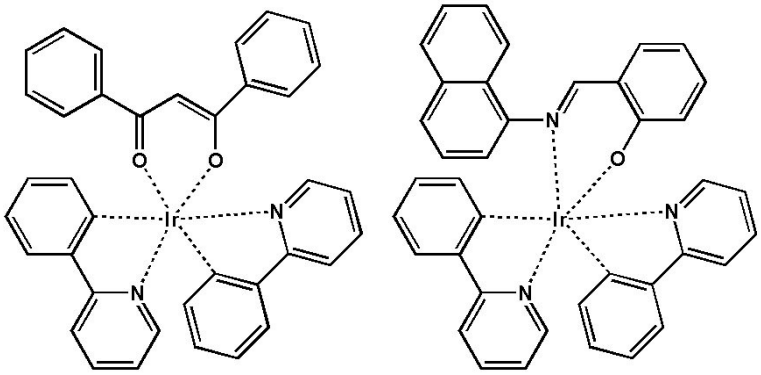
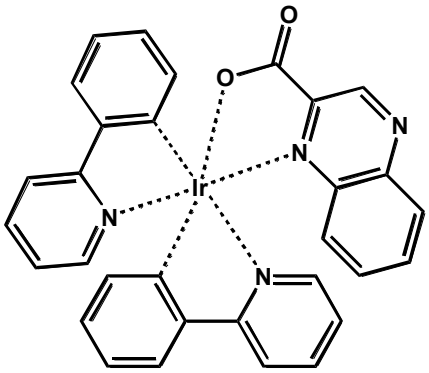
Electronic Supplementary Material (ESI) for Dalton Transactions.

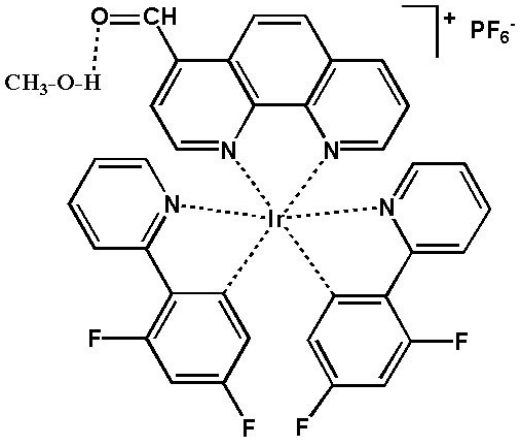
Electronic Supporting Information



Scheme S1 Molecular structures of $(ppy)_2(DBM)$ (left) and $Ir(ppy)_2(SB)$ (right).



Scheme S2 Molecular structure of $[Ir(ppy)_2(qnx)]$.



Scheme S3 Hydrogen bond CH_3O-H···O=CH- between complex **1** and CH_3OH molecule.

Table S1 Crystallographic data and refinement of complex **1**·$CHCl_3$.

	1·$CHCl_3$
Formula	$C_{39}H_{33}N_7O_2F_{12}P_2ClIr$
M	1149.31
Crystal system	Triclinic
Space group	$P\bar{1}$
T /K	296
a /Å	11.5379(7)
b /Å	13.6588(9)
c /Å	15.6212(10)
α / °	86.7990(10)
β /°	69.2010(10)
γ / °	69.0300(10)
V/Å^3	2141.8(2)
Z	2
D_c /g cm^{-3}	1.782
F(000)	1128
GooF on F^2	1.037
R_1, wR_2 [$I>2\sigma(I)$][a]	0.0530, 0.1301
R_1, wR_2 (all data)[a]	0.0728, 0.1472
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	1.386, -1.353

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

Table S2 Selected bond lengths (Å) and bond angles (°) for complex **1**·$CHCl_3$.

Ir1-N1	2.121(6)	Ir1-C24	2.019(7)
Ir1-N2	2.142(5)	Ir1-C31	2.045(6)
Ir1-N3	2.043(6)	O1-C13	1.209(10)
Ir1-N4	2.047(6)		
N1-Ir1-N2	78.0(2)	C24-Ir1-N2	98.1(2)
N3-Ir1-N2	87.5(2)	C31-Ir1-N2	174.7(2)
N4-Ir1-N2	96.9(2)	C24-Ir1-N3	81.4(3)
N4-Ir1-N1	85.3(2)	C31-Ir1-N3	95.2(3)
N3-Ir1-N1	99.5(2)	C24-Ir1-N4	94.1(3)
N3-Ir1-N4	174.1(2)	C31-Ir1-N4	80.7(3)
C24-Ir1-N1	175.9(2)	C24-Ir1-C31	86.9(2)
C31-Ir1-N1	97.0(2)		

Table S3 The UV-vis absorption data of complex **1** in CH_2Cl_2 and in CH_3OH at room temperature.

Complex **1**	absorption bands (nm)
in CH_2Cl_2	260, 290, 362, 382 and 500 nm
in CH_3OH	260, 269 and 362 nm, and an absorption tail towards 488 nm

Table S4 Luminescecne data of **2** in solution at room temperature.

medium	λ_{em} (nm)	quantum yield
CH_2Cl_2	500	12.6%
EA	506	4.5%
THF	507	7.2%
$CHCl_3$	500	10.4%
CH_3CN	507	4.5%
CH_3OH	507	5.9%

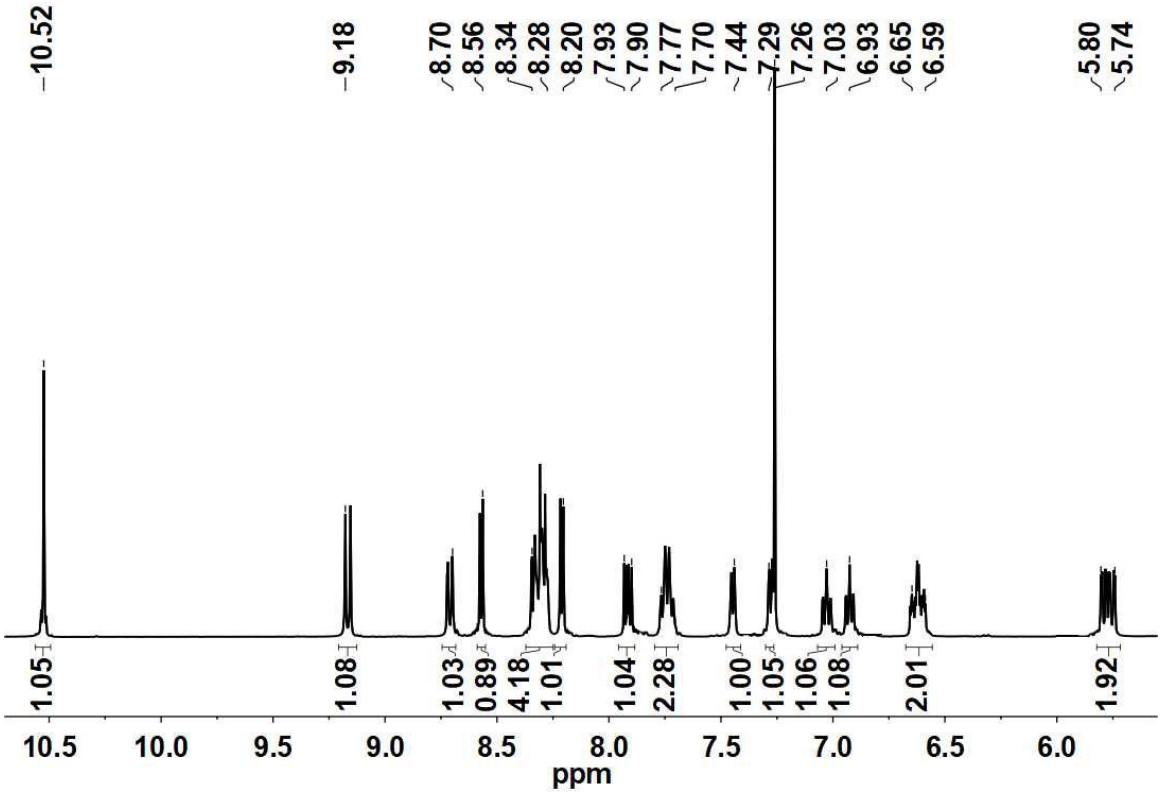


Fig. S1 ^{1}H NMR spectrum of complex **1** (400 MHz, $CDCl_3$, using sample $\mathbf{1^R}$).

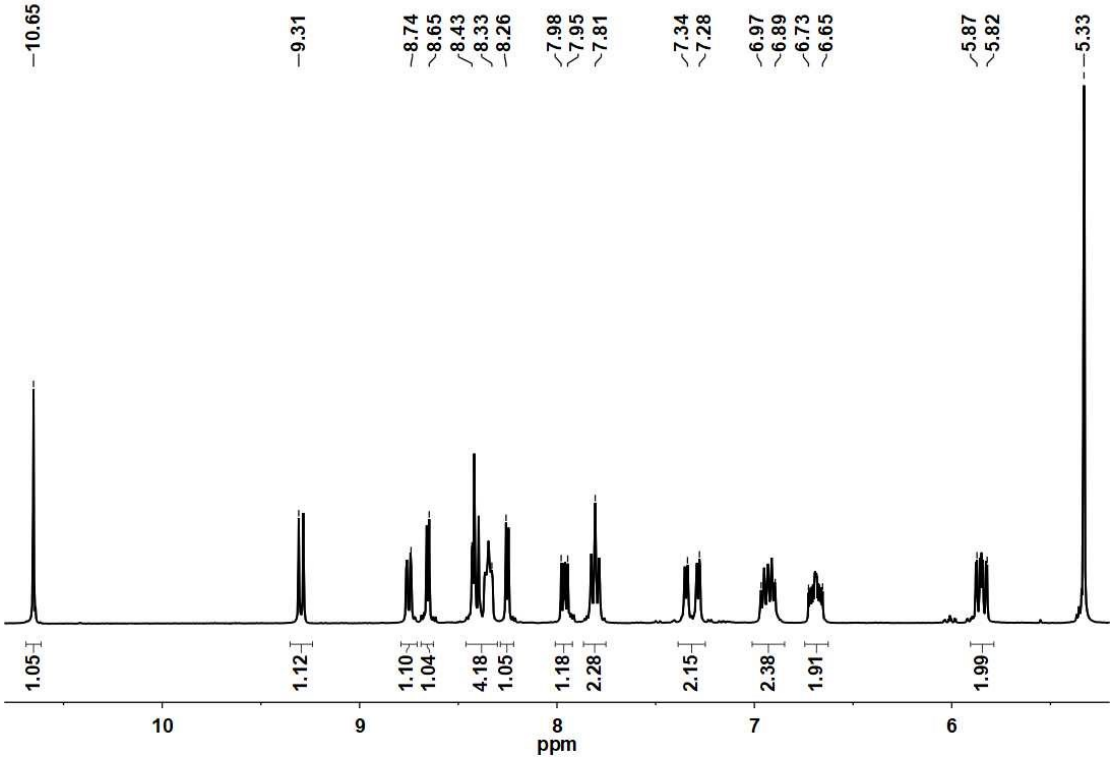


Fig. S2 ^{1}H NMR spectrum of complex **1** (400 MHz, CD_2Cl_2, using sample $\mathbf{1^R}$).

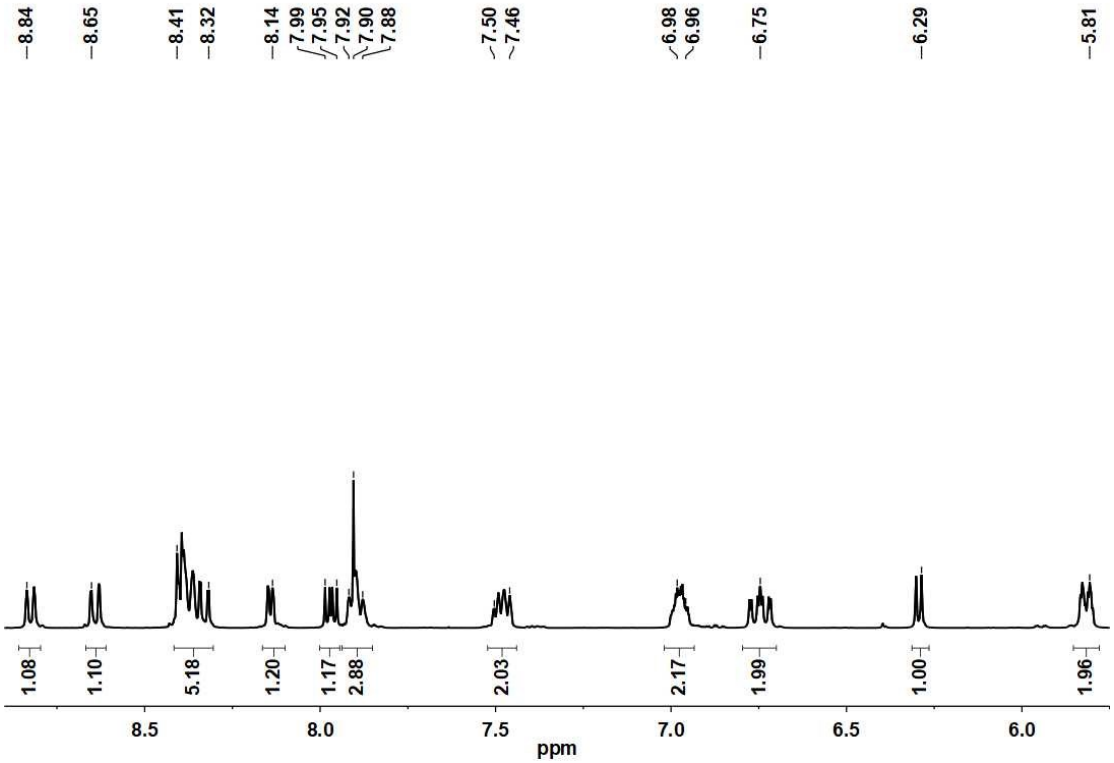


Fig. S3 ^{1}H NMR spectrum of complex **1** (400 MHz, CD_3OD, using sample $\mathbf{1^R}$).

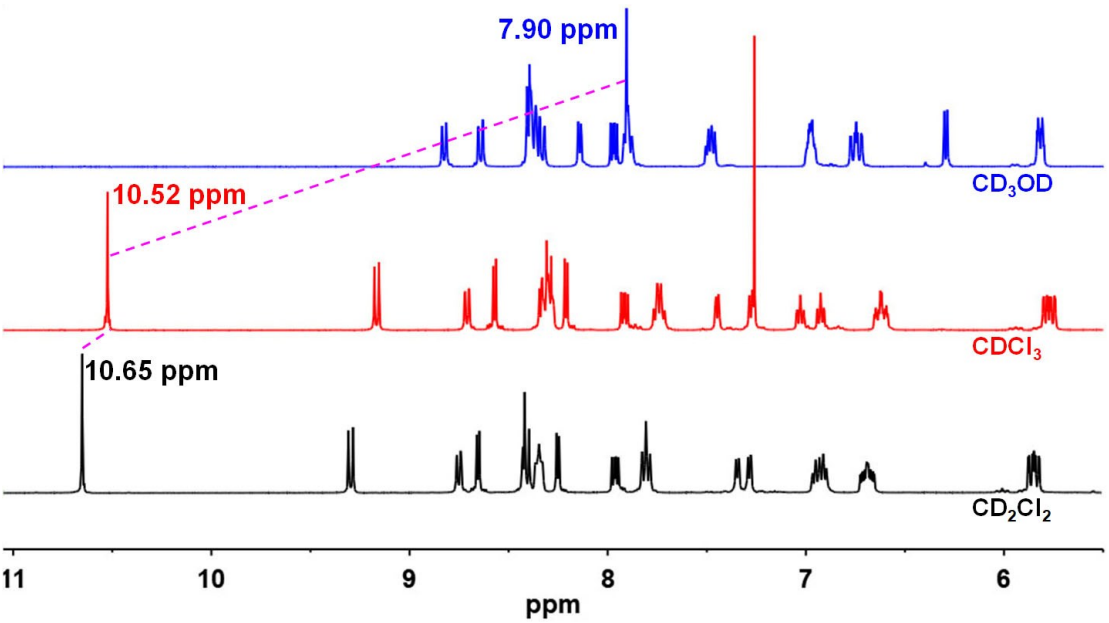


Fig. S4 The ^{1}H NMR signal of –CHO proton in complex **1** measured in CD_2Cl_2, $CDCl_3$ or CD_3OD.

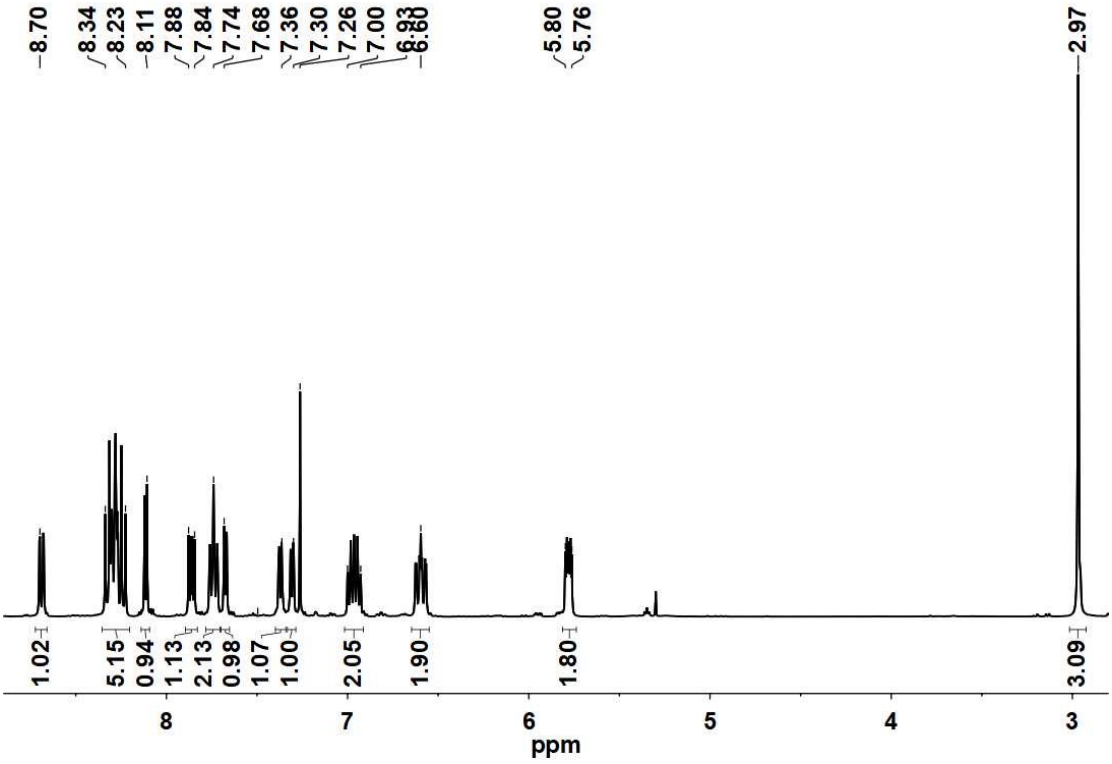


Fig. S5 ^{1}H NMR spectrum of complex **2** (400 MHz, $CDCl_3$).

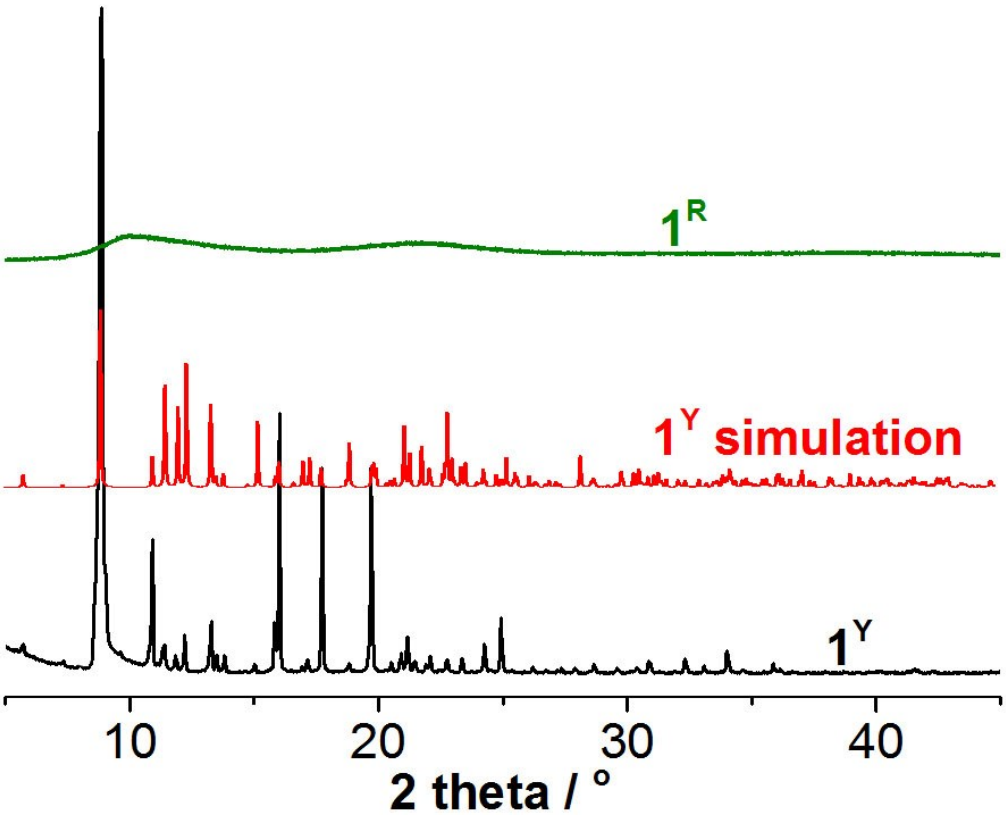


Fig. S6 Experimental XRD patterns of $\mathbf{1^R}$ and $\mathbf{1^Y}$, and simulated XRD patterns of $\mathbf{1^Y}$.

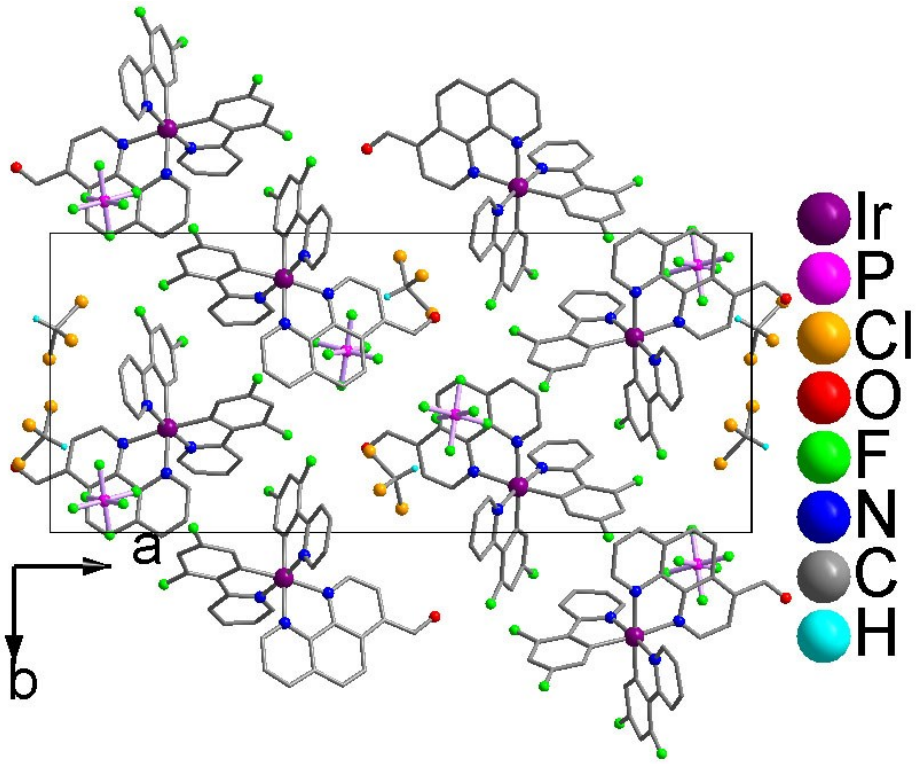


Fig. S7 The packing structure of $\mathbf{1^Y}$. Only the H atoms in $CHCl_3$ molecules are kept.

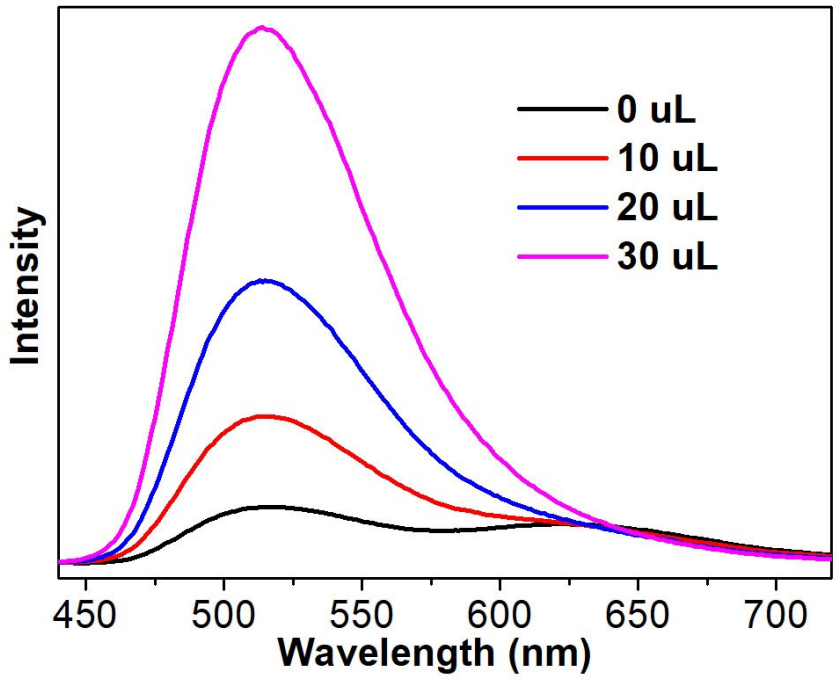


Fig. S8 The changes of luminescence spectra of complex **1** in CH_2Cl_2 (2.5 mL, c = 1 × 10^{-4} M) upon adding CH_3OH (10, 20, 30 uL).

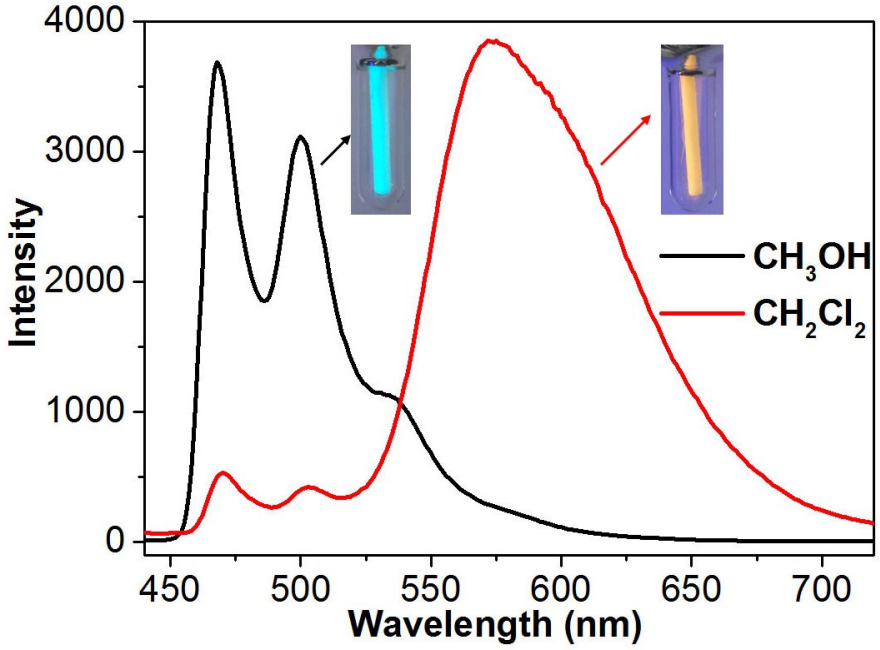


Fig. S9 The luminescence spectra of complex **1** in CH_2Cl_2 and in CH_3OH at 77 K.

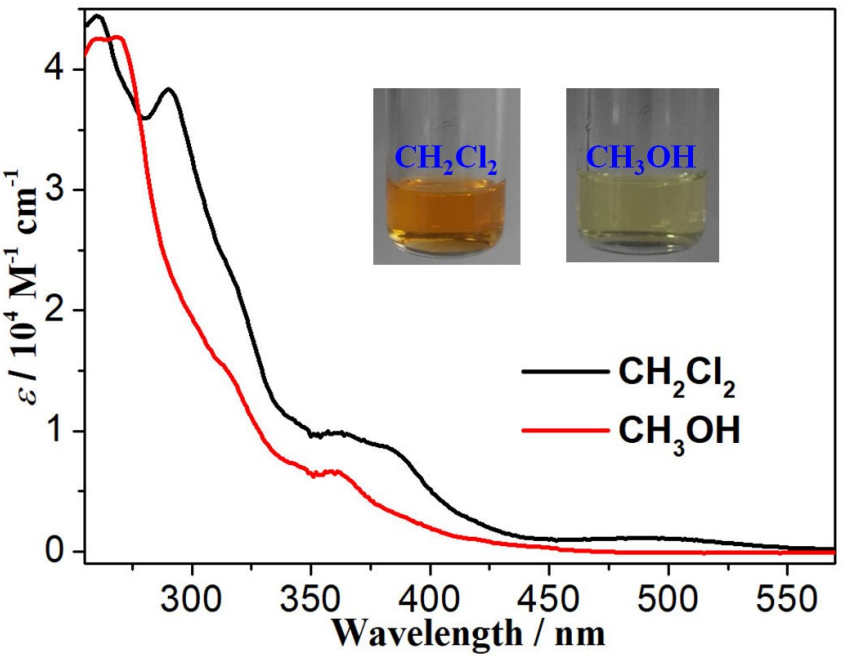


Fig. S10 The UV-vis absorption spectra of complex **1** in CH_2Cl_2 and in CH_3OH. Inset: the photographs of **1** in CH_3OH and in CH_2Cl_2 under room light.

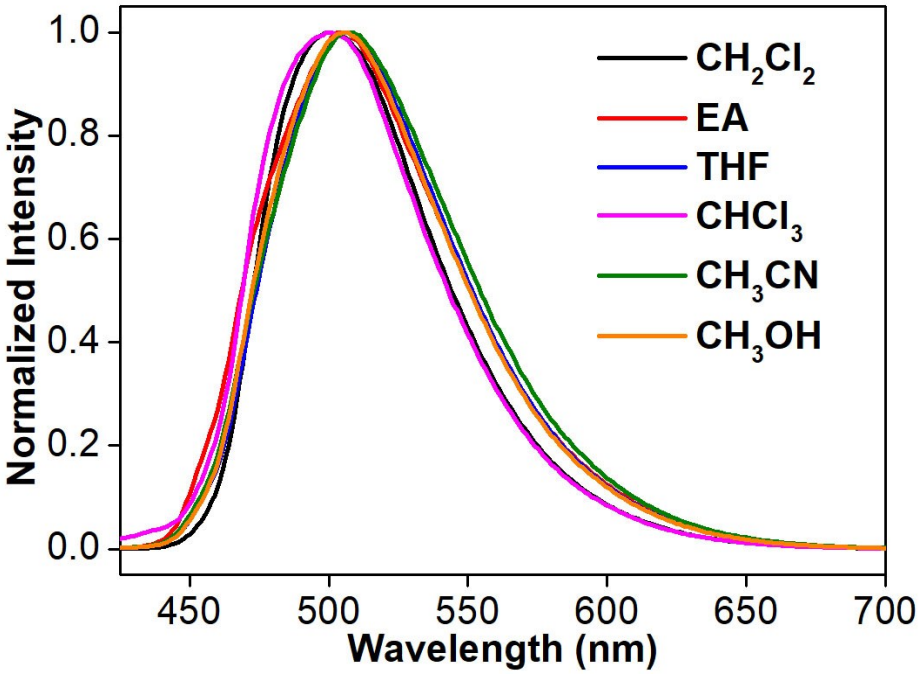


Fig. S11 Luminescence spectra of **2** in different solvents (EA = $CH_3COOC_2H_5$, c = 1 × 10^{-4} M, λ_{ex} = 368 nm).

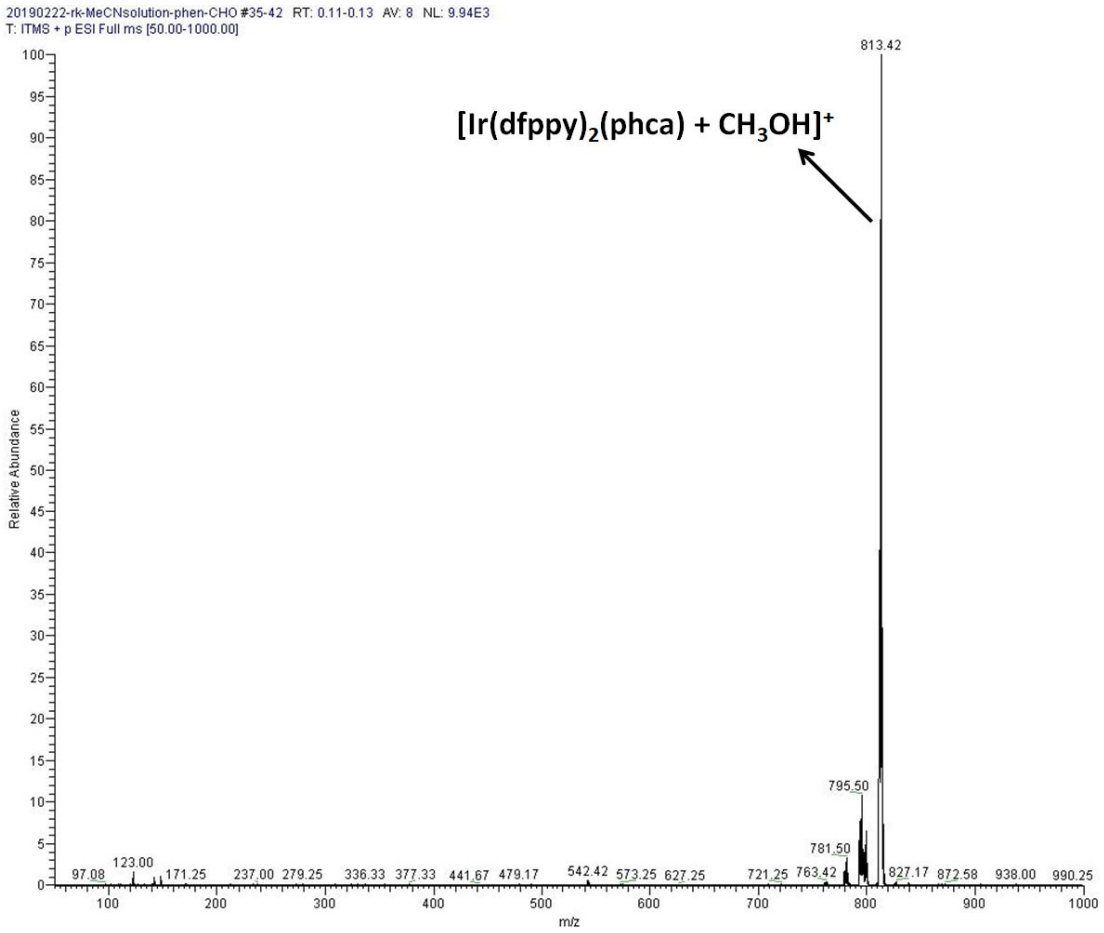


Fig. S12 Electrospray mass spectrometry (ES-MS) of **1** in CH_3CN solution.

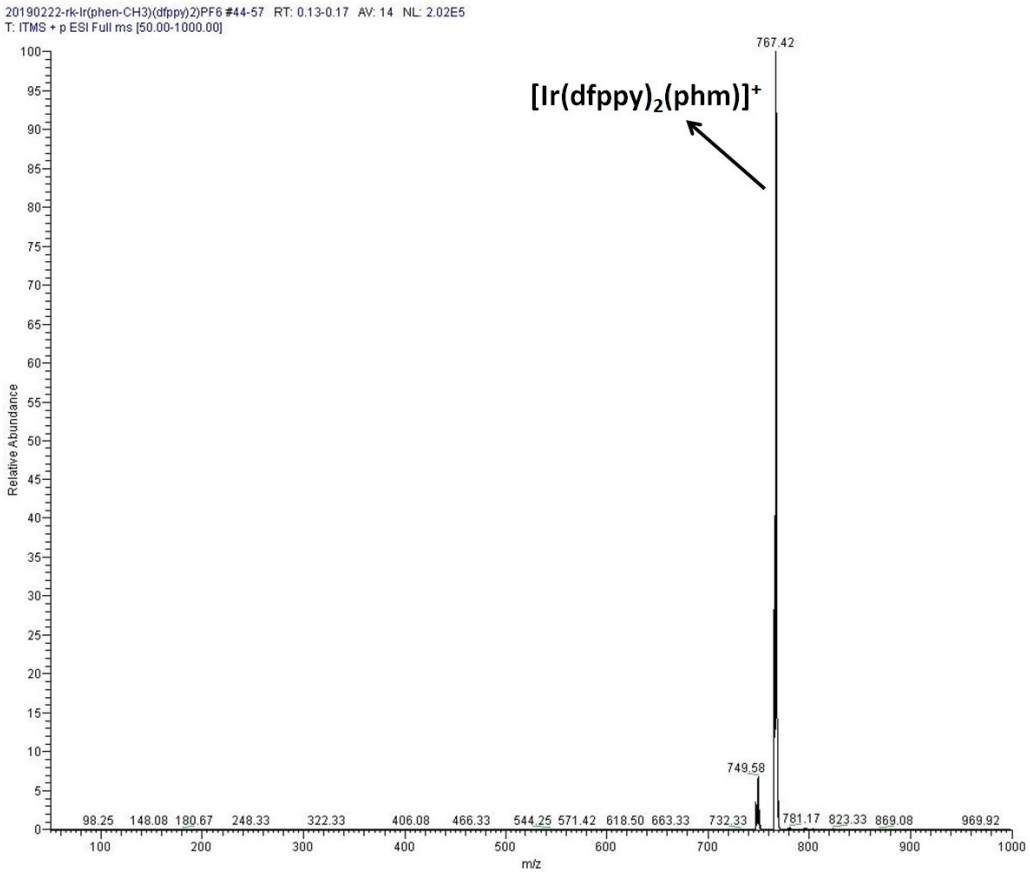


Fig. S13 Electrospray mass spectrometry (ES-MS) of **2** in CH_3CN solution.

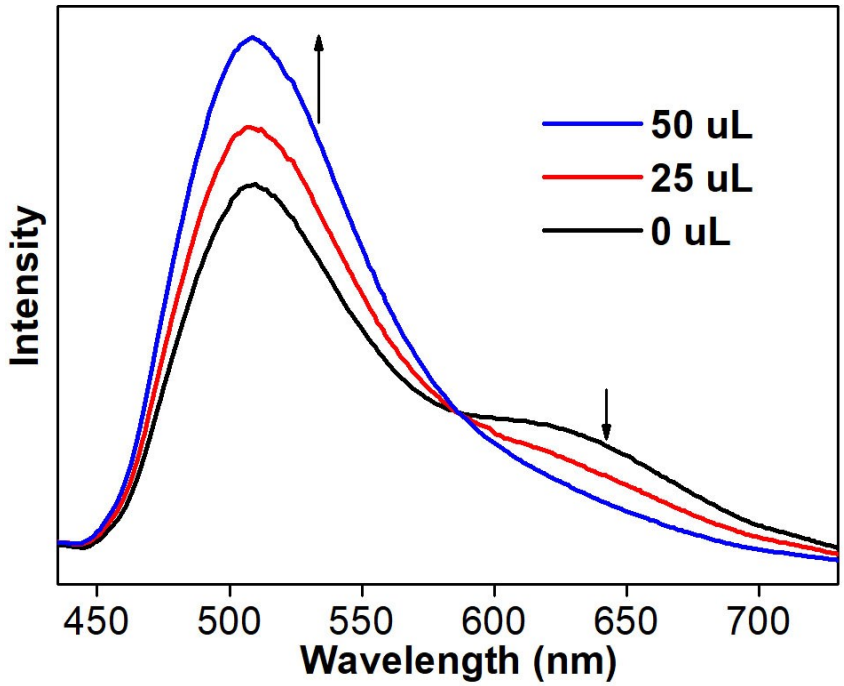


Fig. S14 Luminescence change of complex **1** upon adding in H_2O into its THF solution (2.5 mL, $c = 1 \times 10^{-4}$ M) at room temperature.

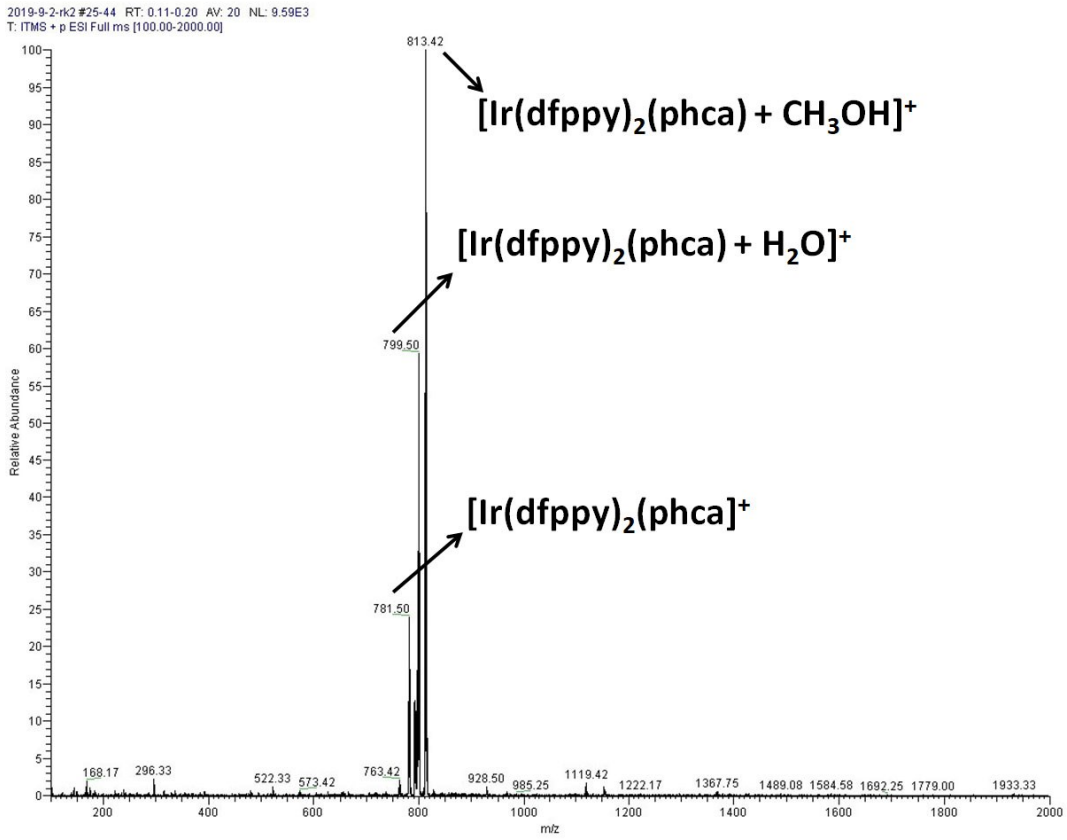


Fig. S15 Electrospray mass spectrometry (ES-MS, using CH_3OH as mobile phase) of complex **1** in CH_3CN-H_2O mixture (v/v = 3/1).

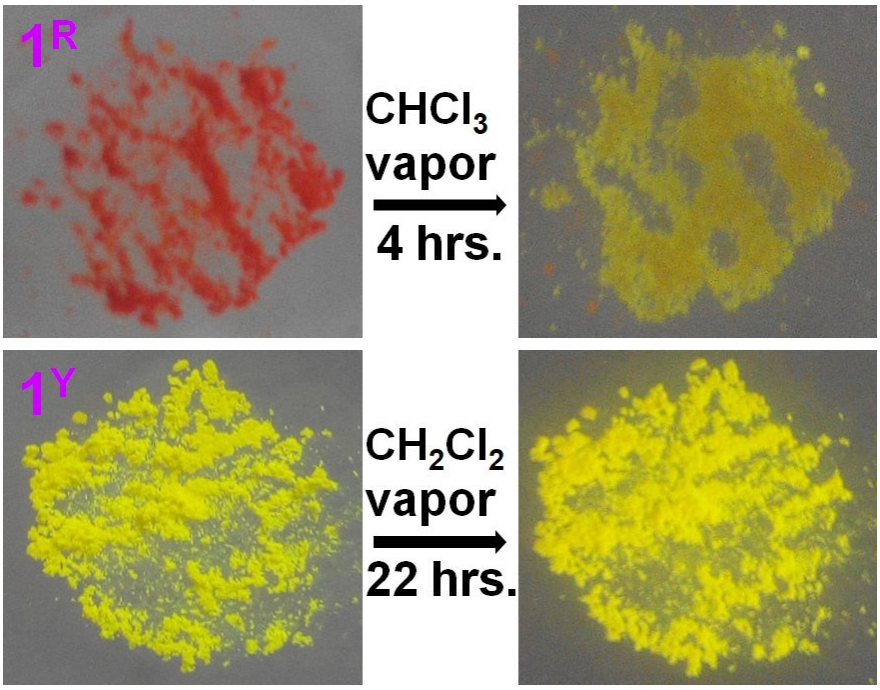


Fig. S16 Influence of $CHCl_3$/CH_2Cl_2 vapor on the emission colors of solids $\mathbf{1}^{\mathbf{R}}$ and $\mathbf{1}^{\mathbf{Y}}$.

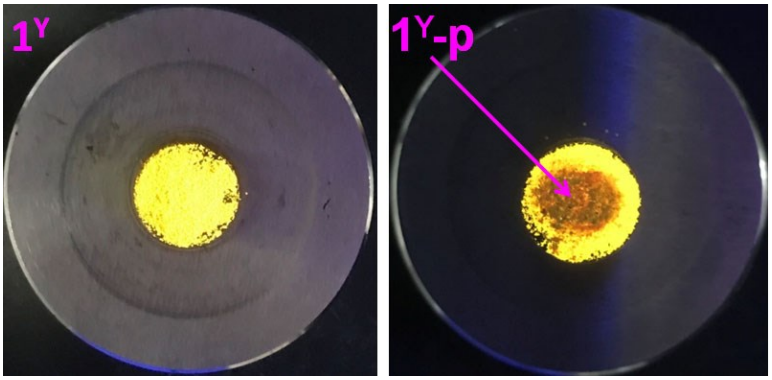


Fig. S17 The photographs of samples $\mathbf{1^Y}$ and $\mathbf{1^Y}$**-p** under 365 nm light (Pressing experiment of $\mathbf{1^Y}$ was performed on a device which can make KBr disks for measuring IR spectra. Sample $\mathbf{1^Y}$ was sandwiched between two steel plates, with more $\mathbf{1^Y}$ at the center of the plate. The applied pressure was 7 tons.).

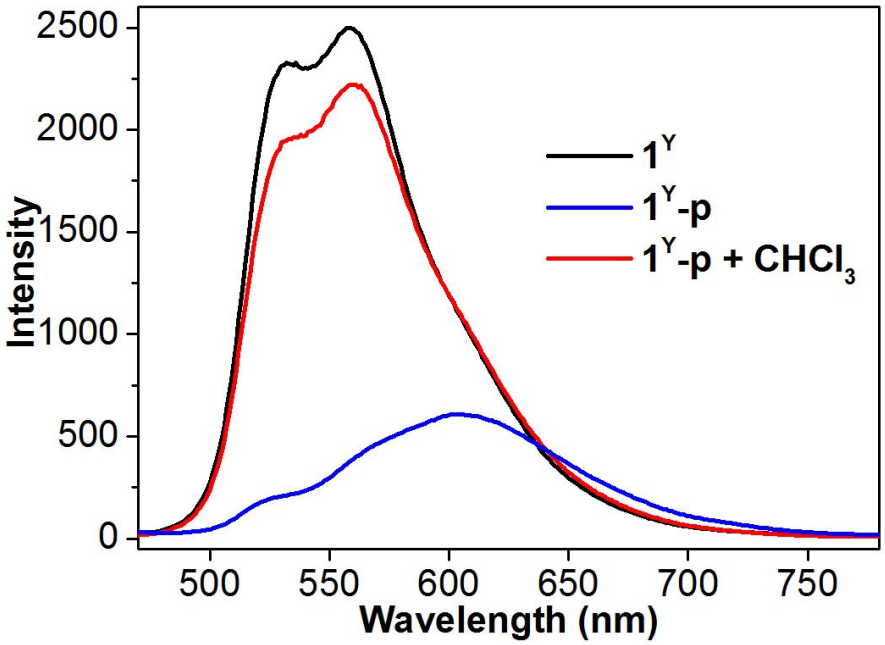


Fig. S18 Solid-state emission spectra of $\mathbf{1^Y}$, $\mathbf{1^Y}$**-p** and "$\mathbf{1^Y}$**-p + CHCl3**".

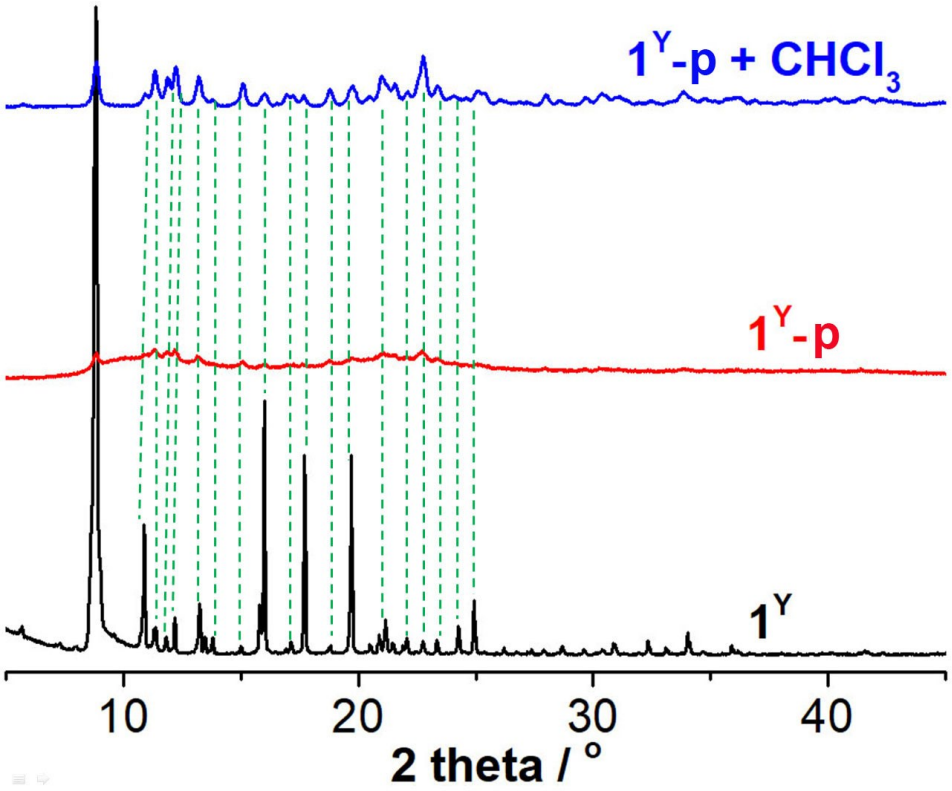


Fig. S19 The XRD patterns of $\mathbf{1^{Y}}$, $\mathbf{1^{Y}}$**-p** and "$\mathbf{1^{Y}}$**-p + CHCl**$_3$".