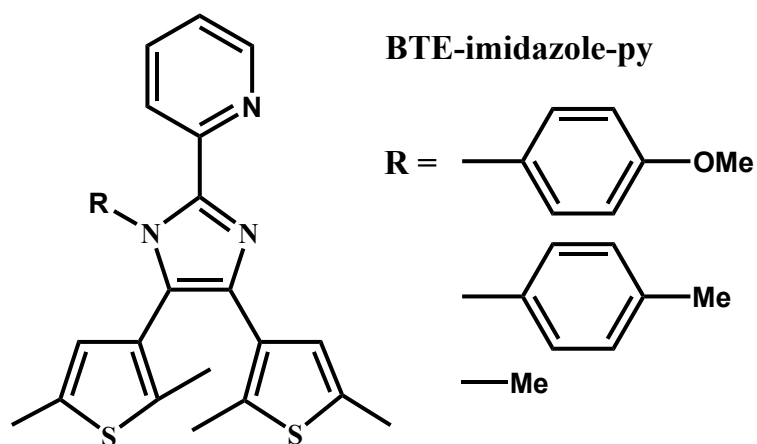
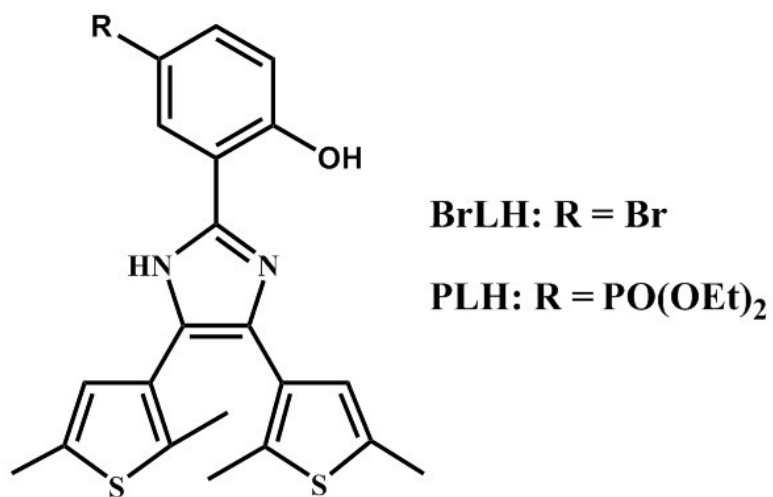


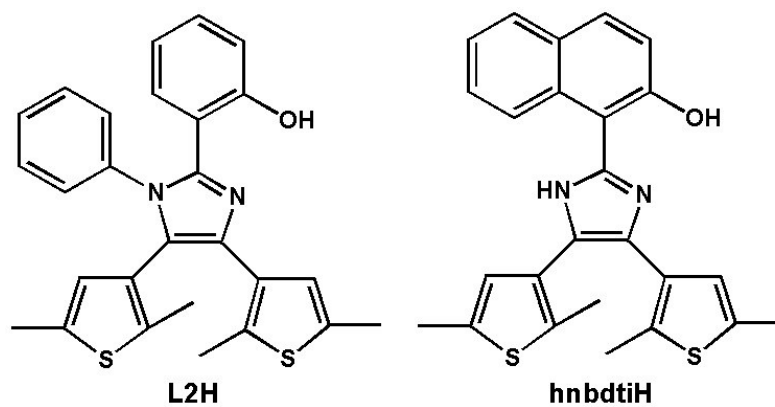
Electronic Supporting Information



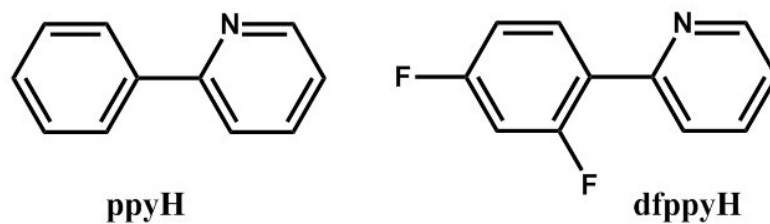
Scheme S1



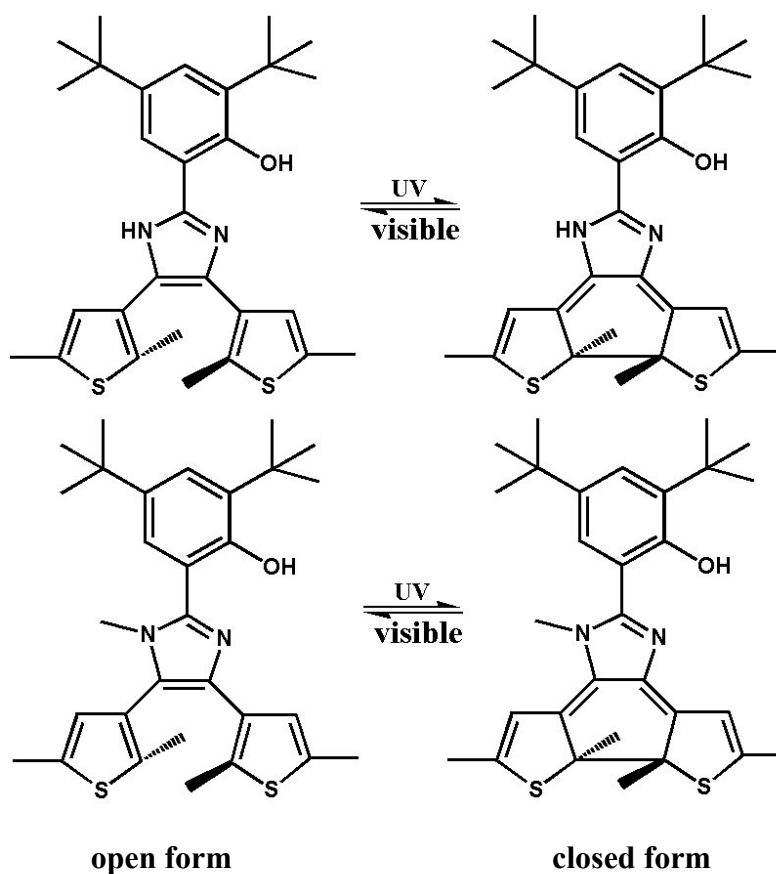
Scheme S2



Scheme S3



Scheme S4



Scheme S5 Structure transition of tBuLH (top) and tBuLMeH (bottom) between the open form and the closed form

Table S1 UV-vis absorption bands of tBuLH, tBuLMeH **1** and **2** in CH₂Cl₂ at room temperature.

Compound	λ_{\max} (nm)
tBuLH	228, 291, 326
tBuLMeH	230, 291, 326
1	248, 379, 450
2	245, 346, 450

Table S2 Emission data of tBuLH, tBuLMeH, **1**, **2** and [Ir(dfppy)₂(L1)]·2CH₃OH in CH₂Cl₂ at room temperature and emission data of **1**, **2** and [Ir(dfppy)₂(L1)]·2CH₃OH in C₂H₅OH-CH₃OH (v/v = 3/1) at 77 K.

Compound	emission wavelength (nm) at room temperature	emission wavelength (nm) at 77 K
L1H	442 nm ^a	-
tBuLH	464 nm	-
tBuLMeH	479 nm	-
[Ir(dfppy) ₂ (L1)]·2CH ₃ OH	508 nm ^a	471, 506 nm ^{a,b}
1	514 nm	498 nm
2	507 nm	492 nm

a: the data from *Dalton Trans.*, 2015, **44**, 4289; *b*: seeing Fig. S19.

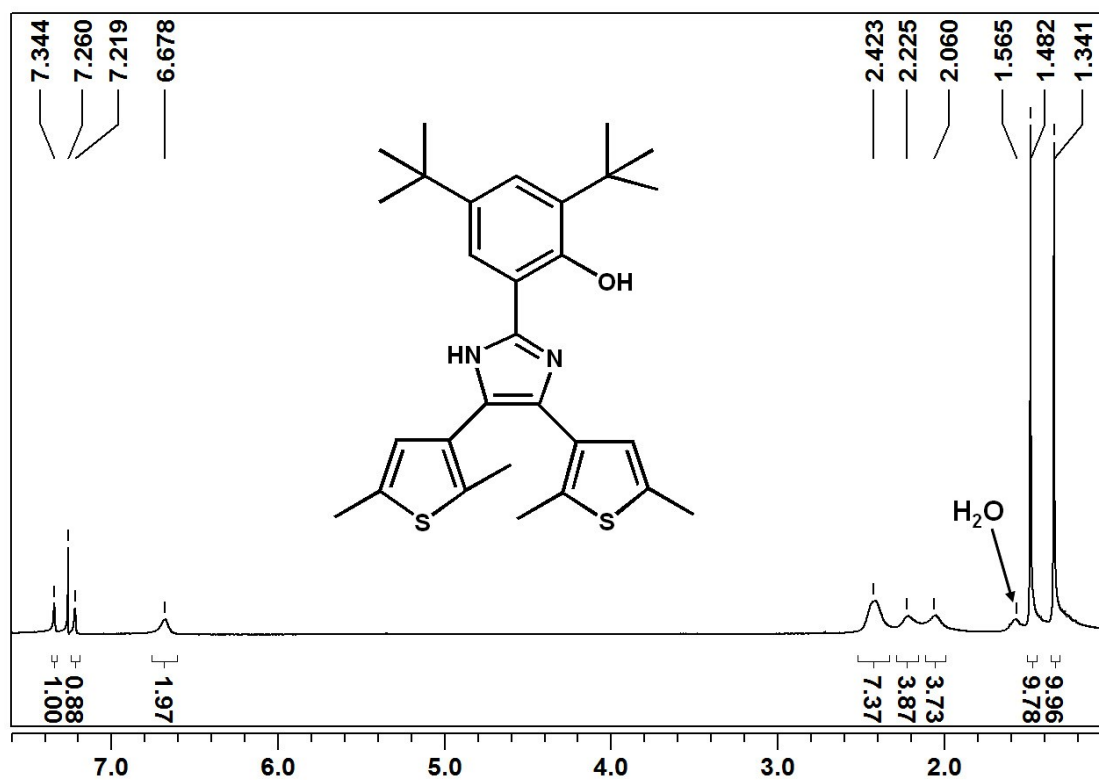


Fig. S1 ¹H NMR spectrum of tBuLH (500 MHz, CDCl₃).

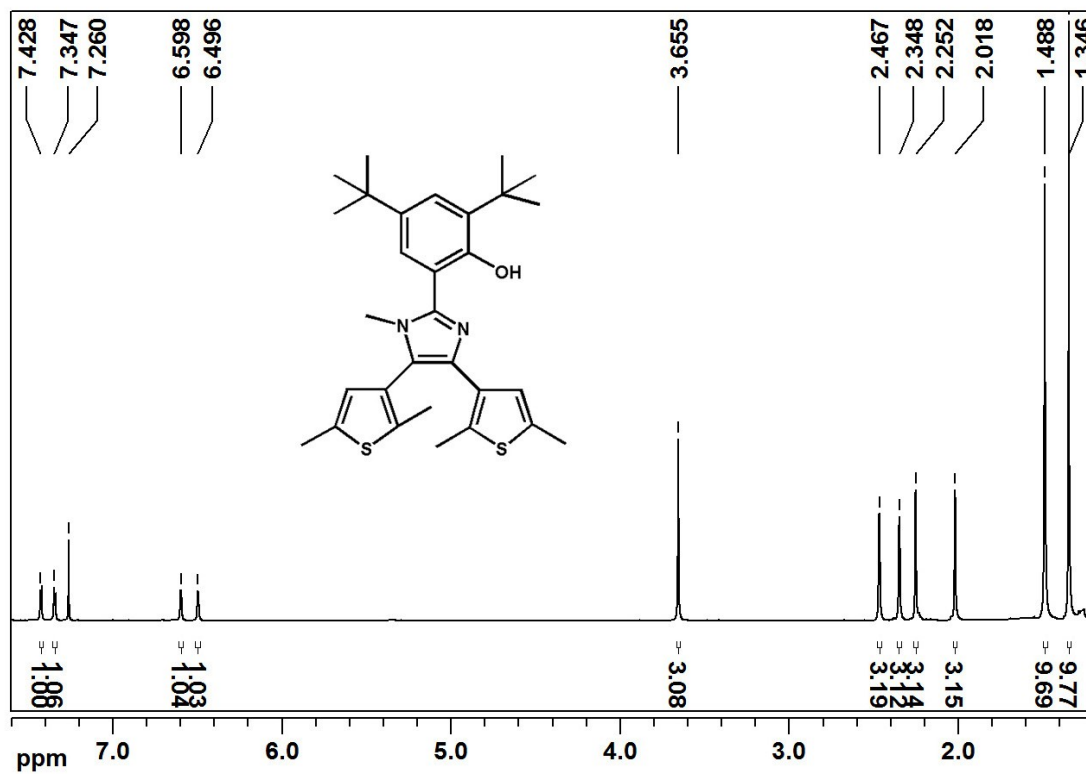


Fig. S2 ¹H NMR spectrum of tBuLMeH (300 MHz, CDCl₃).

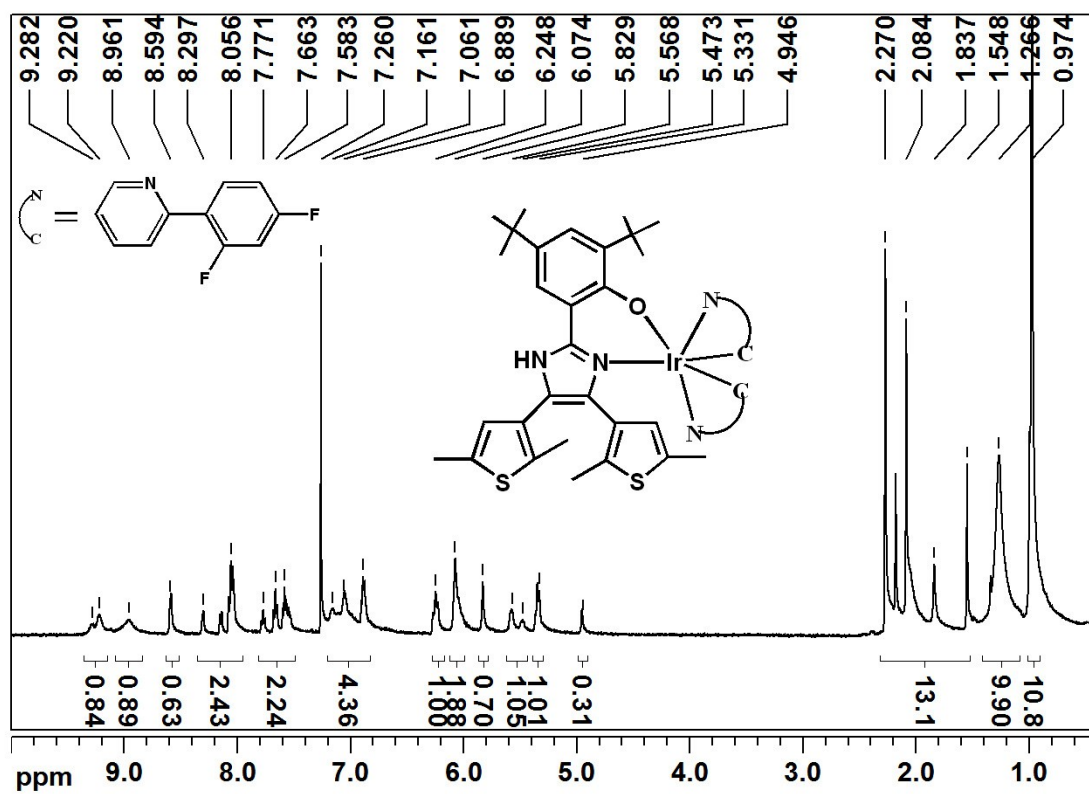


Fig. S3 ¹H NMR spectrum of 1 (500 MHz, CDCl₃).

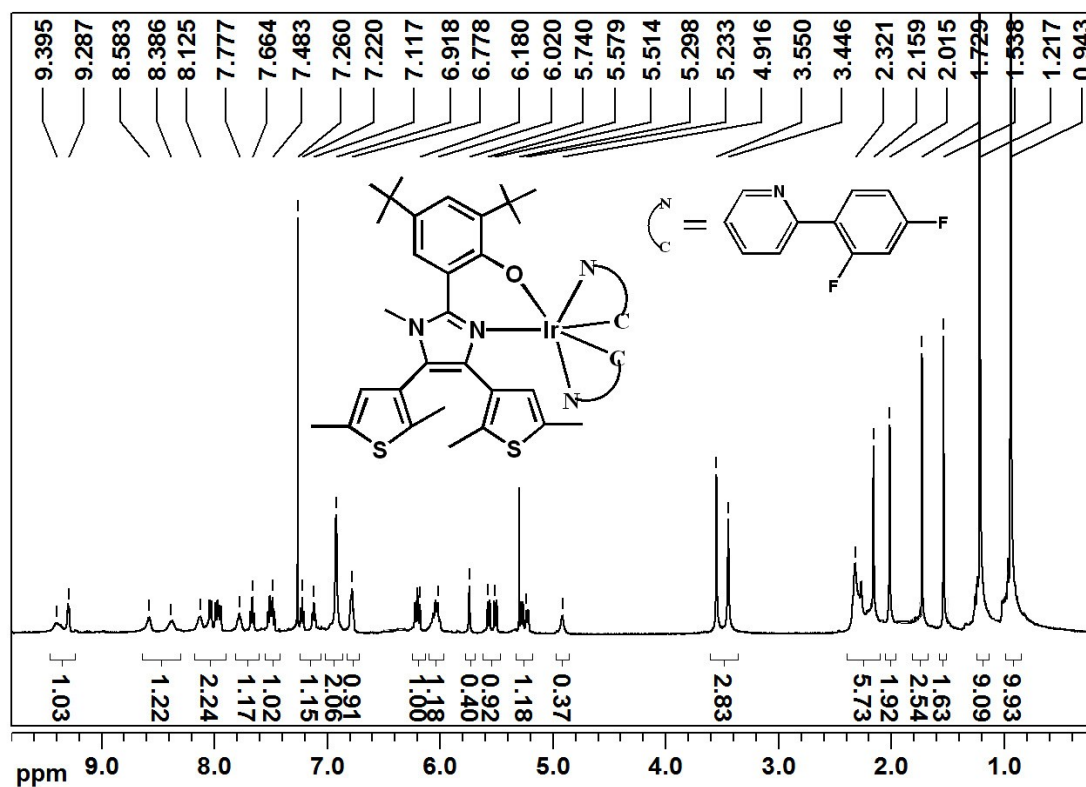


Fig. S4 ^1H NMR spectrum of **2** (500 MHz, CDCl_3).

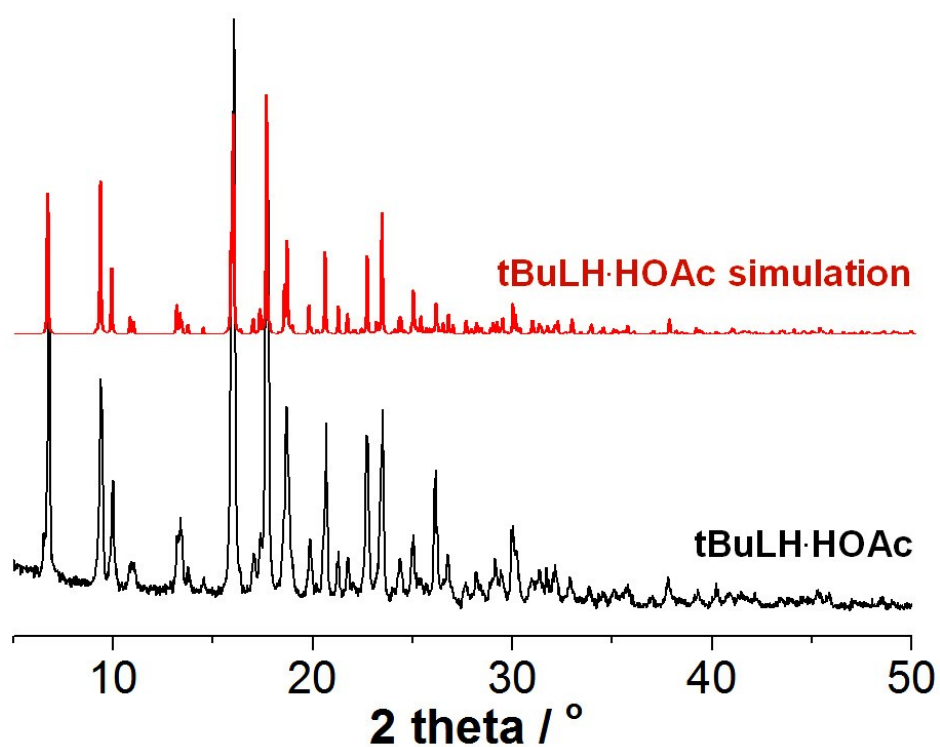


Fig. S5 Experimental and simulated XRD patterns of $\text{tBuLH}\cdot\text{HOAc}$.

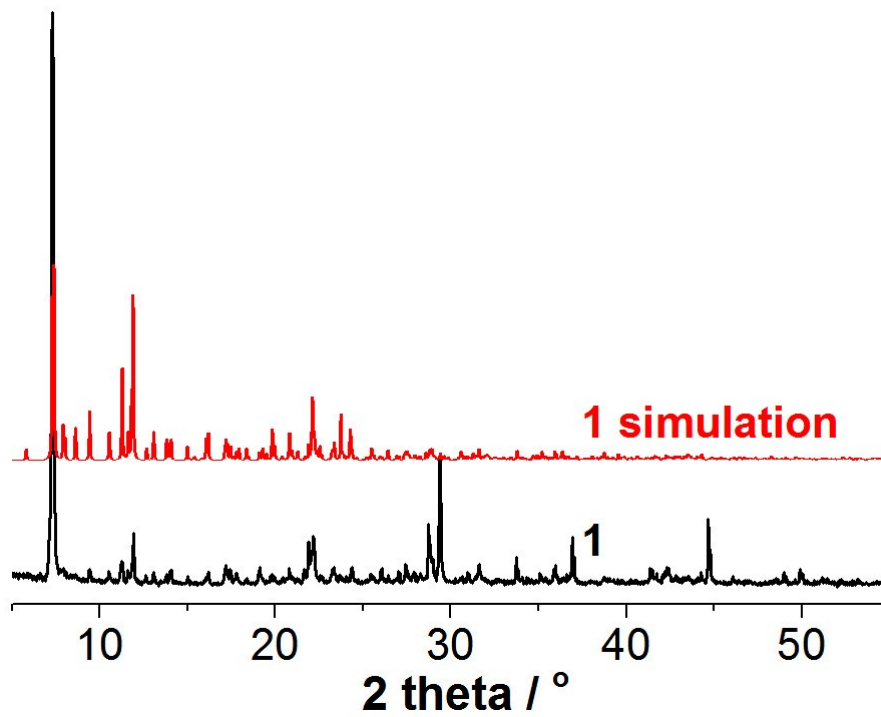


Fig. S6 Experimental and simulated XRD patterns of 1.

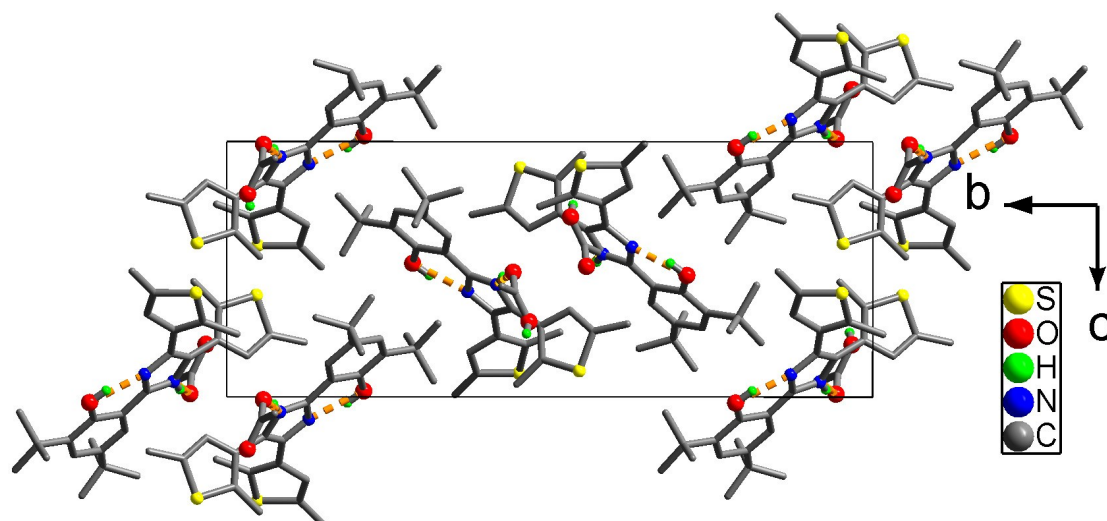


Fig. S7 Packing structure of tBuLH·HOAc.

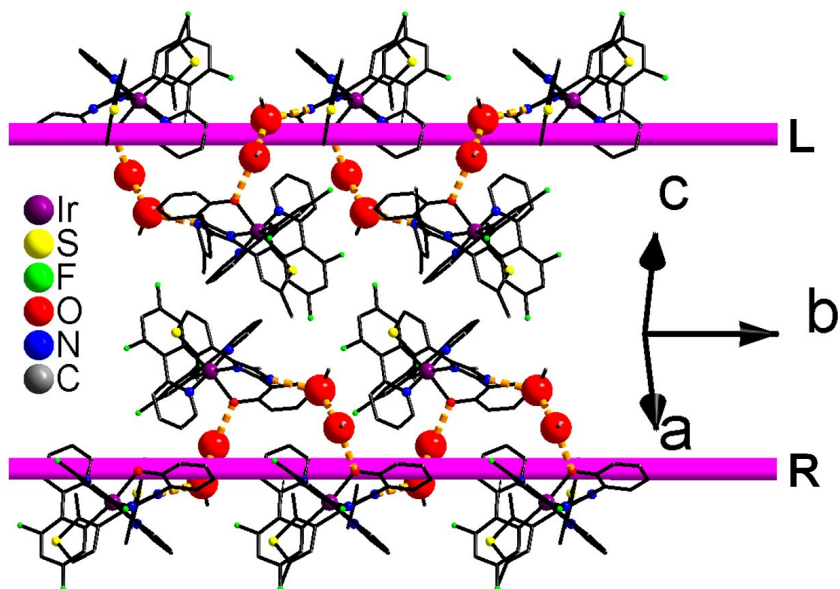


Fig. S8 Packing structure of $[\text{Ir}(\text{dfppy})_2(\text{L1})]\cdot 2\text{CH}_3\text{OH}$ containing right- and left-handed helical chains (denoted as R and L, respectively). Red balls are O atoms from CH_3OH molecules or phenolate groups.

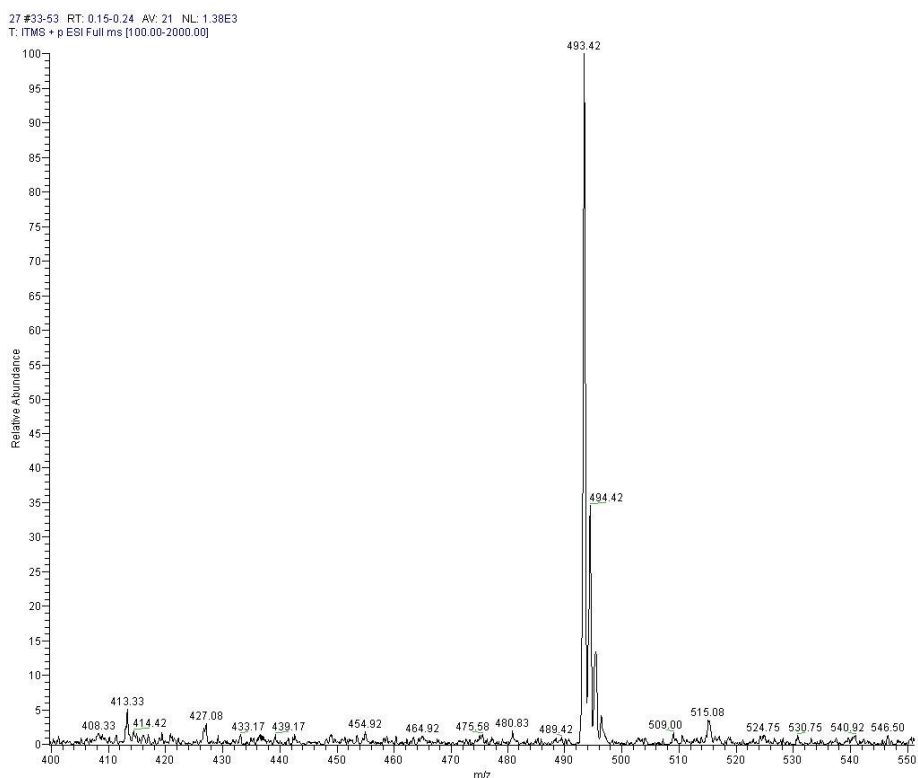


Fig. S9 Electrospray mass spectrometry (ES-MS) of tBuLH in $\text{CH}_3\text{OH}-\text{CH}_2\text{Cl}_2$ solution before UV irradiation ($\lambda = 326 \text{ nm}$).

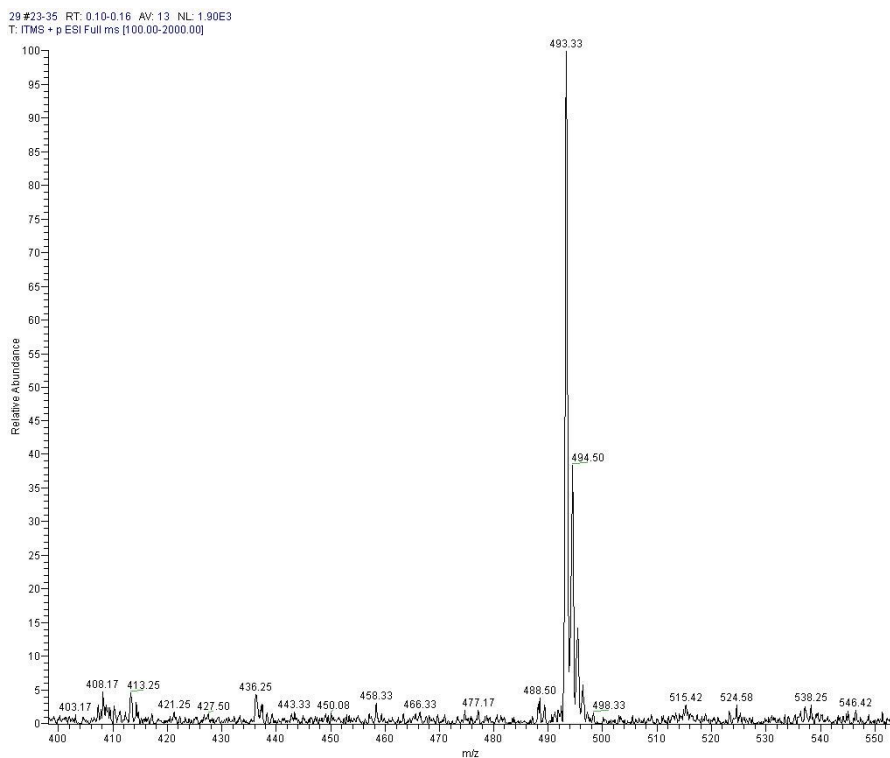


Fig. S10 Electrospray mass spectrometry (ES-MS) of tBuLH in $\text{CH}_3\text{OH-CH}_2\text{Cl}_2$ solution after 2.5-minute UV irradiation ($\lambda = 326 \text{ nm}$).

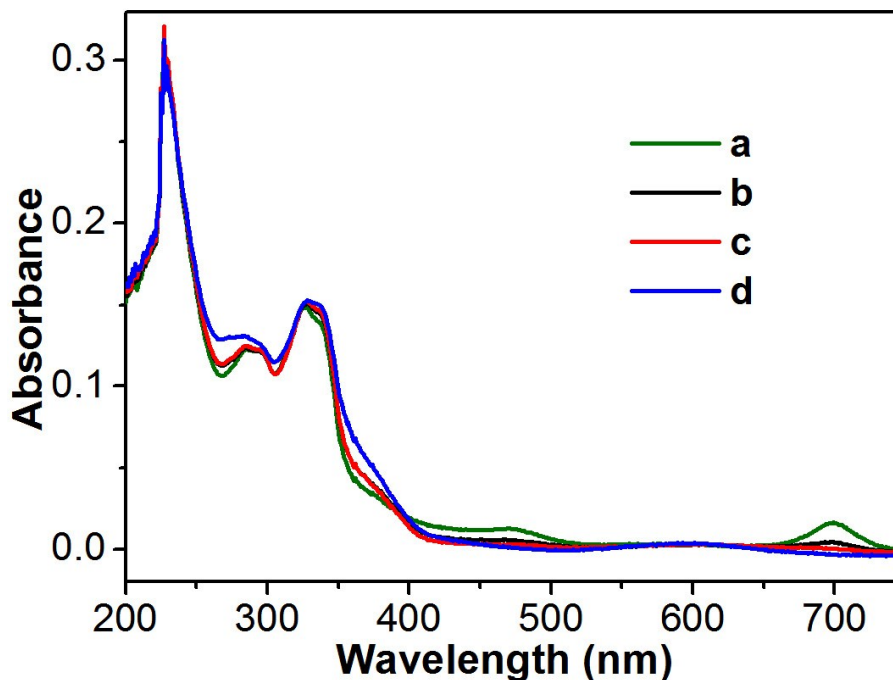


Fig. S11 Plot a: irradiating ($\lambda = 326 \text{ nm}$) the CH_2Cl_2 solution of tBuLH ($c = 1.0 \times 10^{-5} \text{ M}$) for 2.5 minutes; plots b and c: irradiating ($\lambda = 700 \text{ nm}$) the solution corresponding to plot a for 1 and 2 minutes, respectively; plot d: placing the solution corresponding to plot a in the dark for 45 minutes.

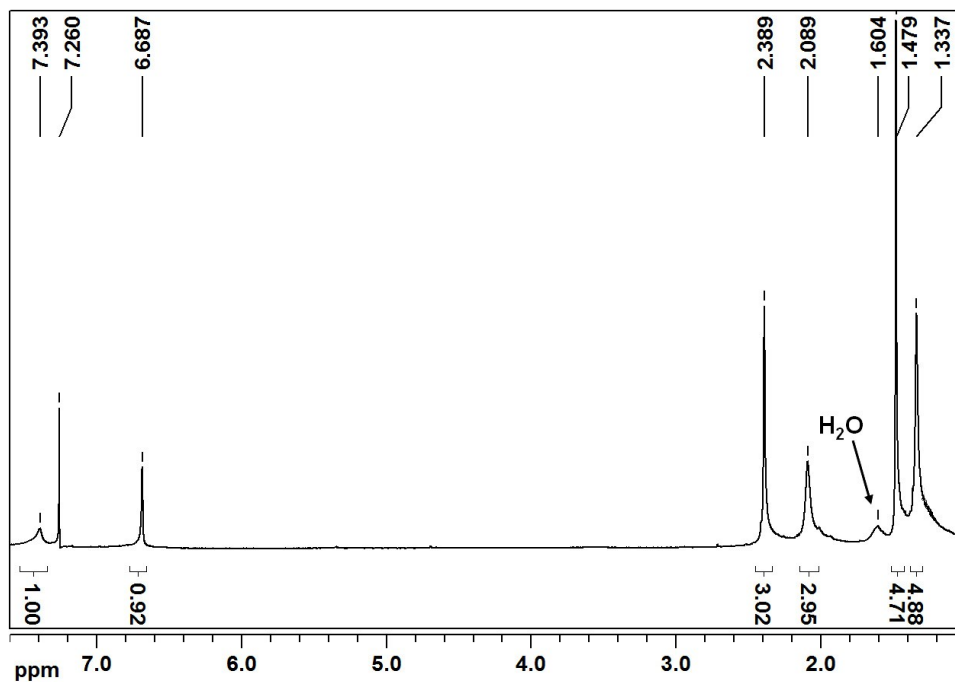


Fig. S12 ¹H NMR spectrum of tBuLH after irradiation with 326 nm light (500 MHz, CDCl₃).

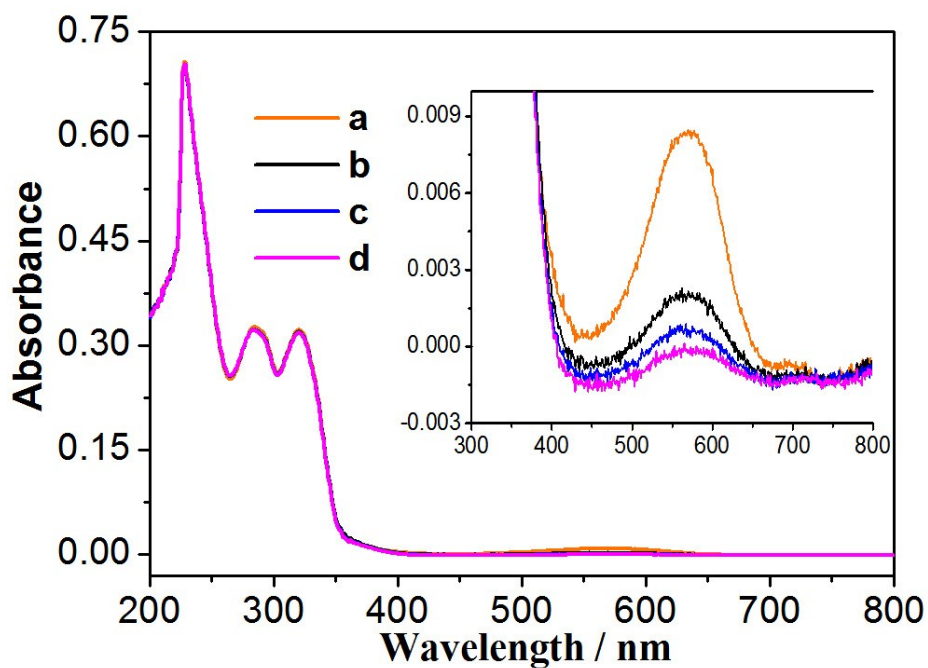


Fig. S13 Plot a: irradiating ($\lambda = 321$ nm) the CH₂Cl₂ solution of tBuLMeH ($c = 1.0 \times 10^{-5}$ M) for 2 minutes; plots b and c: irradiating ($\lambda = 570$ nm) the solution corresponding to plot a for 0.5 and 1 minute, respectively; plot d: placing the solution corresponding to plot a in the dark for one hour.

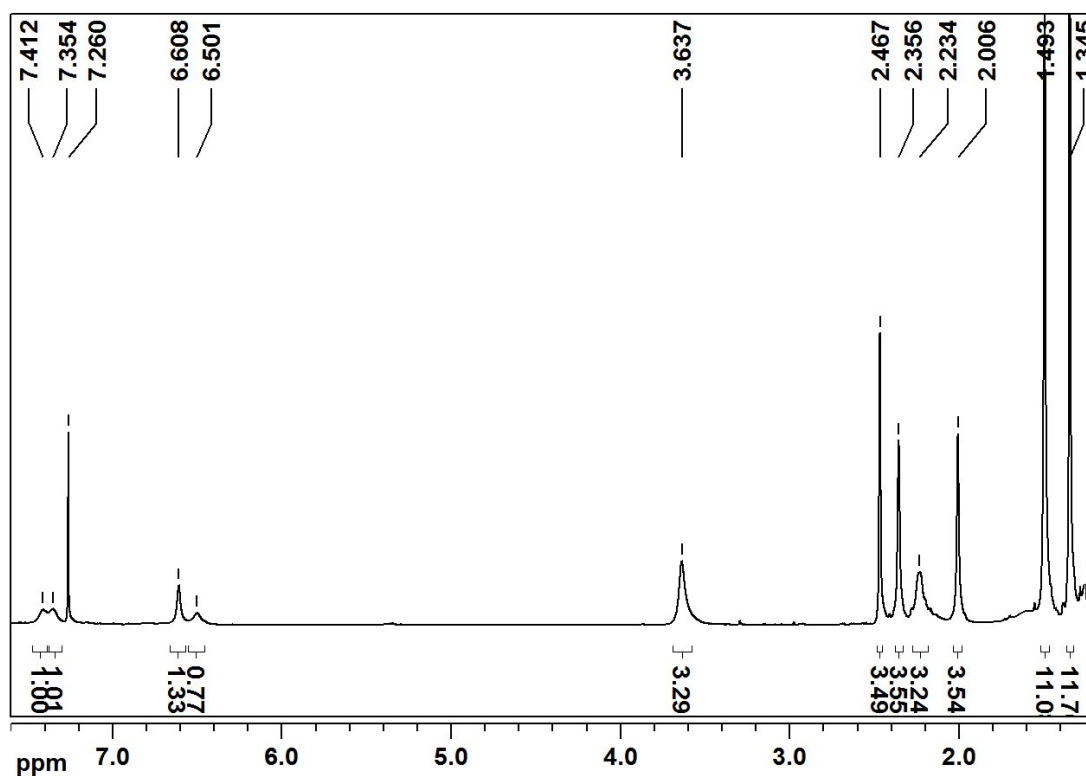


Fig. S14 ^1H NMR spectrum of tBuLMeH after irradiation with 321 nm light (300 MHz, CDCl_3).

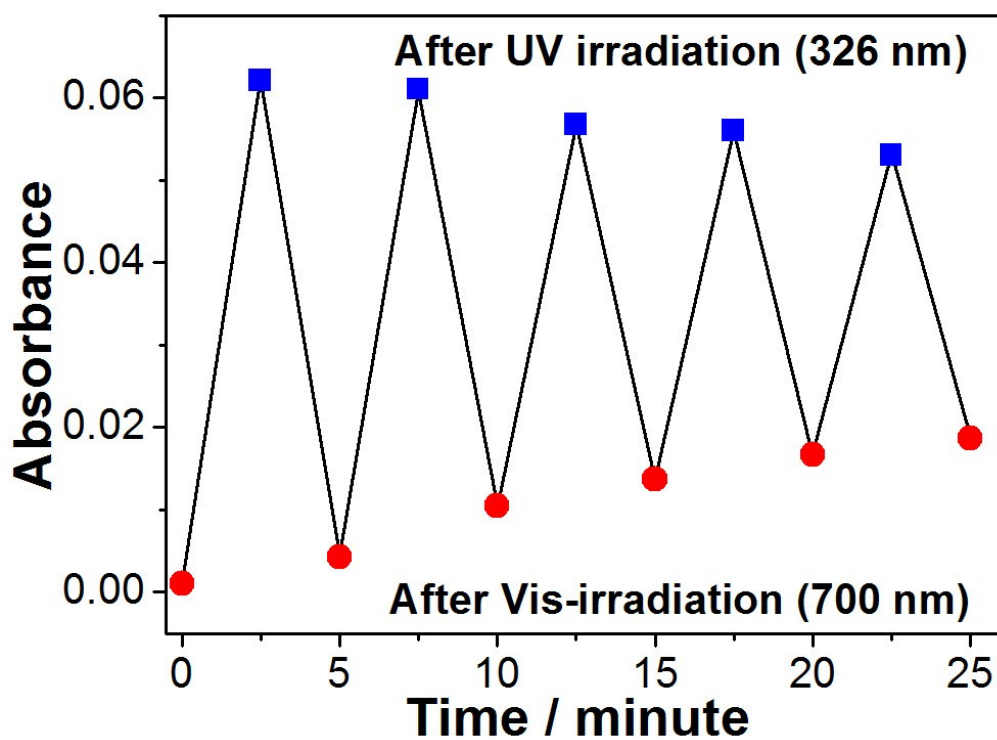


Fig. S15 UV-vis absorbance change of tBuLH at 700 nm in CH_2Cl_2 at room temperature, upon alternative irradiation with 326 and 700 nm light (total 5 cycles).

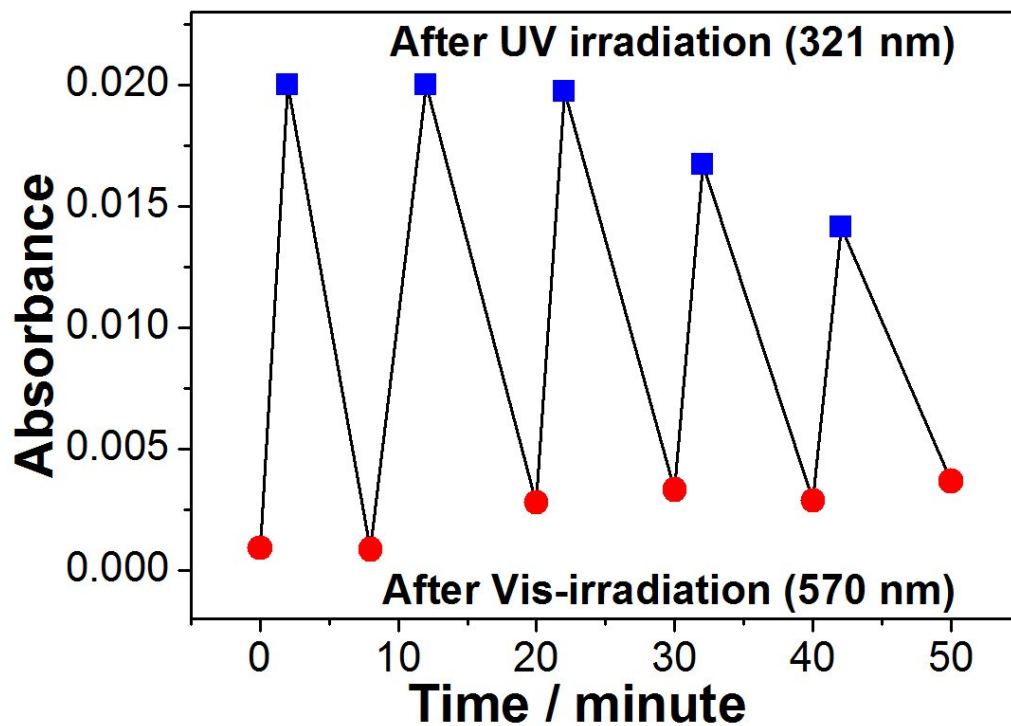


Fig. S16 UV-vis absorbance change of tBuLMeH at 570 nm in CH₂Cl₂ at room temperature, upon alternative irradiation with 321 and 570 nm light (total 5 cycles).

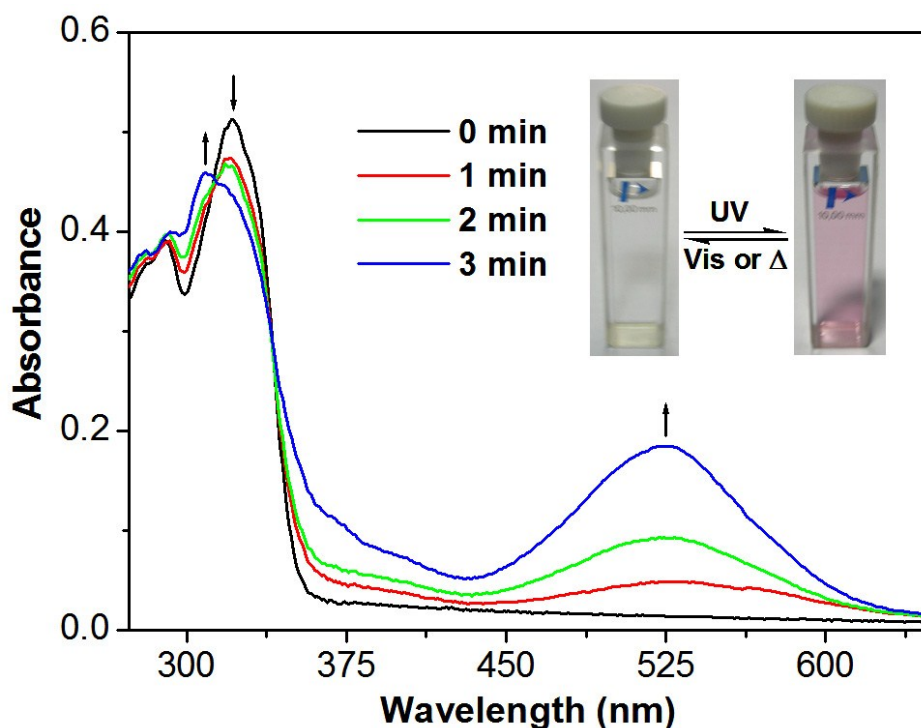


Fig. S17 Absorption-spectra changes of hpbdtiH in CH₂Cl₂-CH₃CN (v/v = 1/4) solution ($c = 2.5 \times 10^{-5}$ M) upon UV irradiation ($\lambda = 321$ nm) for 0 - 3 minutes, from the ESI of *Chem. Commun.*, 2013, **49**, 8863.

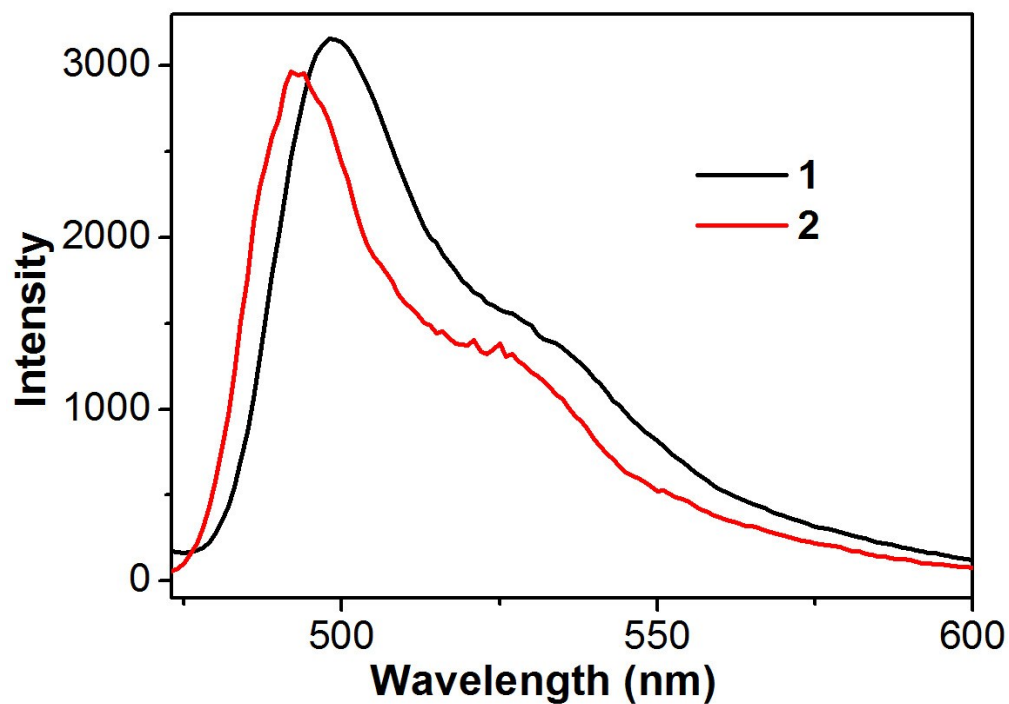


Fig. S18 Phosphorescence spectra of **1** and **2** in C₂H₅OH-CH₃OH (v/v = 3/1) at 77 K ($c = 1.5 \times 10^{-4}$ M, $\lambda_{\text{ex}} = 370$ nm).

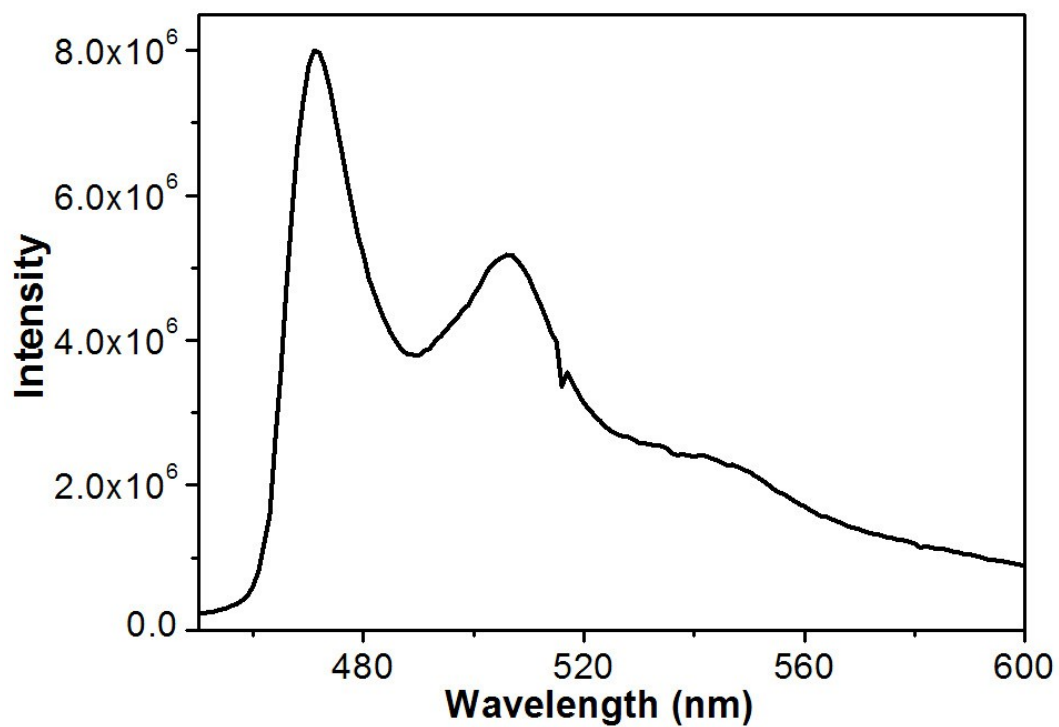


Fig. S19 Phosphorescence spectra of [Ir(dfppy)₂(L1)]·2CH₃OH in C₂H₅OH-CH₃OH (v/v = 3/1) at 77 K ($\lambda_{\text{ex}} = 405$ nm), from the ESI of *Dalton Trans.*, 2015, **44**, 4289.

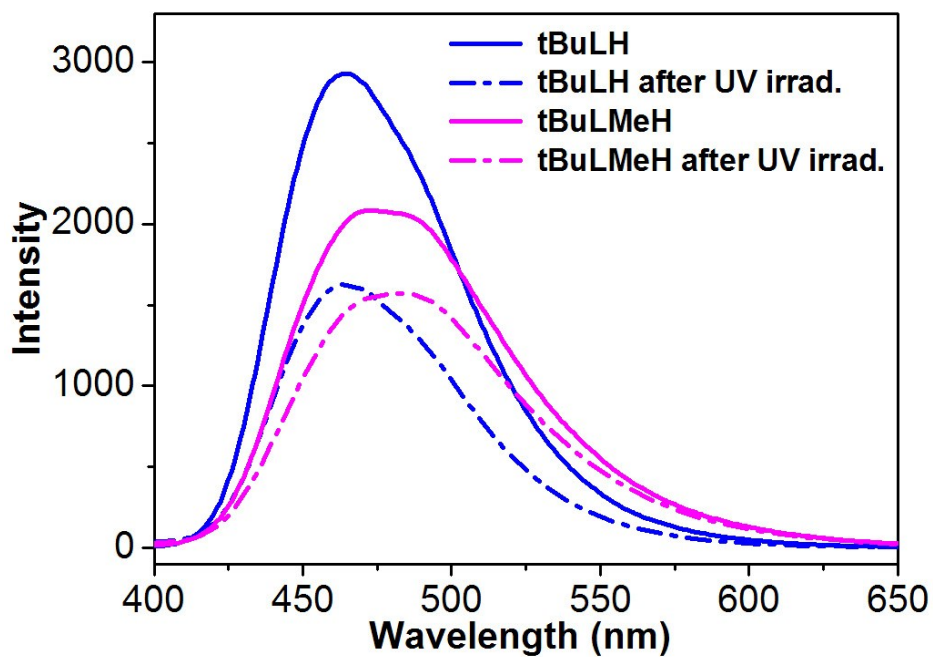


Fig. S20 Luminescence spectra of tBuLH and tBuLMeH in CH₂Cl₂ at room temperature before and after three-minute UV irradiation with 326 nm light for the former, and 321 nm light for the latter ($c = 4 \times 10^{-5}$ M, $\lambda_{\text{ex}} = 340$ nm for **2**).