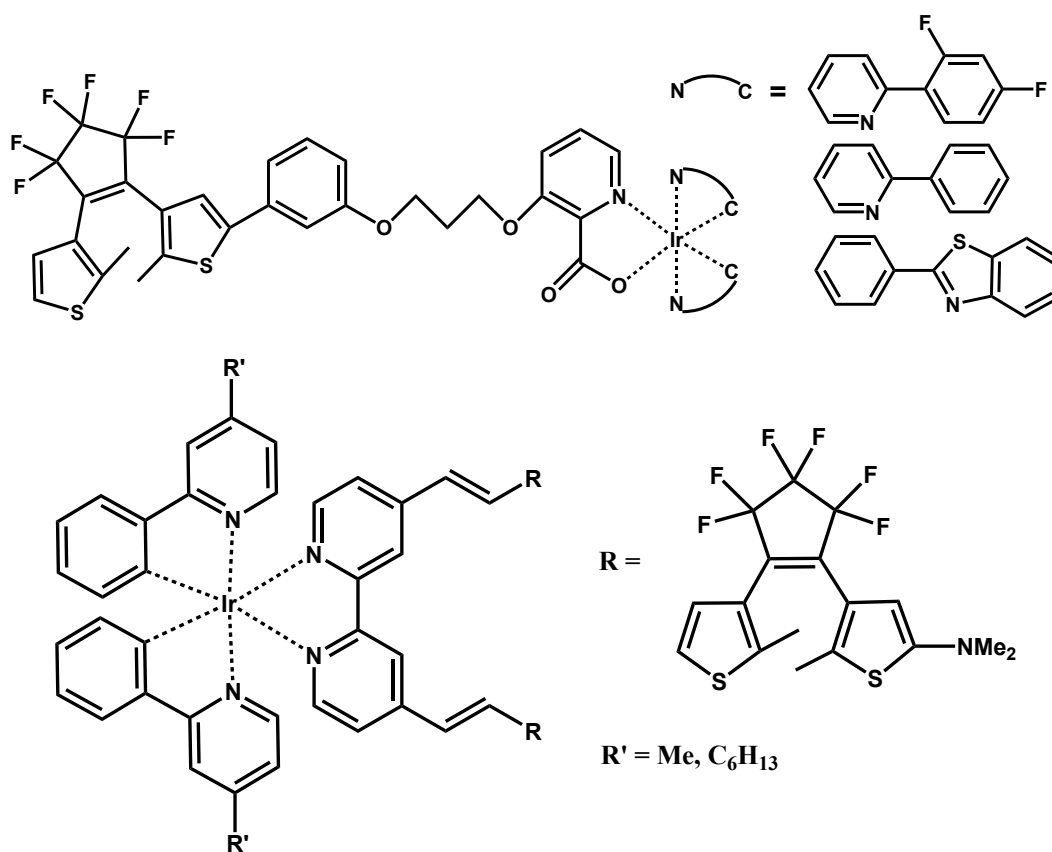


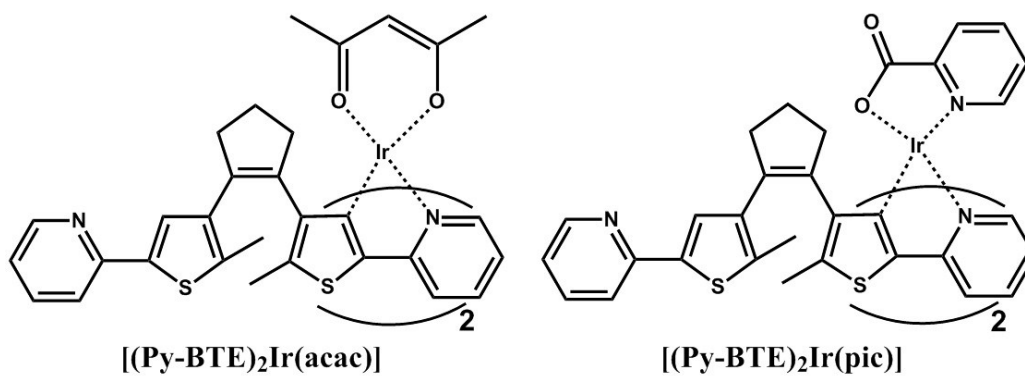
## Electronic Supporting Information

**Table S1** UV-vis absorption bands of BrLH, **1** and **2** in CH<sub>2</sub>Cl<sub>2</sub> at room temperature.

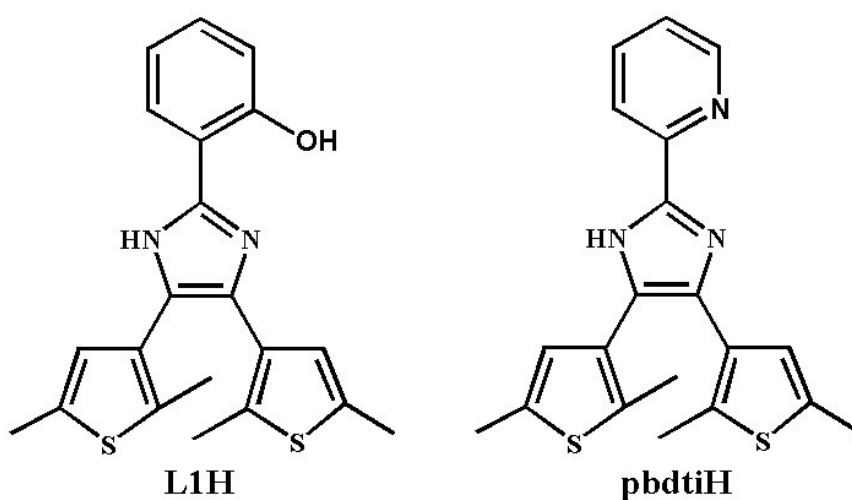
Compound	$\lambda_{\max}$ (nm)
BrLH	224, 245, 292, 338 (< 370 nm)
<b>1</b>	230, 251, 283, 380, 477
<b>2</b>	231, 270, 381, tail to 440



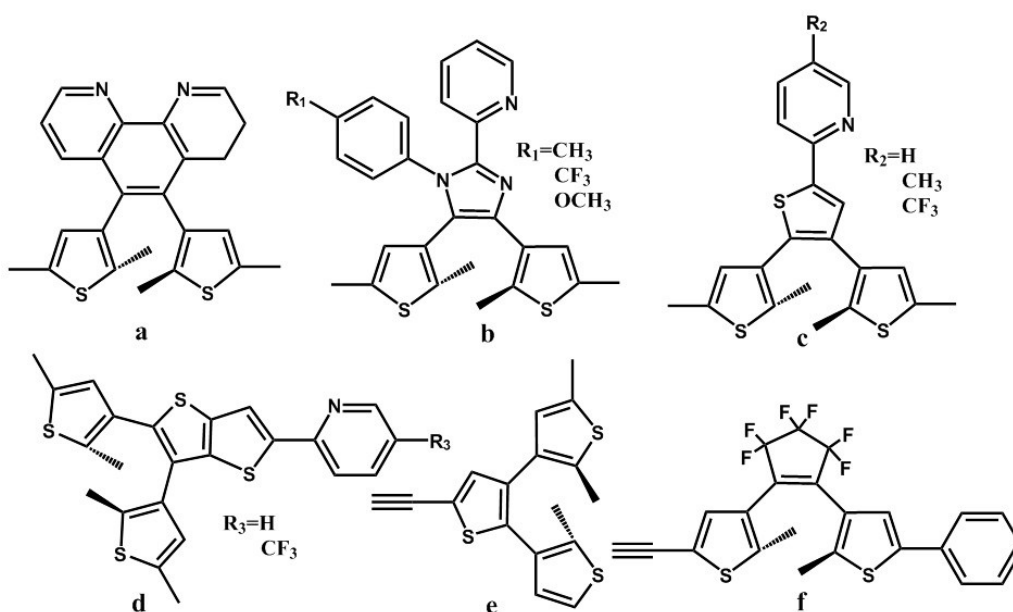
**Scheme S1**



Scheme S2



Scheme S3



**Scheme S4** a: L; b: BTE with diimine unit; c and d: BTE with C<sup>N</sup> moiety; e and f: BTE with alkynyl group.

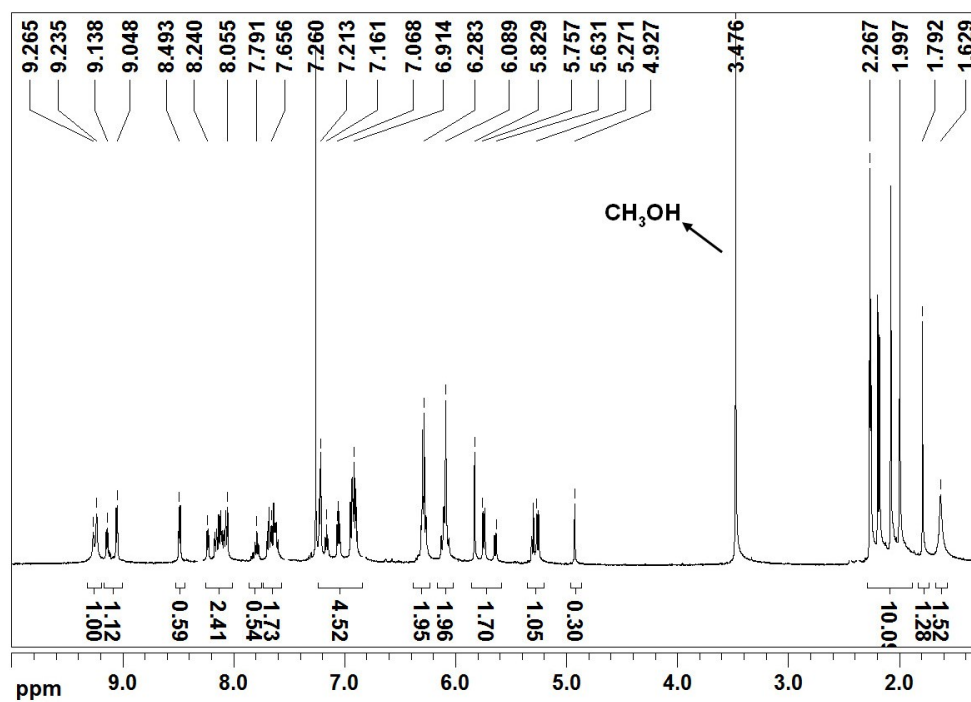


Fig. S1  $^1\text{H}$  NMR spectrum of **1** (500 MHz,  $\text{CDCl}_3$ , signal at 3.48 ppm from  $\text{CH}_3\text{OH}$ ).

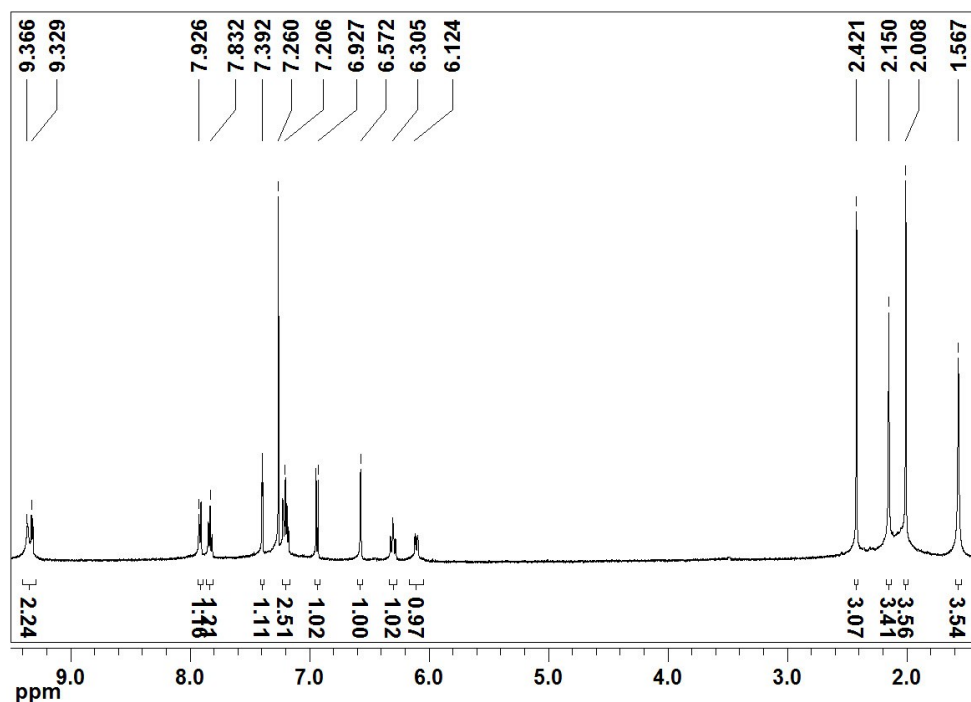
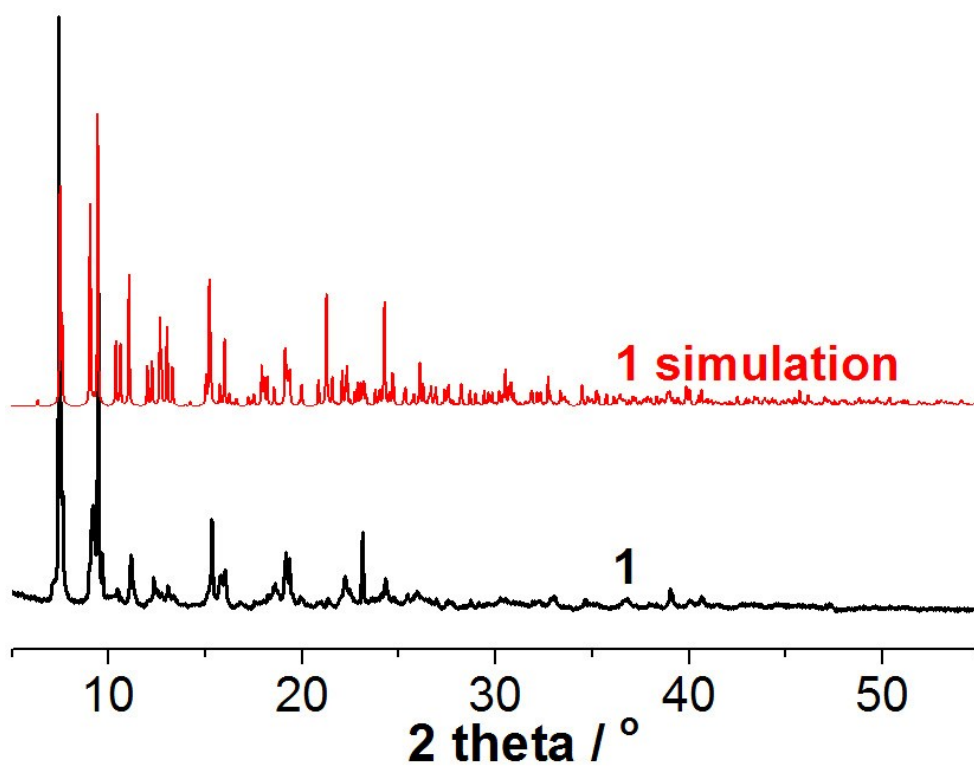
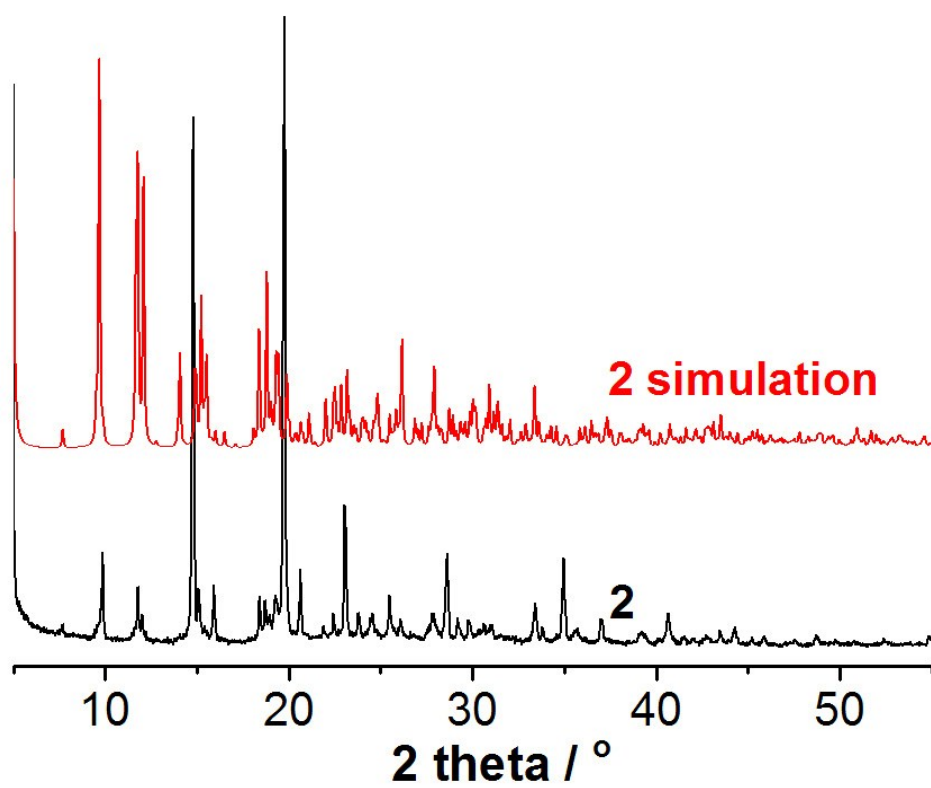


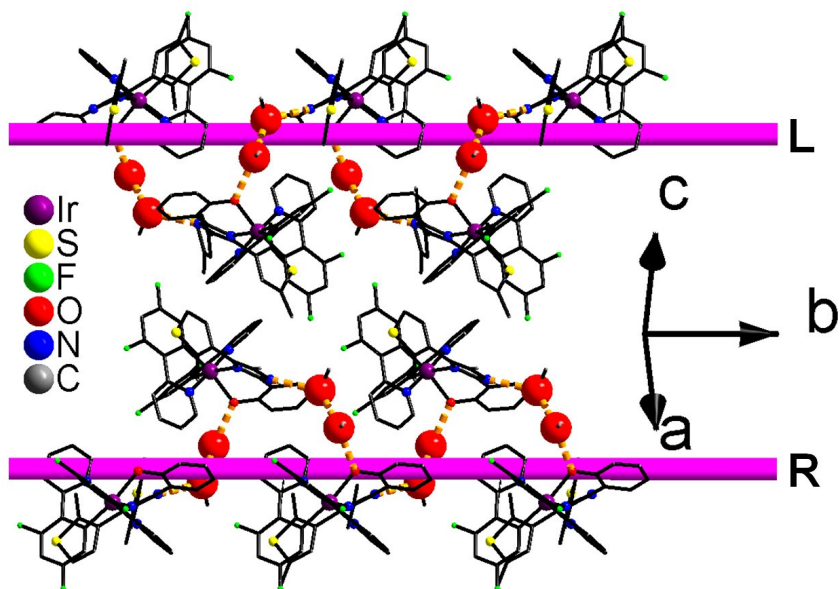
Fig. S2  $^1\text{H}$  NMR spectrum of **2** (500 MHz,  $\text{CDCl}_3$ ).



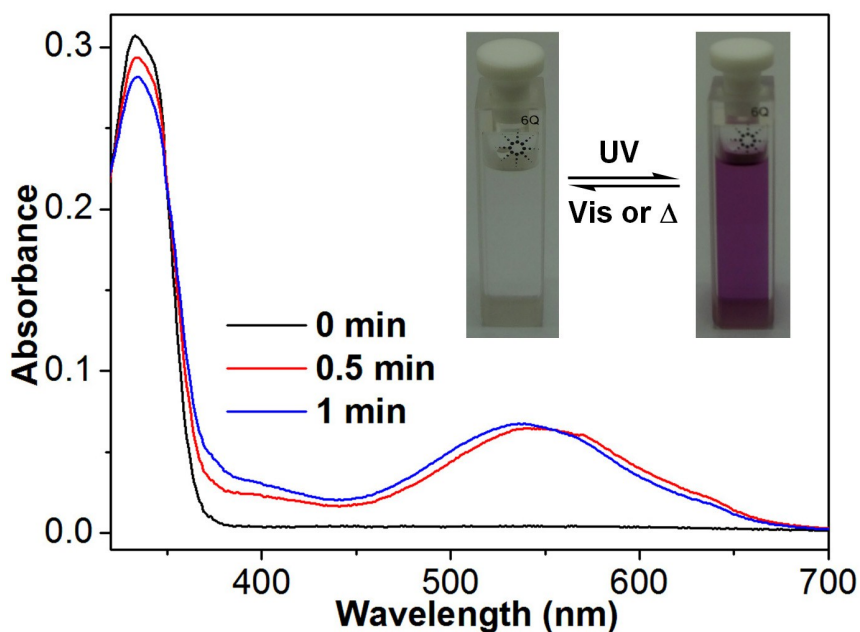
**Fig. S3** Experimental and simulated XRD patterns of 1.



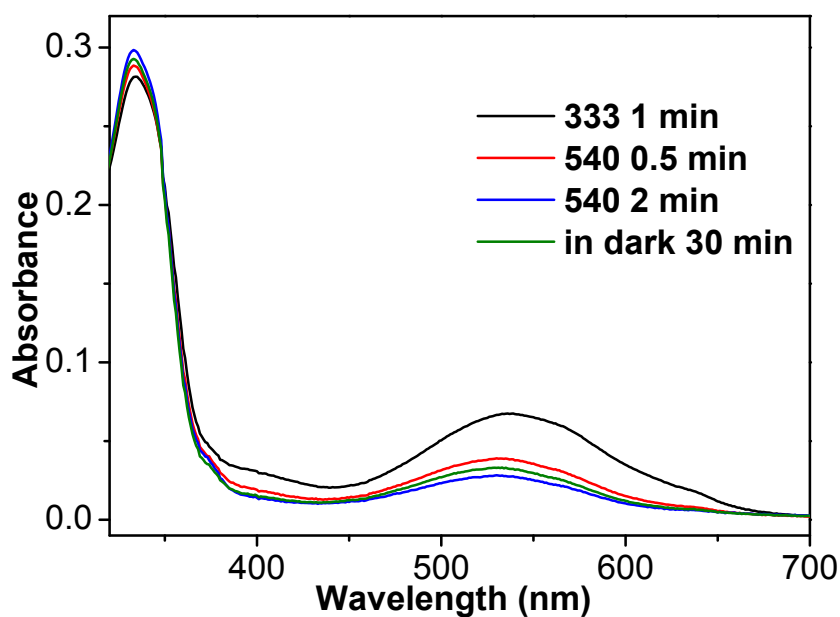
**Fig. S4** Experimental and simulated XRD patterns of 2.



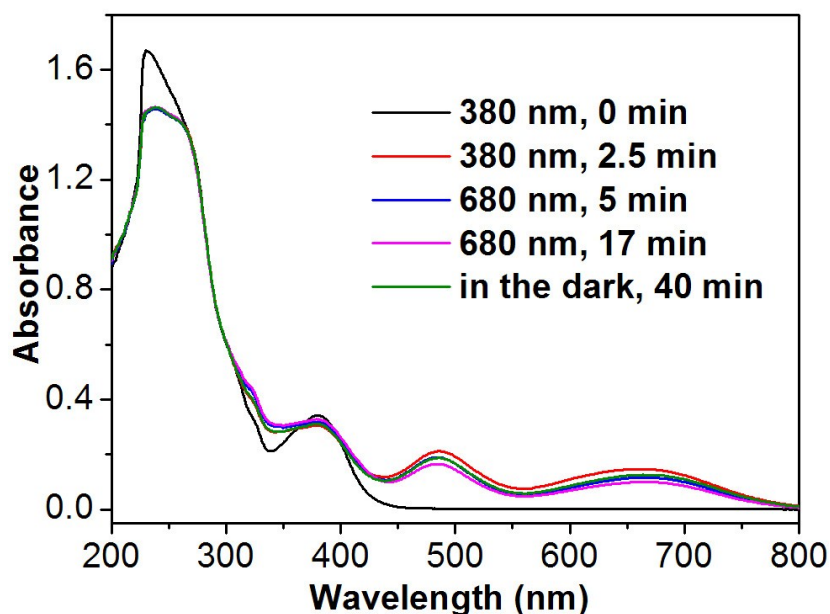
**Fig. S5** Packing structure of [Ir(dfppy)<sub>2</sub>(L1)]·2CH<sub>3</sub>OH containing right- and left-handed helical chains (denoted as R and L, respectively). Red balls are O atoms from CH<sub>3</sub>OH molecules or phenolate groups, from the ESI of *Dalton. Trans*, 2015, 44, 4289.



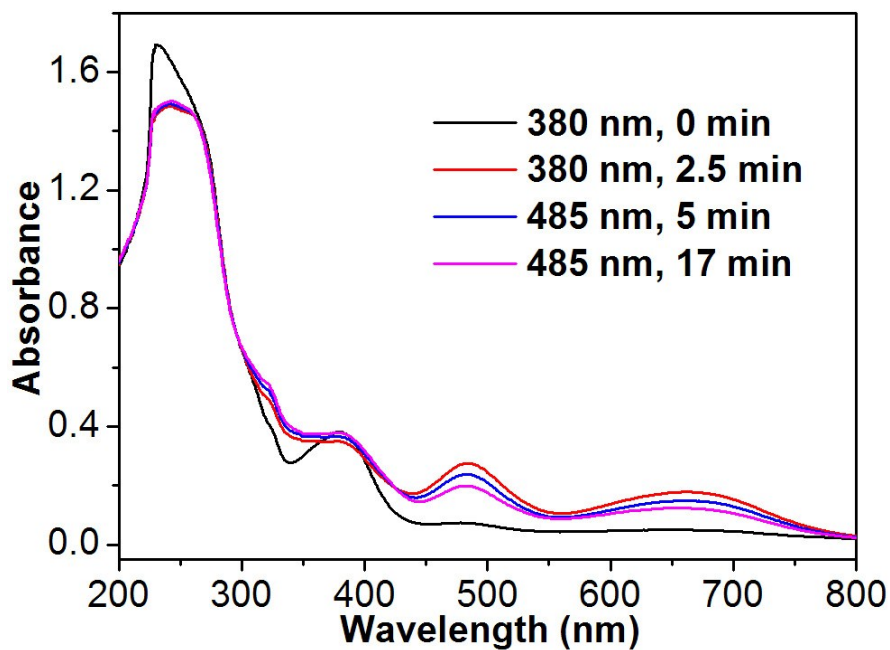
**Fig. S6** Absorption-spectra changes of BrLH in CH<sub>2</sub>Cl<sub>2</sub>-CH<sub>3</sub>CN solution (c = 2.0 × 10<sup>-5</sup> M) upon UV irradiation (λ = 333 nm) for 0-1 minutes, from the ESI of *Dalton. Trans*, 2015, 44, 5755.



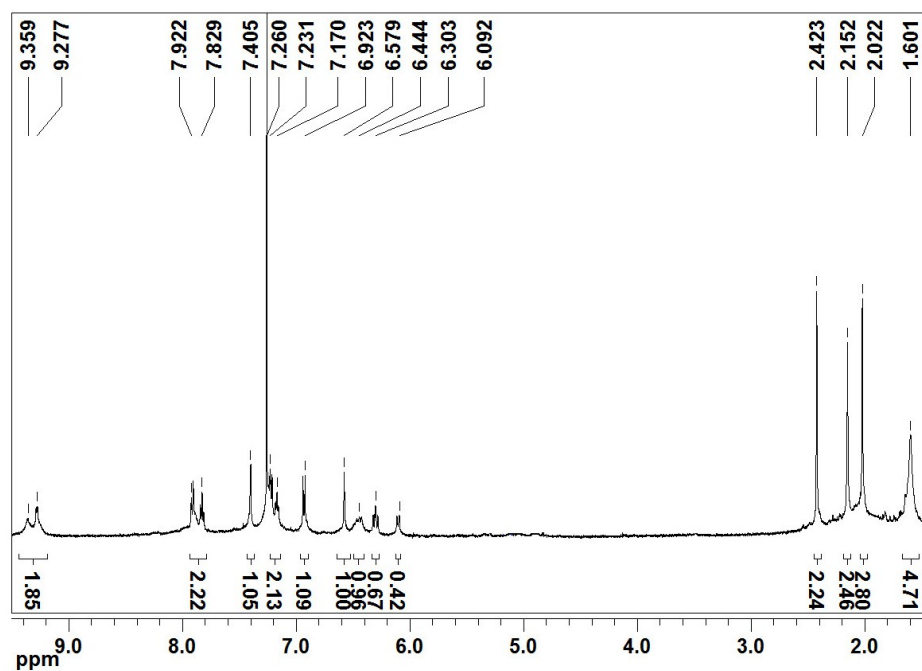
**Fig. S7** Black line: irradiating ( $\lambda = 333$  nm) the solution of BrLH for 1 minute; red line and blue line: irradiating ( $\lambda = 540$  nm) the solution corresponding to black line for 0.5 and 2 minutes, respectively; olive line: placing the solution corresponding to black line in the dark for 30 minutes, from the ESI of *Dalton. Trans*, 2015, 44, 5755.



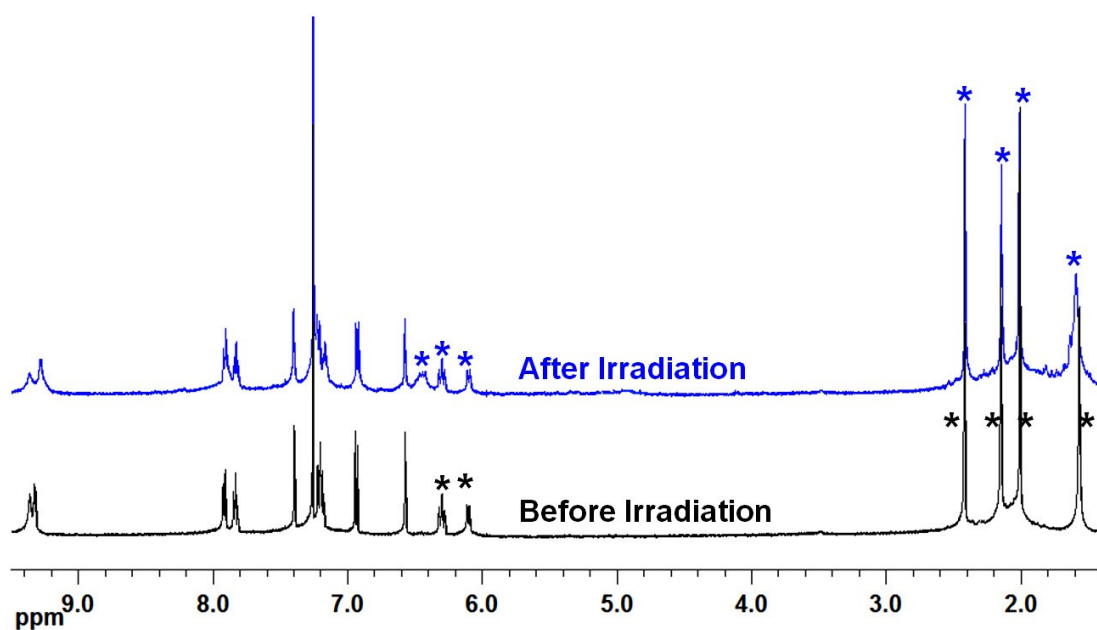
**Fig. S8** Black and red lines: irradiating ( $\lambda = 380$  nm) the  $\text{CH}_2\text{Cl}_2$  solution of **2** for 0 and 2.5 minutes, respectively; blue and magenta lines: irradiating ( $\lambda = 680$  nm) the solution corresponding to red line for 5 and 17 minutes, respectively; green line: placing the solution corresponding to red line in the dark for 40 minutes.



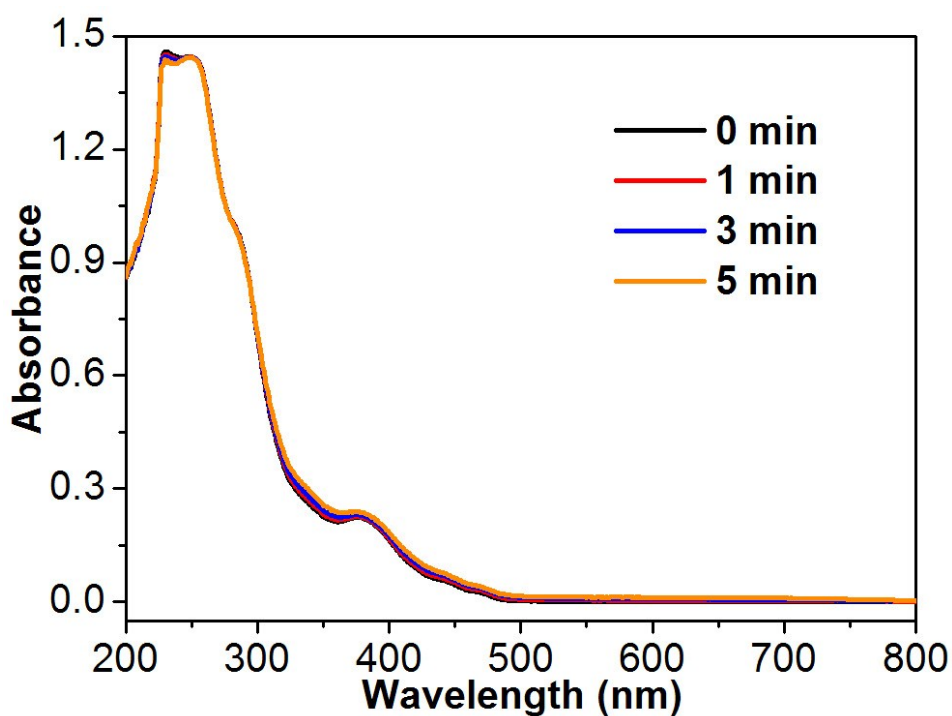
**Fig. S9** Black and red lines: irradiating ( $\lambda = 380$  nm) the  $\text{CH}_2\text{Cl}_2$  solution of **2** for 0 and 2.5 minutes, respectively; blue and magenta lines: irradiating ( $\lambda = 485$  nm) the solution corresponding to red line for 5 and 17 minutes, respectively.



**Fig. S10**  $^1\text{H}$  NMR spectrum of **2** after irradiation with 365 nm light (500 MHz,  $\text{CDCl}_3$ ).

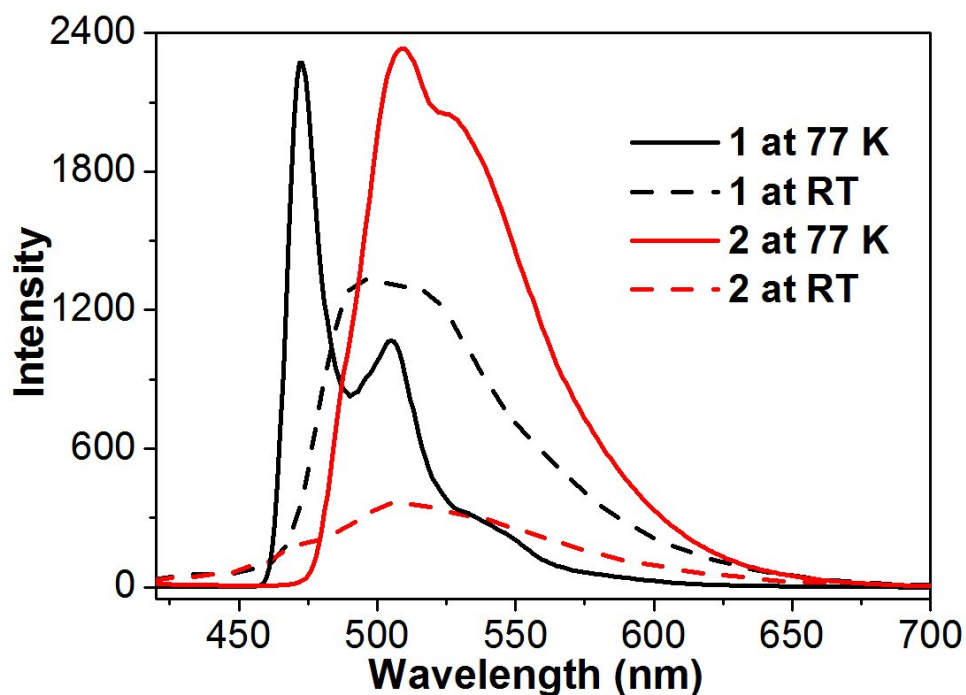


**Fig. S11**  $^1\text{H}$  NMR spectra of **2** before and after irradiation, where peaks with \* indicate partial conversion from open form (before irradiation) to closed form (after irradiation).

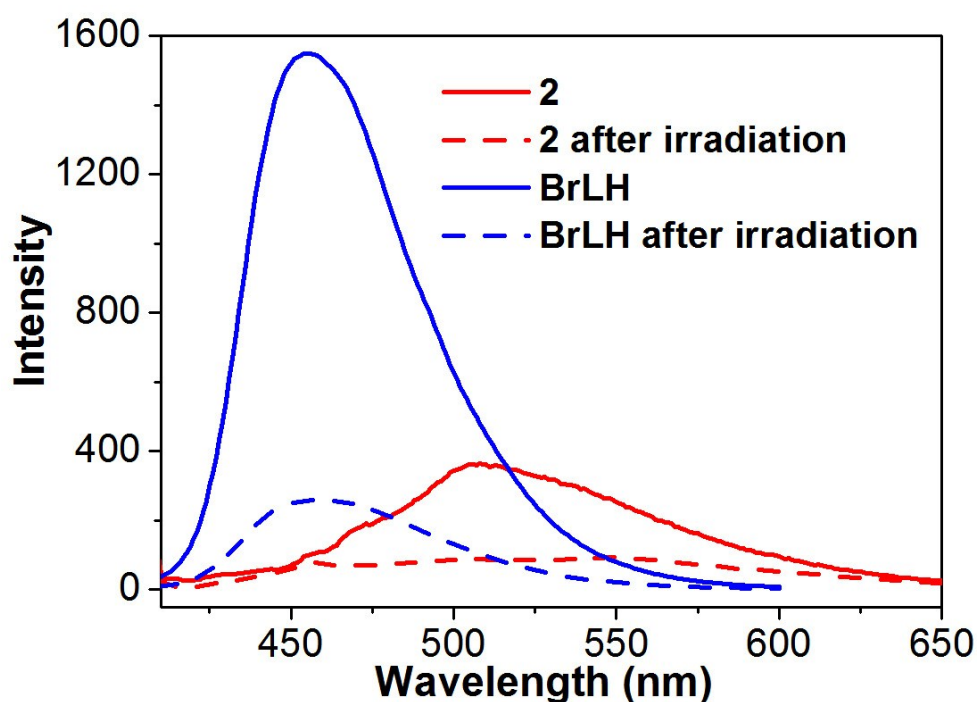


**Fig. S12** Absorption spectra changes of **1** in  $\text{CH}_2\text{Cl}_2$  solution ( $c = 2.0 \times 10^{-5}$  M) upon UV irradiation ( $\lambda = 380$  nm) for 0-5 minutes.

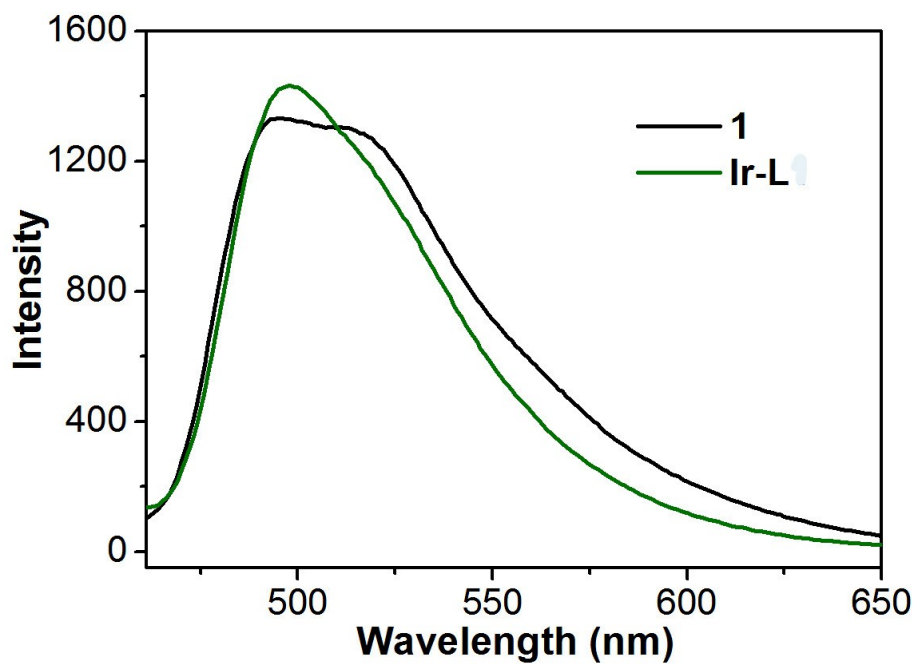




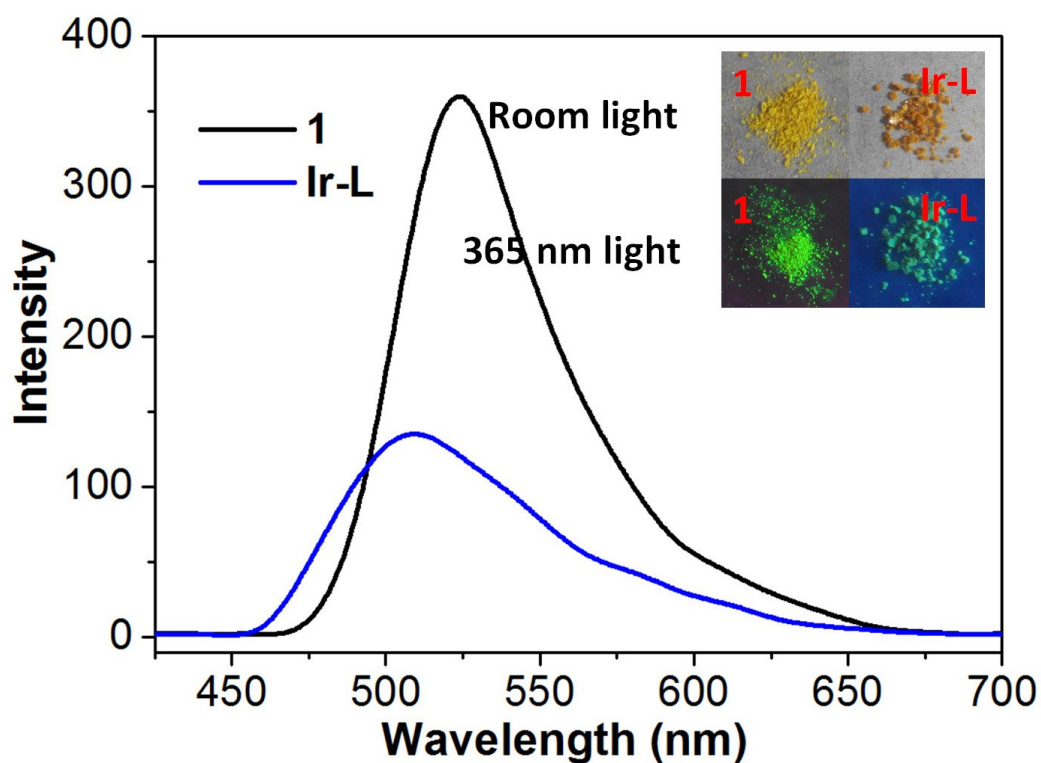
**Fig. S13** Phosphorescence spectra of **1** and **2** in  $\text{C}_2\text{H}_5\text{OH}-\text{CH}_3\text{OH}$  (v/v = 3/1) at 77 K, and in  $\text{CH}_2\text{Cl}_2$  at room temperature (RT) ( $c = 1.5 \times 10^{-4}$  M,  $\lambda_{\text{ex}} = 400$  nm).



**Fig. S14** Luminescence spectra of **2** and BrLH in  $\text{CH}_2\text{Cl}_2$  at room temperature before and after irradiation with 380 nm light for the former, and 333 nm light for the latter ( $c = 1.5 \times 10^{-4}$  M,  $\lambda_{\text{ex}} = 400$  and 350 nm for **2** and BrLH, respectively).



**Fig. S15** Luminescence spectra of **1** and  $[\text{Ir}(\text{dfppy})_2(\text{L1})]\cdot 2\text{CH}_3\text{OH}$  (denoted as **Ir-L**) in  $\text{CH}_2\text{Cl}_2$  at room temperature ( $c = 1.5 \times 10^{-4} \text{ M}$ ,  $\lambda_{\text{ex}} = 400 \text{ nm}$ ).



**Fig. S16** Solid-state emission spectra of **1** and  $[\text{Ir}(\text{dfppy})_2(\text{L1})]\cdot 2\text{CH}_3\text{OH}$  (denoted as **Ir-L**) ( $\lambda_{\text{ex}} = 400 \text{ nm}$ ). Inset: the photographs under the irradiation with room light or 365 nm light.