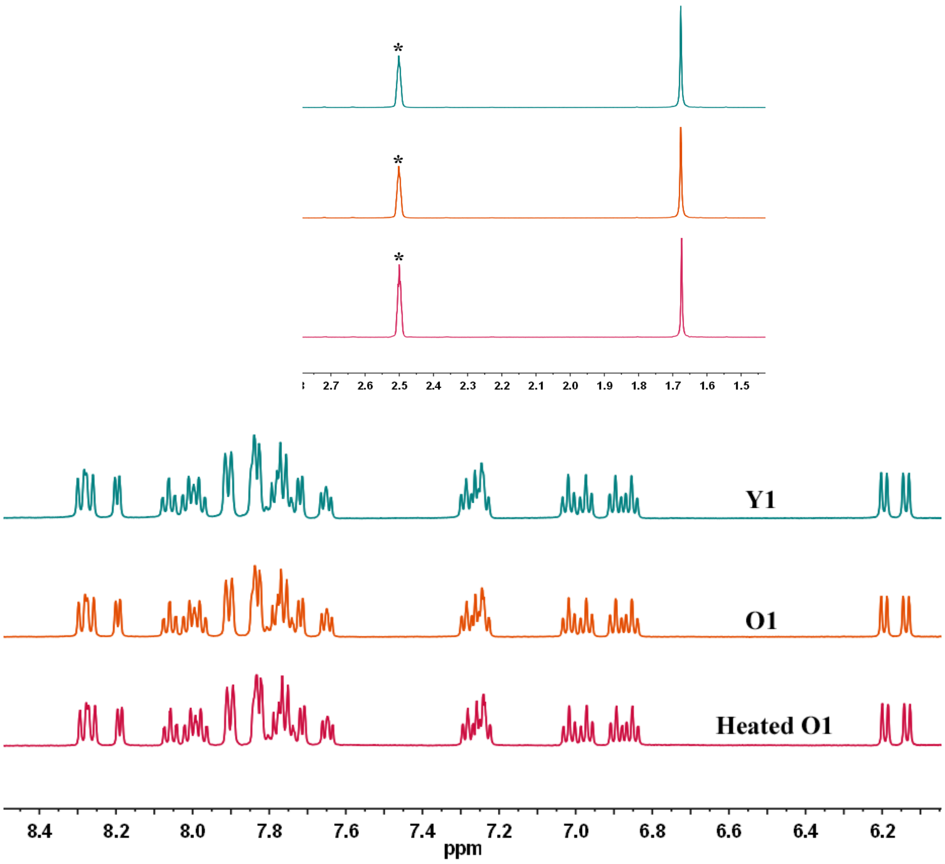


Fig. S9 ^{1}H NMR spectra of **Y1** in different states.

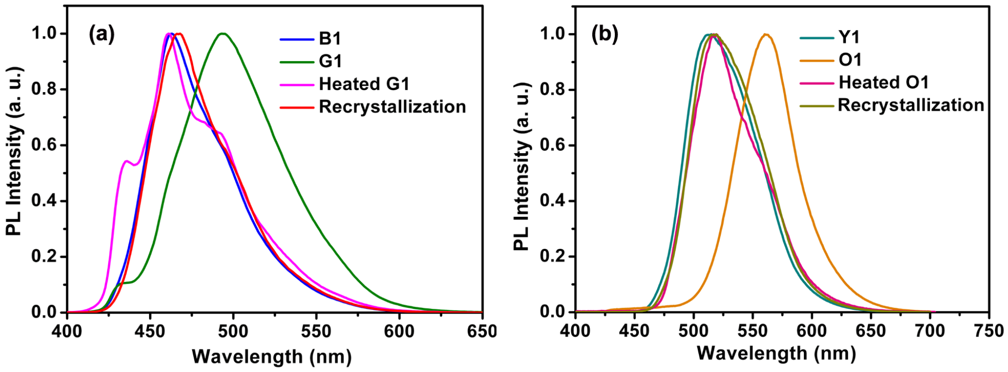


Fig. S10 Emission spectra of **B1** (a) and **Y1** (b) in different states at room temperature.

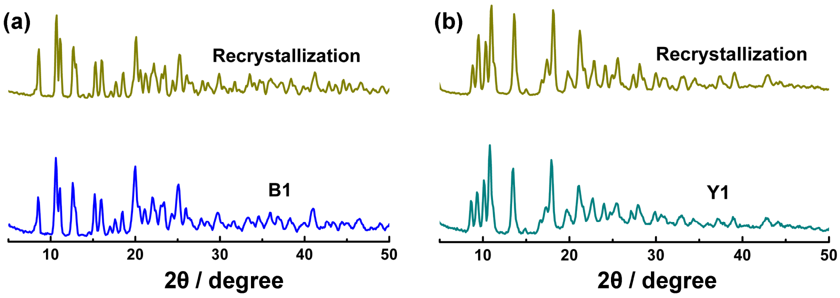


Fig. S11 PXRD curves of recrystallization on ground samples.

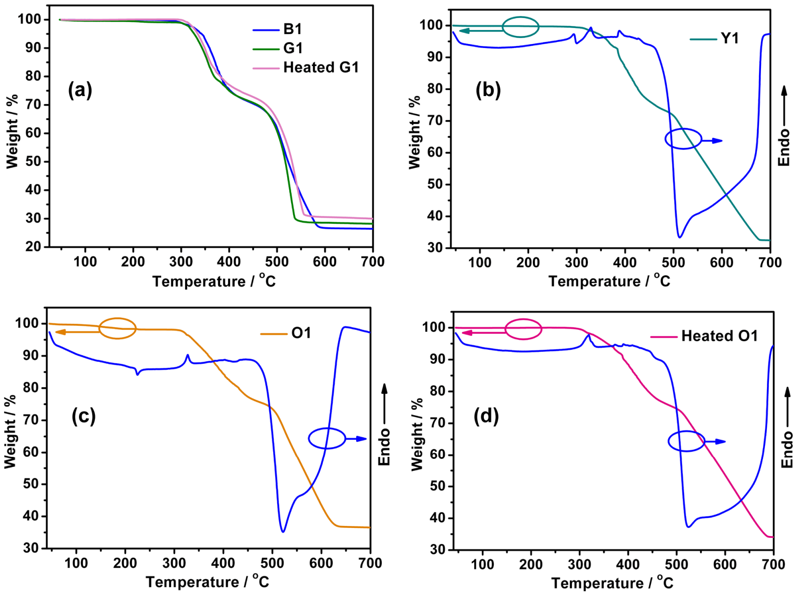


Fig. S12 (a) TGA curves of **B1** in difference state, (b) TGA/DTA curves of **Y1** (c) **O1** (d) and Heated **O1**.

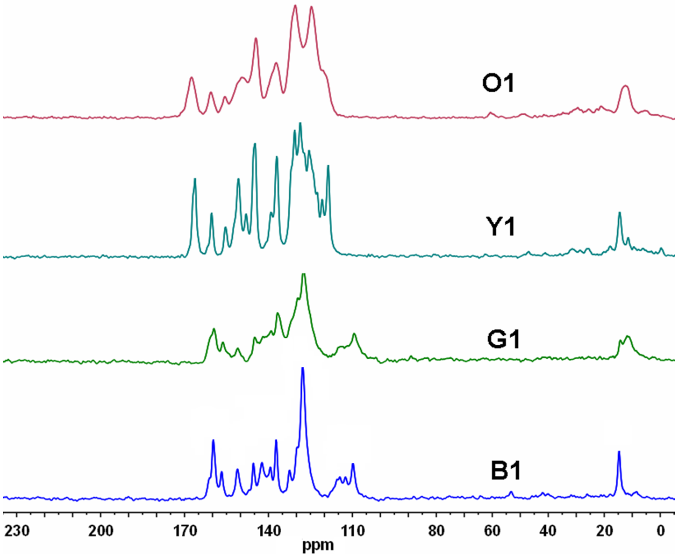


Fig. S13 ^{13}C CP/MAS spectra of **B1**, **G1**, **Y1** and **O1**.

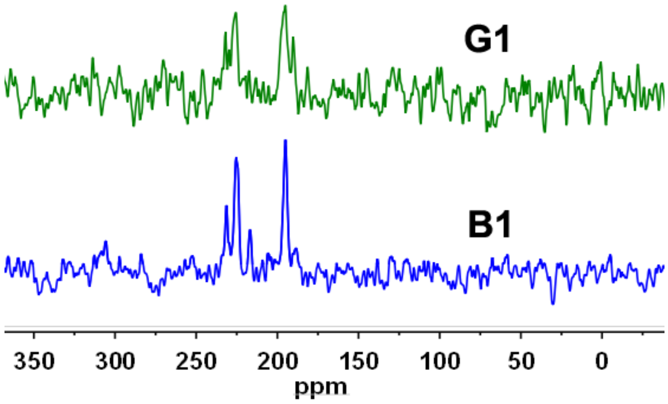


Fig. S14 ^{15}N CP/MAS spectra of **B1** and **G1**.

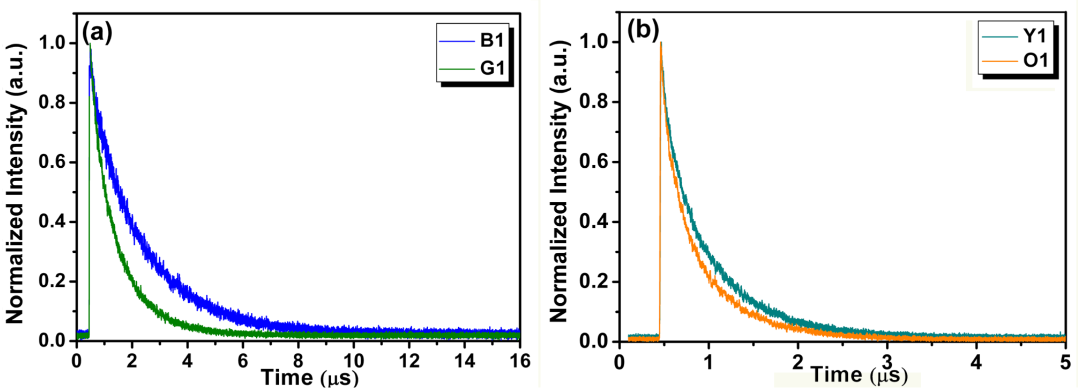


Fig. S15 Solid state photoluminescence decay curves of **B1**, **G1**, **Y1** and **O1**. (Monitor wavelengths are 461, 493, 517 and 560 nm for **B1**, **G1**, **Y1** and **G1**, respectively)

References

1. G. M. Sheldrick, SHELXL-97, *Program for Crystal Structure Refinement*, University of Göttingen, 1997.
2. L. J. Farrugia, WINGX, *A Windows Program for Crystal Structure Analysis;* University of Glasgow; Glasgow, UK, 1988.
3. L. He, J. Qiao, L. Duan, G. F. Dong, D. Q. Zhang, L. D. Wang and Y. Qiu, *Adv. Funct. Mater.*, 2009, **19**, 2950.