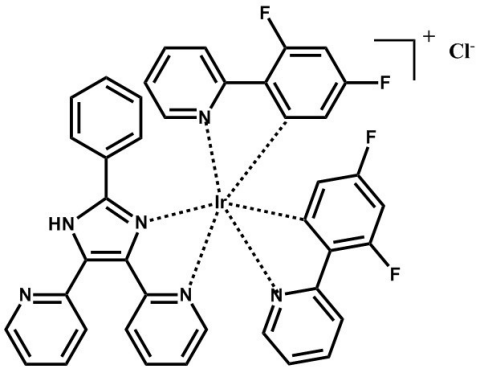
Electronic Supporting Information

1. Synthesis of 2,2'-(2-phenyl-1H-imidazole-4,5-diyl)dipyridine (pidpyH)

A mixture of benzaldehyde (2.5 mmol, 0.2653 g), 1,2-bis(2-pyridine)ethane-1,2-dione (2.0 mmol, 0.4240 g), ammonium acetate (40 mmol, 3.1040 g) and HOAc (20 mL) was heated in an oil bath (120 ^{o}C) for one day. This mixture was extracted by benzene (30 mL), and then organic phase was evaporated under vacumm. The resultant residue was purified using silica gel column and petroleum ether-ethyl acetate as eluent, obtaining light yellow solid with a yield of 297 mg [50% based on 1,2-bis(2-pyridine)ethane-1,2-dione]. Anal. found (calcd) for $C_{19}H_{14}N_4$: C, 76.57 (76.49); H, 5.94 (4.73), N, 18.86 (18.78). IR (KBr, cm^{-1}): 3366(w), 3127(m), 1589(m), 1534(w), 1489(w), 1472(w), 1460(m), 1442(w), 1421(w), 1400(s), 1270(w), 1219(w), 1091(w), 1002(w), 977(w), 784(m), 742(w), 699(w), 691(m), 664(w). ^{1}H NMR (300 MHz, $CDCl_3$), δ (ppm): 7.16 and 7.26 (2d, 2H from phenyl group), 7.37-7.49 (m, 3H from phenyl group), 7.68, 7.81, 8.00 and 8.02 (4t, 4H from two pyridyl groups), 8.14-8.69 (4d, 4H from two pyridyl groups).

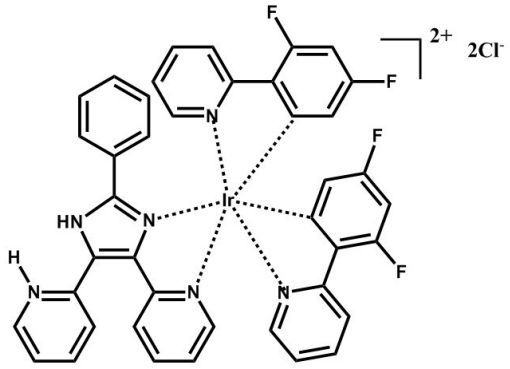
2. Synthesis of [Ir(dfppy)$_2$(pidpyH)]Cl (1·Cl)



A mixture of pidpyH (0.2 mmol, 0.0629 g) and $[Ir(dfppy)_2Cl]_2$ (0.1 mmol, 0.1216 g) in CH_2Cl_2 (15 mL) and CH_3OH (12 mL) was heated in an oil bath (50 ^{o}C) under argon for one day. After evaporation under vacuum, the resultant residue was purified through silica column chromatography using CH_3OH-CH_2Cl_2 (v/v = 0-3/100) solution, obtaining a yellow solid of [Ir(dfppy)$_2$(pidpy)]Cl (**1·Cl**) (181mg, 78% based on

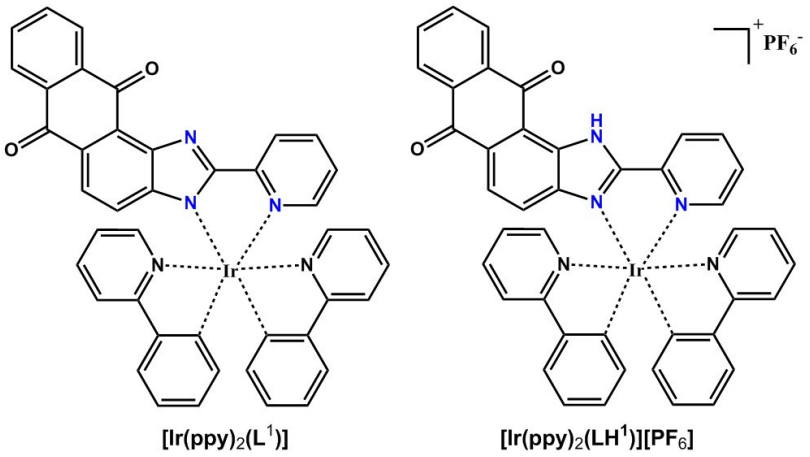
[Ir(dfppy)$_2$Cl]$_2$). Anal. Found (calcd) for $C_{41}H_{26}N_6F_4ClIr$: C, 54.42 (54.33); H, 3.03 (2.89), N, 9.41 (9.27). IR (KBr, cm^{-1}): 3127(w), 1605(s), 1572(m), 1557(m), 1478(s), 1448(s), 1401(w), 1292(w), 1248(w), 1228(w), 1163(w), 1112(w), 1102(w), 987(m), 845(w), 828(w), 784(w), 757(w), 728(w), 702(w). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 5.18 and 5.20 (d, 1H), 5.65 and 5.68 (d, 1H), 6.07 (t, 1H), 6.42 (t, 1H) [5.18-6.42 ppm: total 4H from two 2,4-difluorophenyl rings of the dfppy$^-$ units], 6.83-6.97 (m, total 7H: 5H from the phenyl group of pidpyH ligand and 2H from two pyridyl rings of the dfppy$^-$ units), 7.03-7.18 (2t, 2H from two pyridyl groups of pidpyH ligand), 7.60-7.78 (m, 6H: 4H from two pyridyl rings of the dfppy$^-$ units and 2H from two pyridyl groups of pidpyH ligand). 8.00-8.20 (d and m, total 4H: 2H from two pyridyl rings of the dfppy$^-$ units and 2H from a pyridyl group of pidpyH ligand), 8.65 and 9.34 (2d, 2H from two pyridyl groups of pidpyH ligand).

3. Synthesis of [Ir(dfppy)$_2$(pidpyH$_2$)]2Cl (1H·2Cl)

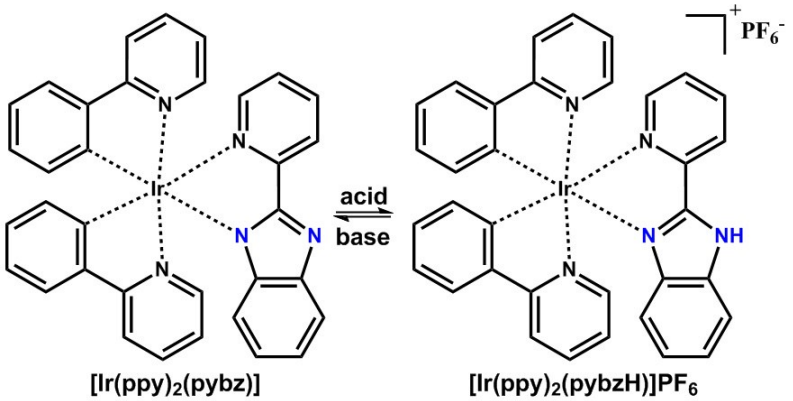


A mixture of **1·Cl** (0.024 mmol, 24 mg) in $CHCl_3$ (5 mL) and HCl (6M, 2 mL) was stirred for 2 hours at room temperature. The mixture was allowed to slowly evaporated, obtaining yellow needlike crystals of **1H·2Cl** (22 mg, 89% based on **1·Cl**). Anal. found (calcd) for $C_{41}H_{27}N_6F_4Cl_2Ir$: C, 52.38 (52.23); H, 3.07 (2.89), N, 9.06 (8.91). IR (KBr, cm^{-1}): 3382(w), 3134(m), 2975(w), 1604(w), 1576(w), 1559(w), 1477(w), 1402(s), 1294(w), 1248(w), 1162(w), 1090(w), 1050(m), 991(w), 881(w), 829(w), 787(w), 759(w), 699(w), 569(w). ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 5.38 and 5.40 (d, 1H), 5.69 and 5.71 (d, 1H), 6.11 (t, 1H), 6.52 (t, 1H) [5.38-6.52 ppm: total 4H from two 2,4-difluorophenyl rings of the dfppy$^-$ units], 6.97-7.16 (two broad

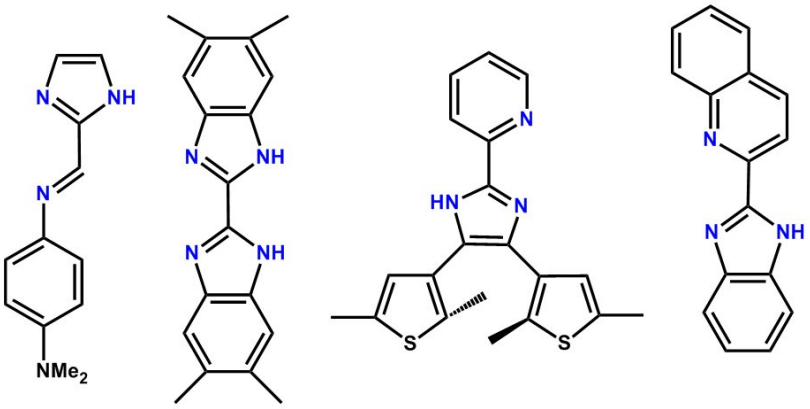
peaks, 8H), 7.52 (one broad peak, 1H), 7.71-8.03 (m, 6H), 8.30-8.85 (m, 6H) [6.97-7.16 ppm and 7.71-8.85 pm: total 21H: 8H from two pyridyl rings of two $dfppy^-$ units and 13 H from pidpyH ligand)



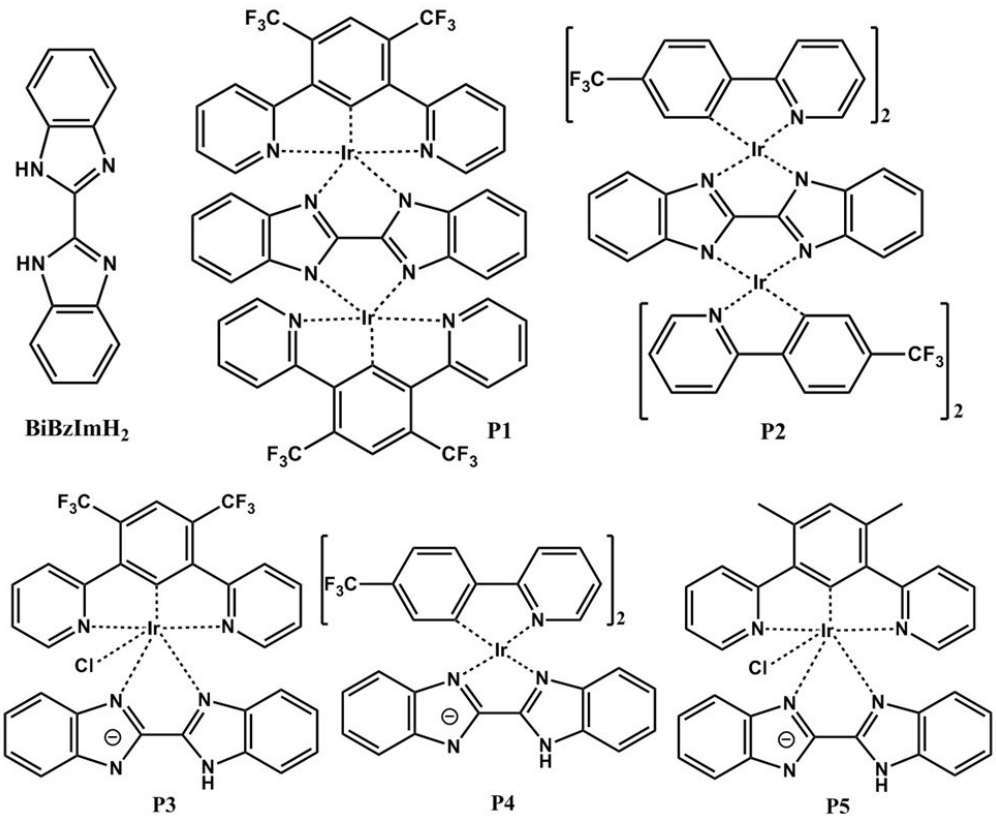
Scheme S1



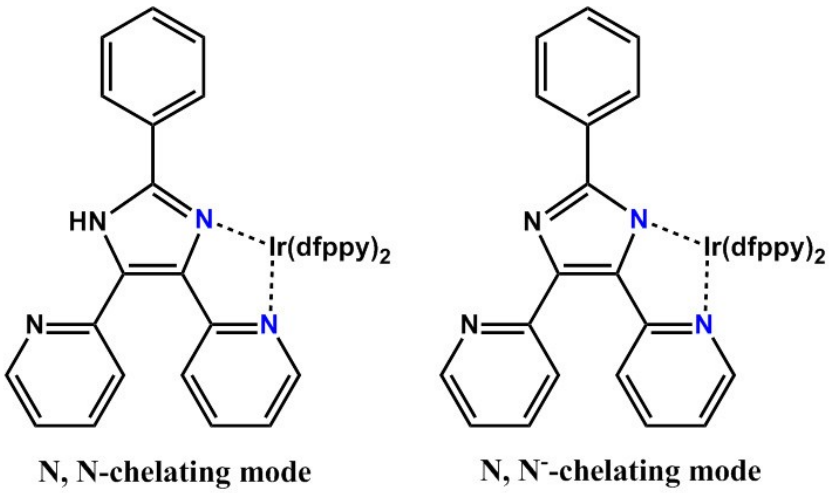
Scheme S2



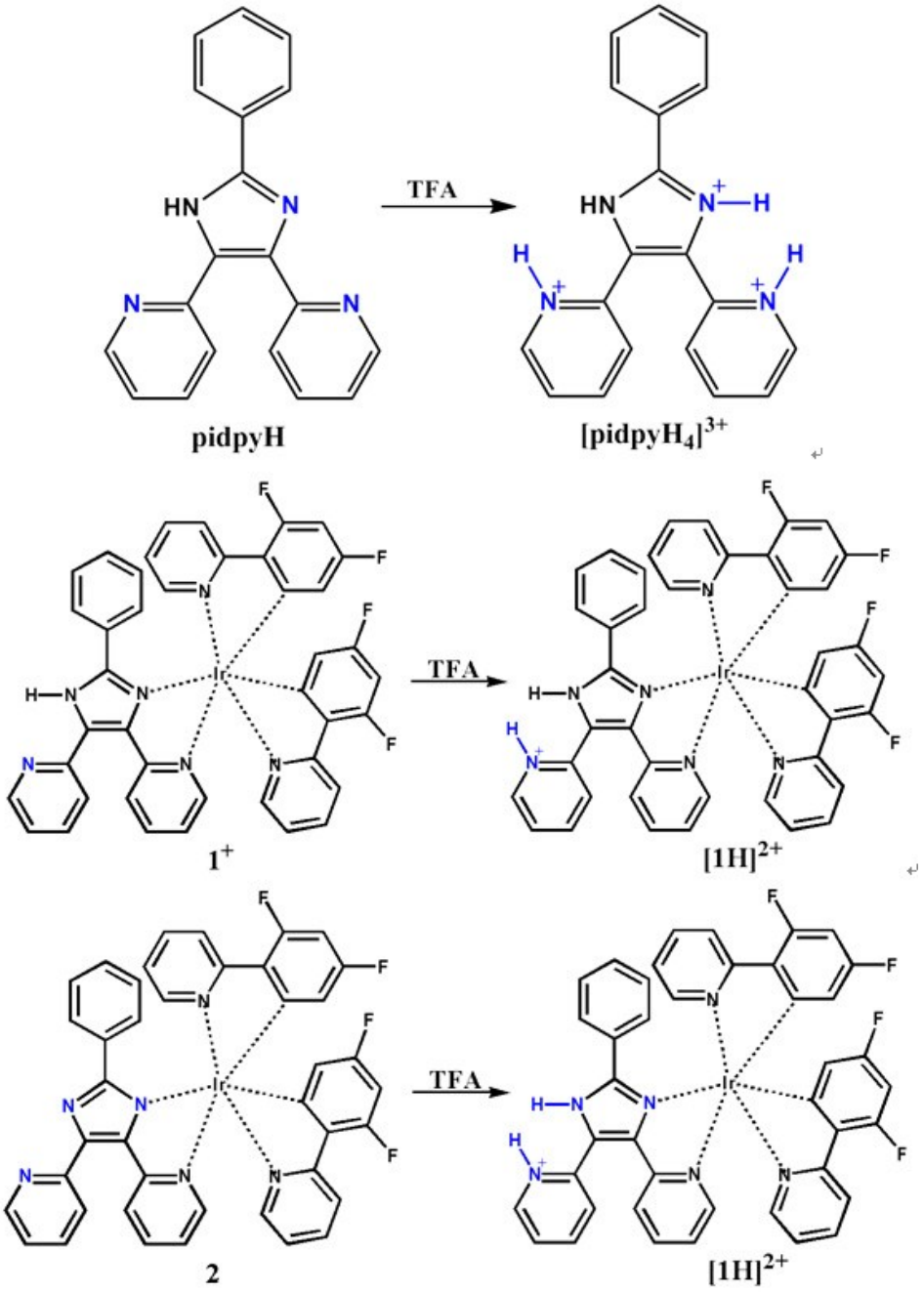
Scheme S3



Scheme S4



Scheme S5



Scheme S6

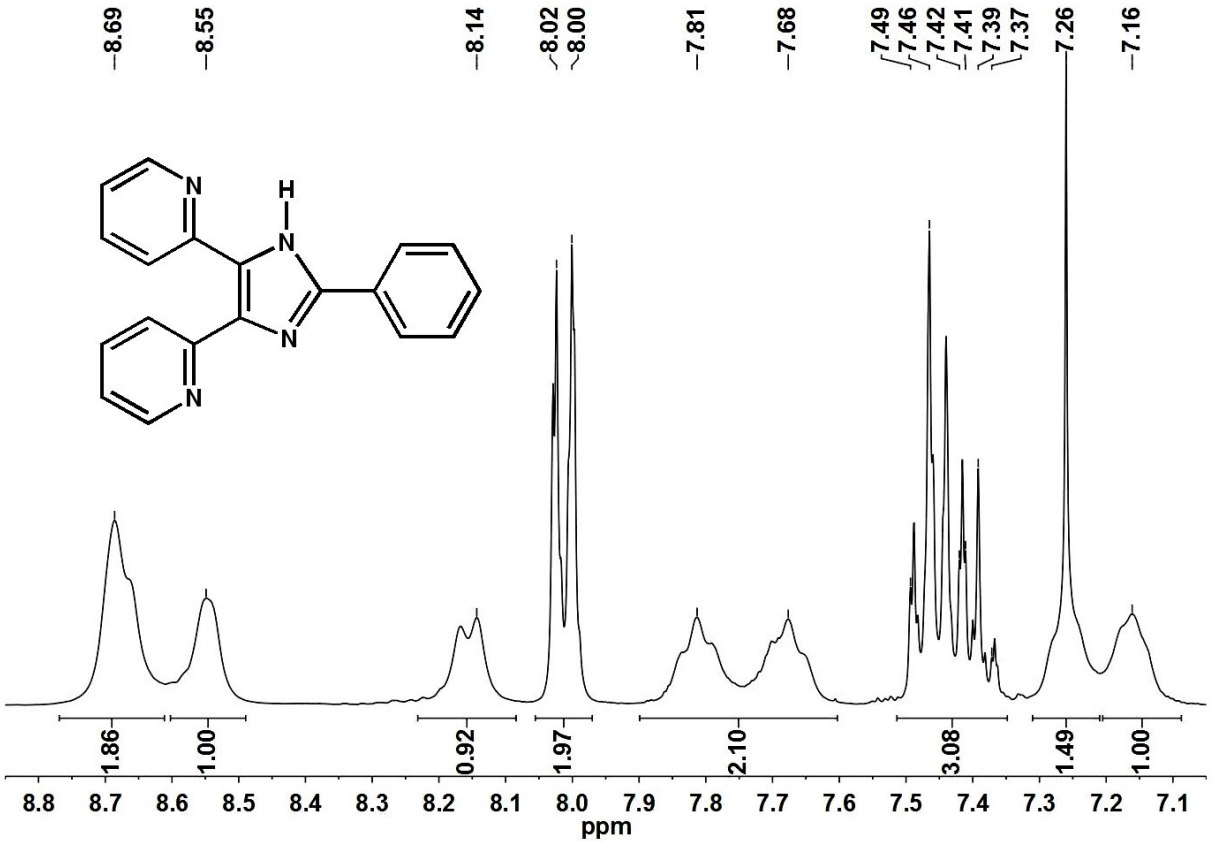


Fig. S1 ^{1}H NMR spectrum of pidpyH (300 MHz, $CDCl_3$).

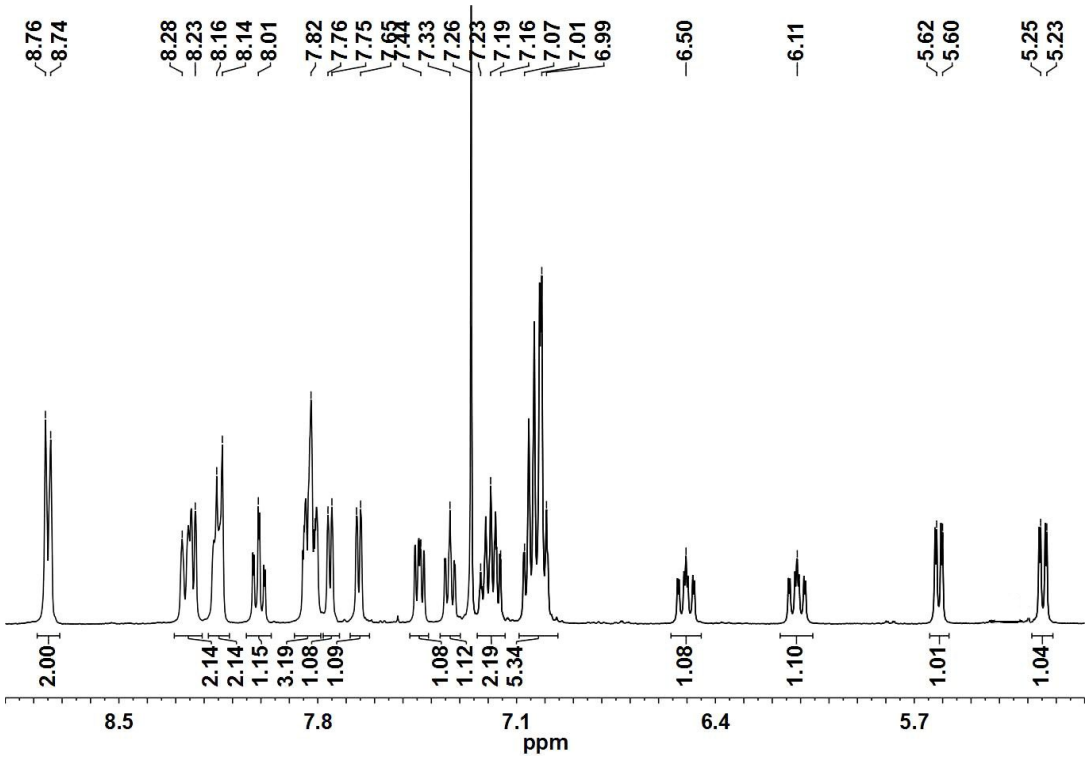


Fig. S2 ^{1}H NMR spectrum of **1·PF$_6$** (400 MHz, $CDCl_3$).

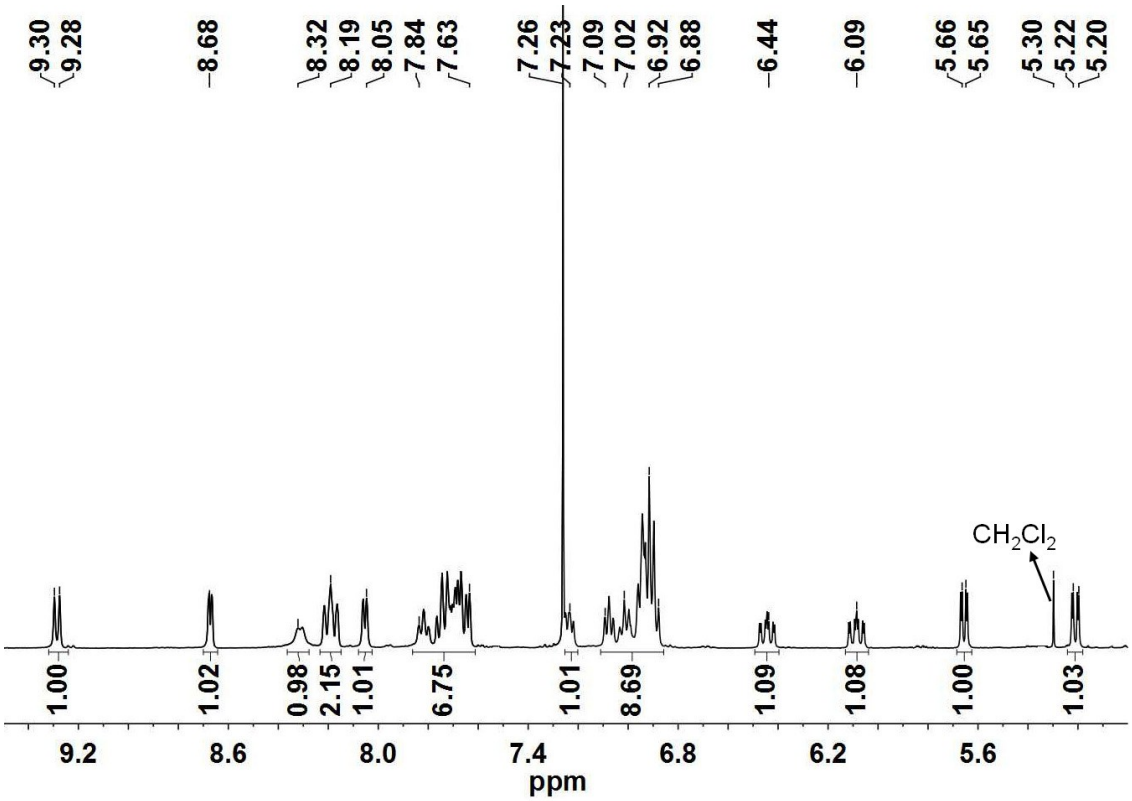


Fig. S3 ^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$).

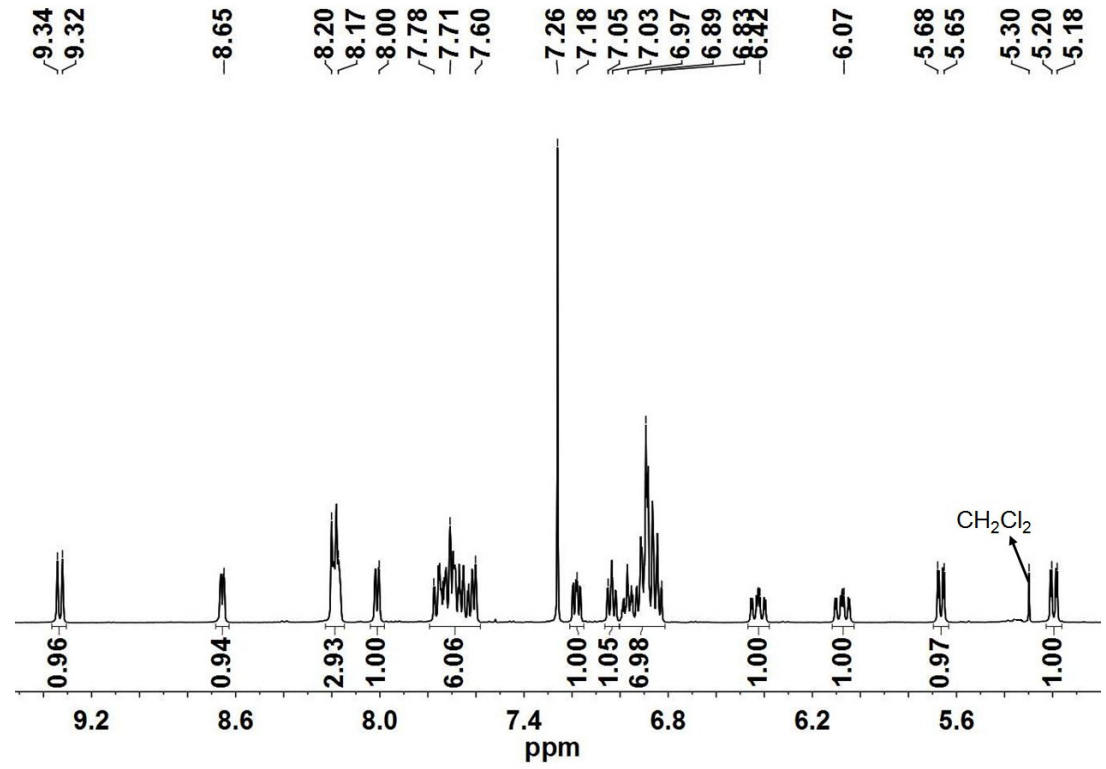


Fig. S4 ^{1}H NMR spectrum of **1·Cl** (400 MHz, $CDCl_3$).

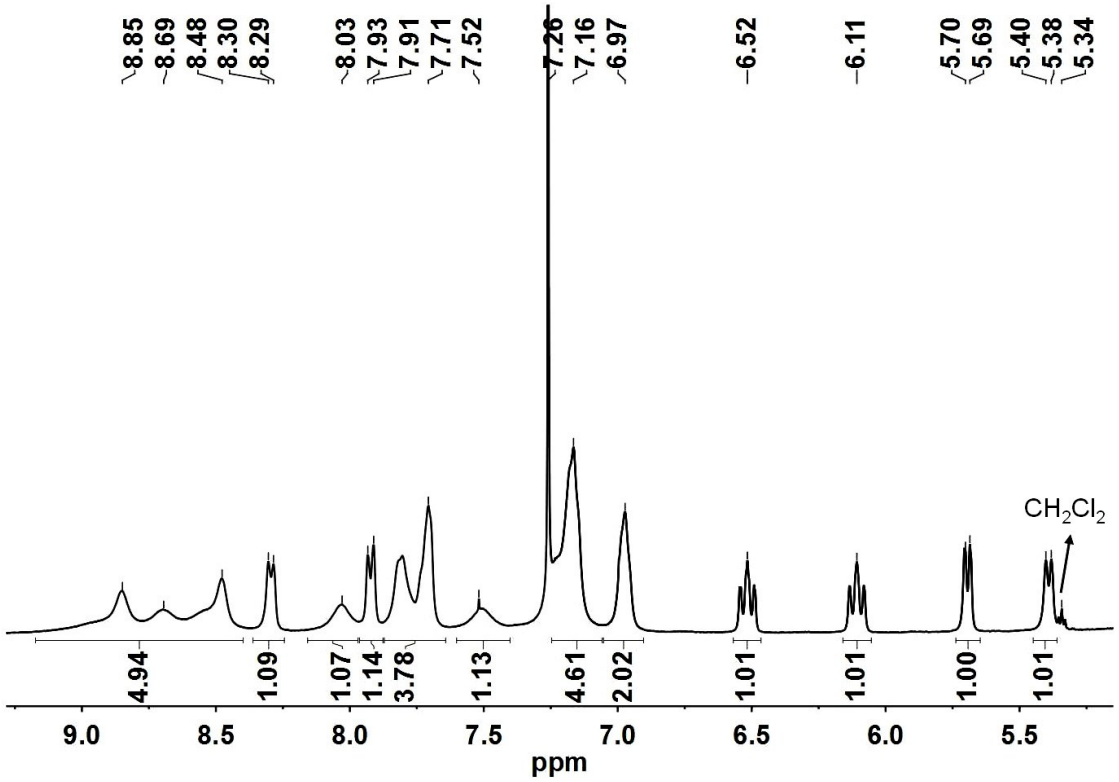


Fig. S5 ^{1}H NMR spectrum of **1H·2Cl** (400 MHz, $CDCl_3$).

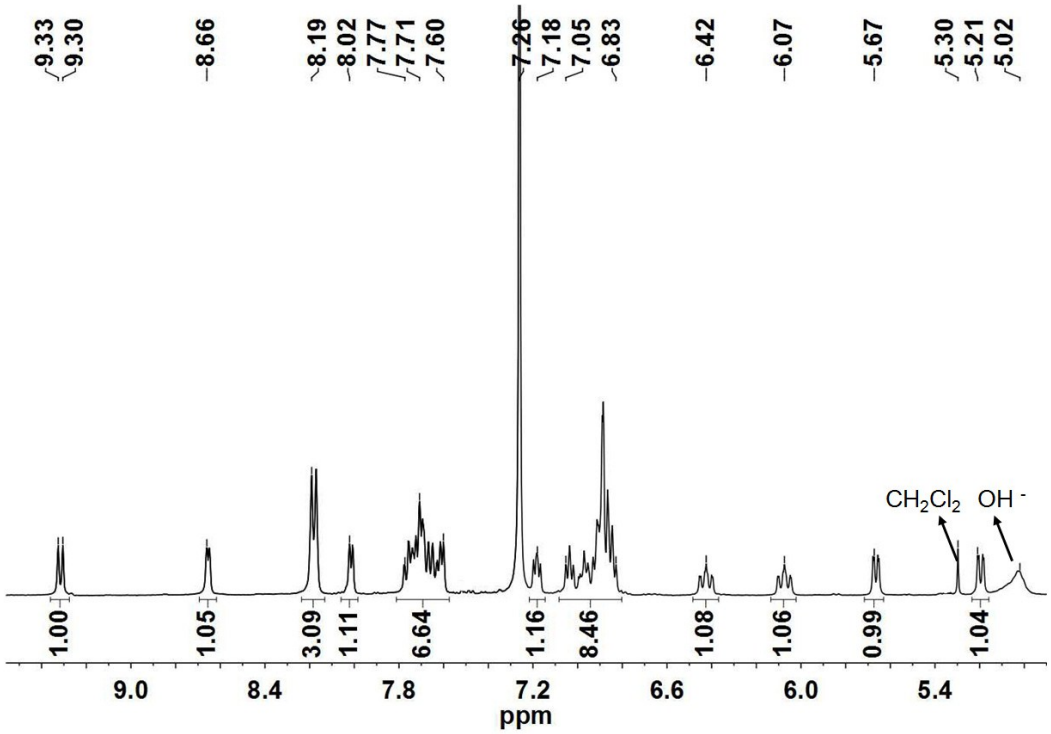


Fig. S6 ^{1}H NMR spectrum of **1·PF6** (400 MHz, $CDCl_3$) after adding a D_2O solution of NaOH (The signal at 5.02 ppm could be from OH^- in the solution, seeing *J. Org. Chem.*, 1997, 62, 7512.).

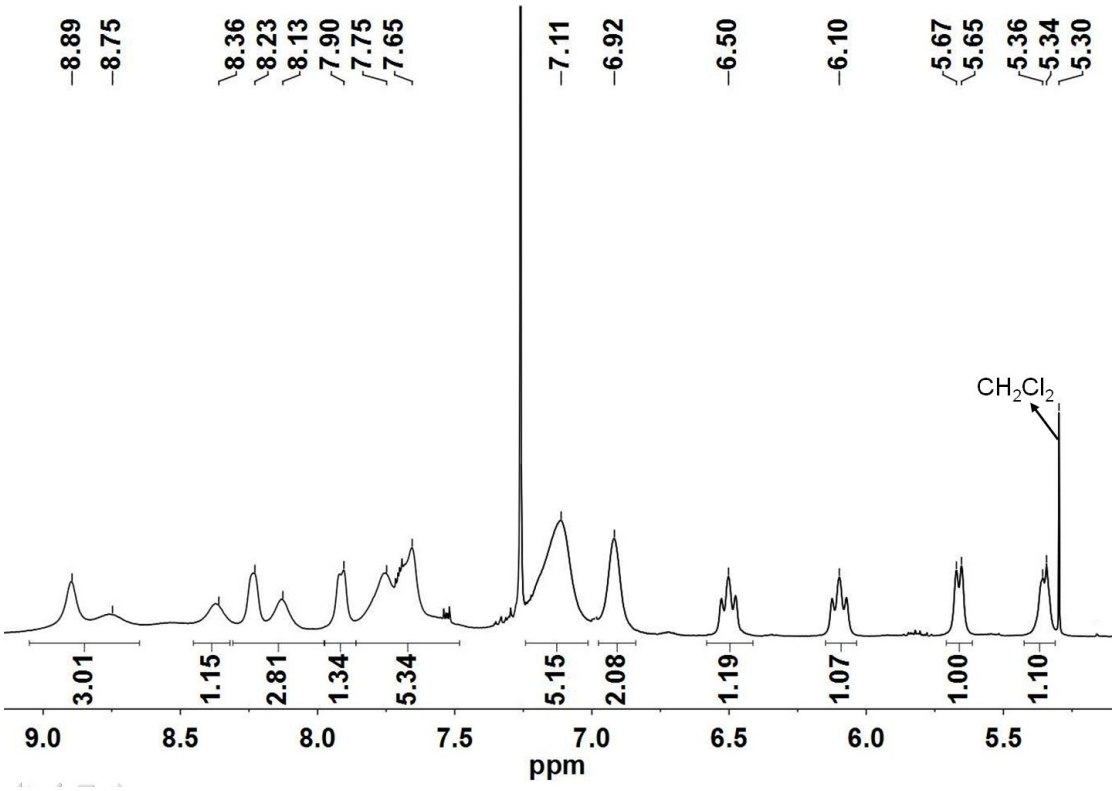


Fig. S7 ^{1}H NMR spectrum of **2** (400 MHz, $CDCl_3$) after adding DCl.

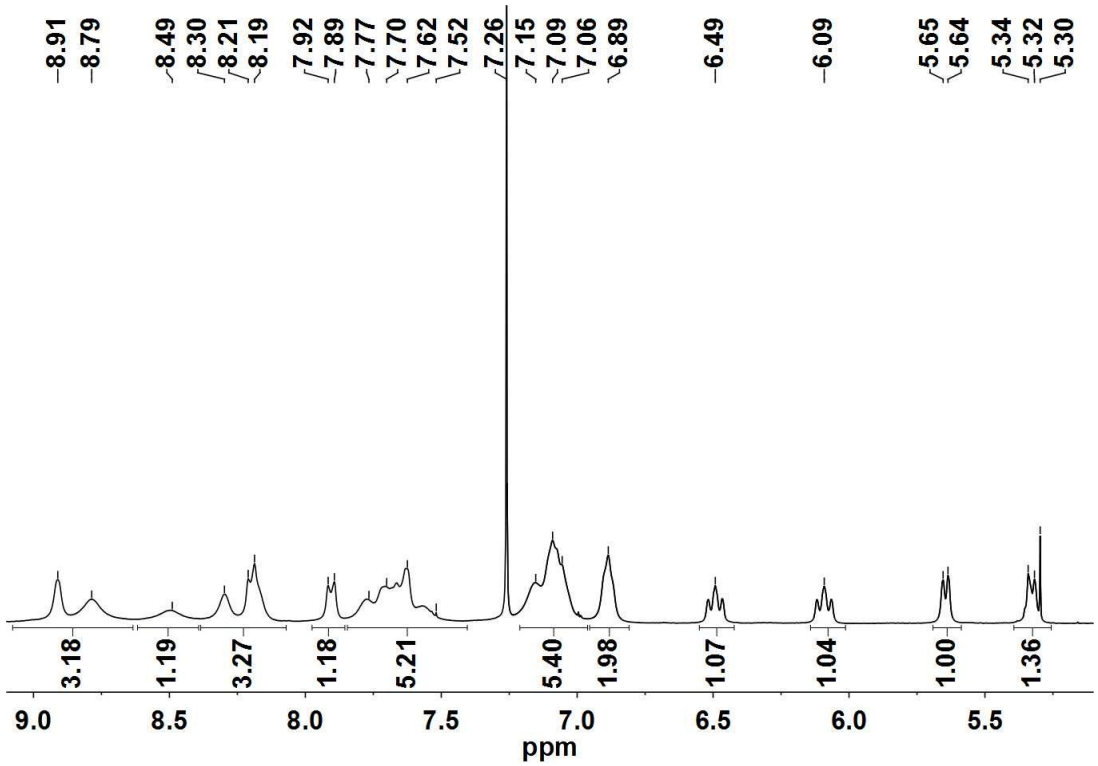


Fig. S8 ^{1}H NMR spectrum of **1·Cl + DCl** (400 MHz, $CDCl_3$).

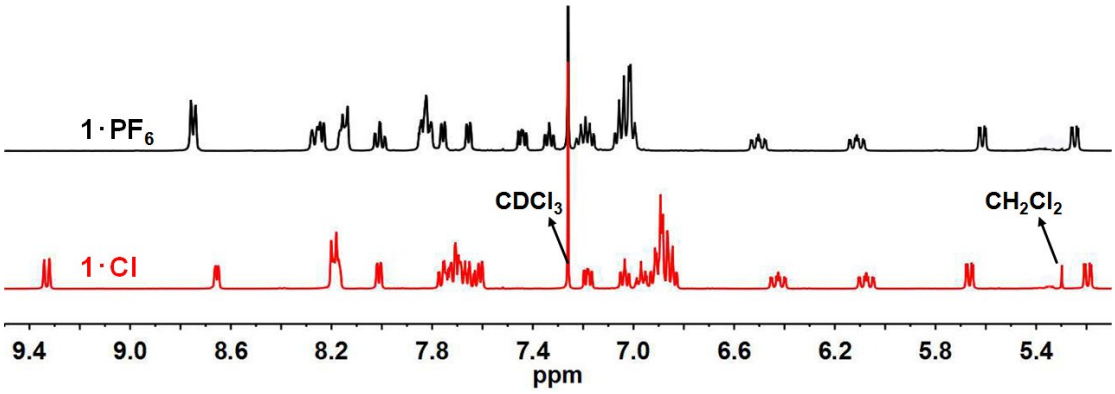


Fig. S9 ^{1}H NMR spectra comparison between **1·PF$_6$** and **1·Cl** .

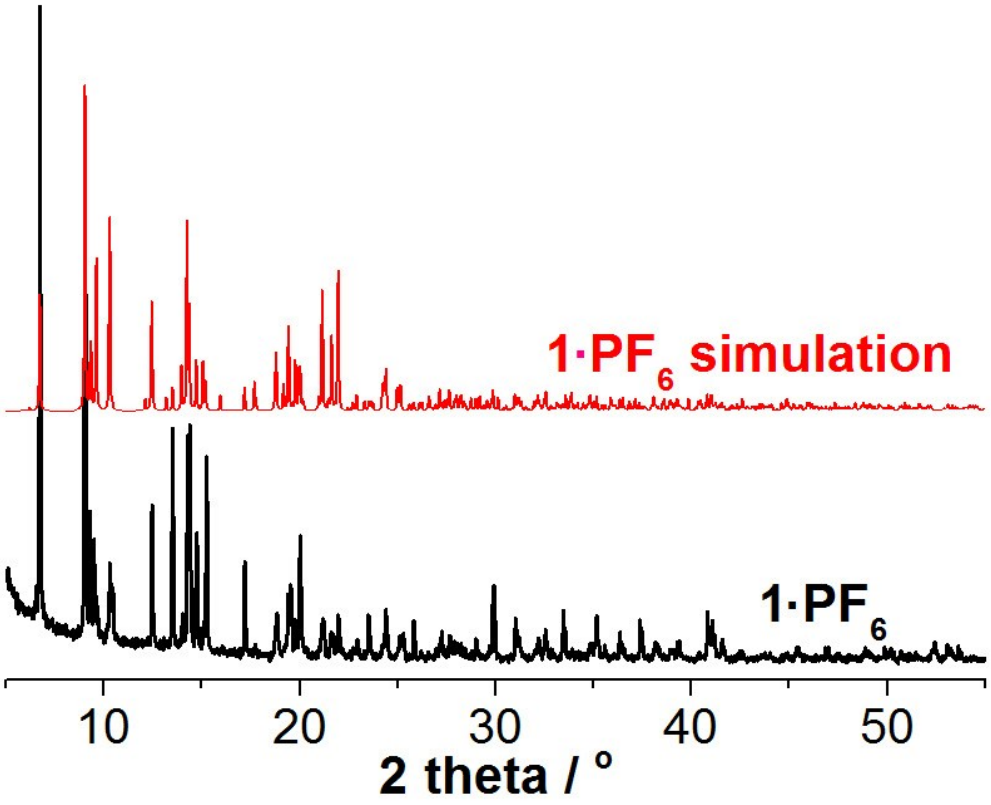


Fig. S10 Experimental and simulated XRD patterns of **1·PF$_6$**.

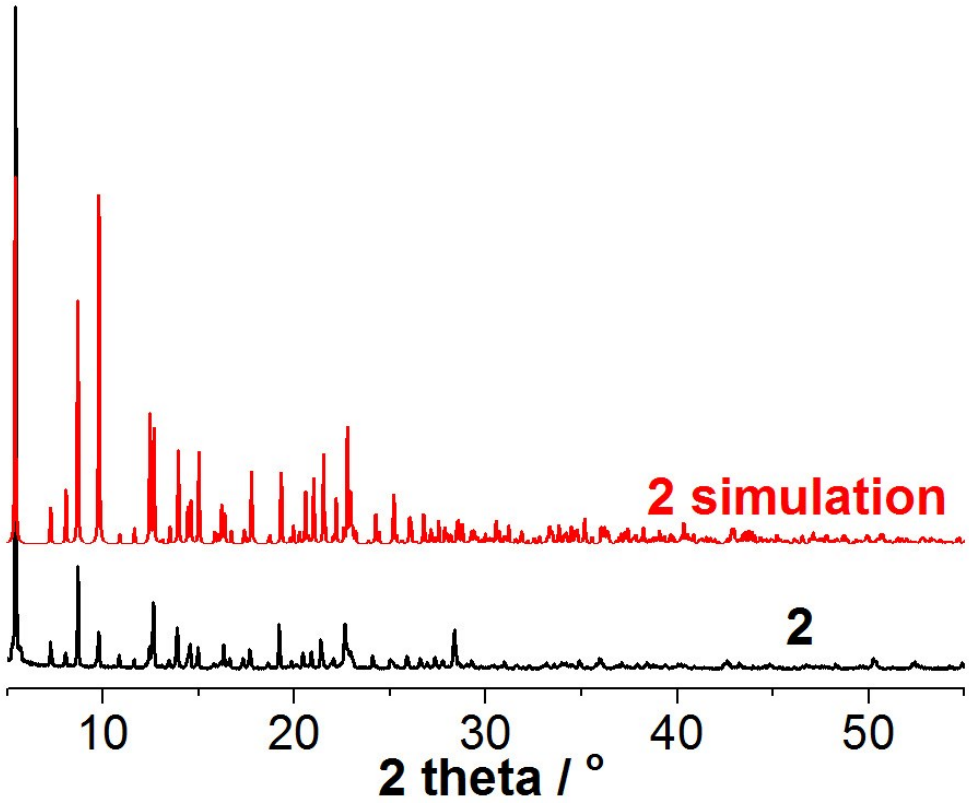


Fig. S11 Experimental and simulated XRD patterns of **2**.

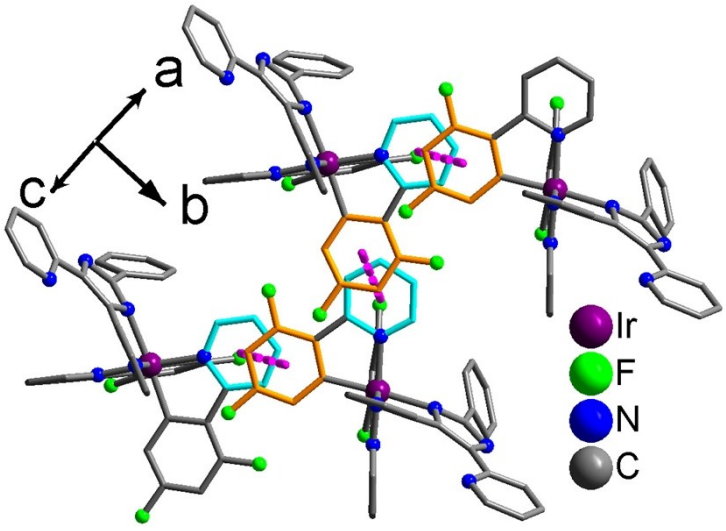


Fig. S12 Supramolecular chain structure in **2** with aromatic stacking interactions. All H atoms are omitted for clarity.

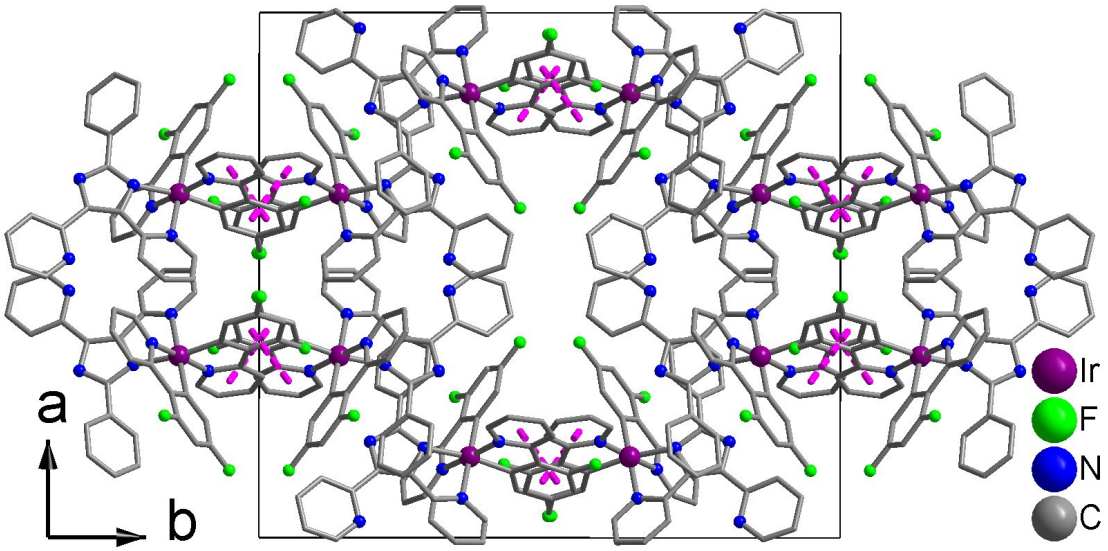


Fig. S13 Packing structure of **2**.

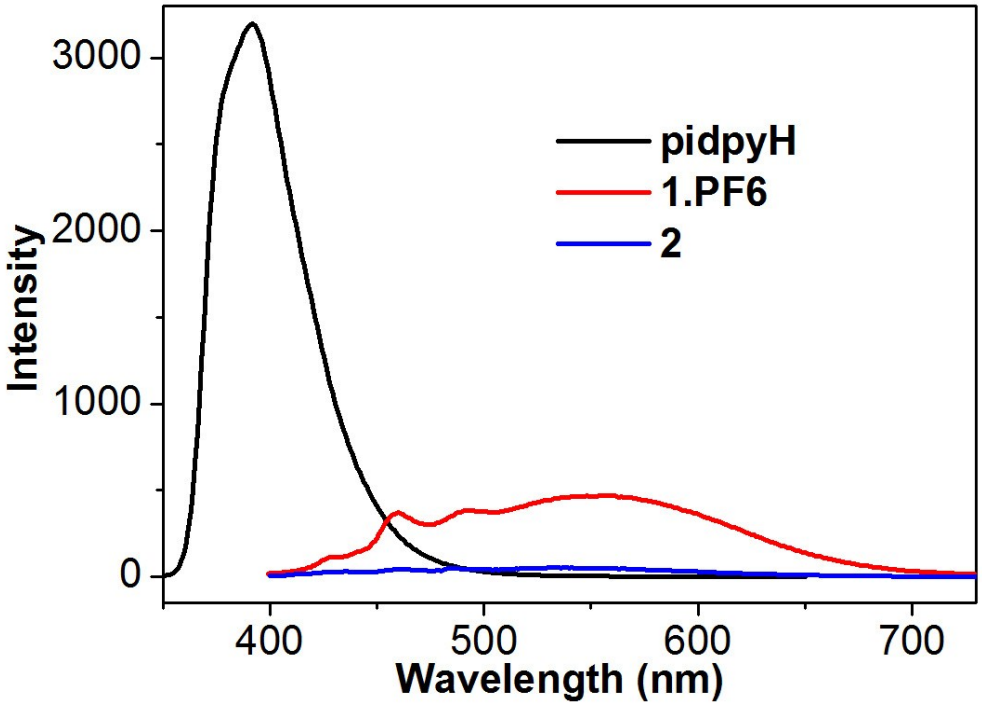


Fig. S14 Luminescence spectra of pidpyH, **1·PF$_6$** and **2** in CH_2Cl_2 (c = 1 × 10^{-4} M, λ_{ex} = 332 nm for pidpyH, and λ_{ex} = 377 nm for **1·PF$_6$** and **2**).

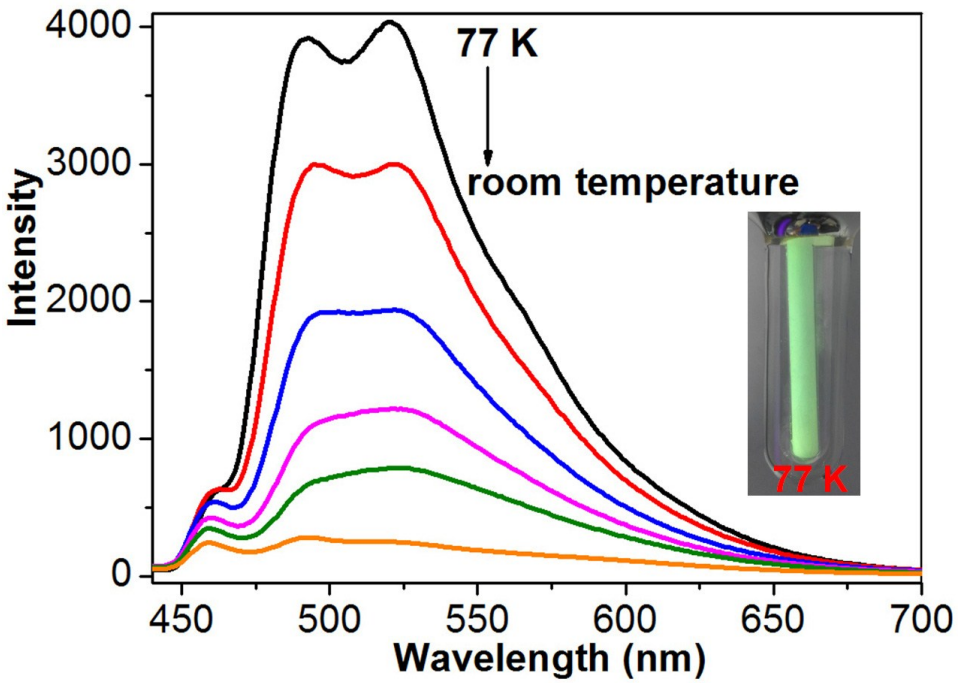


Fig. S15 Luminescence spectral changes of **1·PF$_6$** in CH_2Cl_2 upon increasing temperature from 77 K to room temperature (c = 1.0 × 10^{-4} M, λ_{ex} = 377 nm).

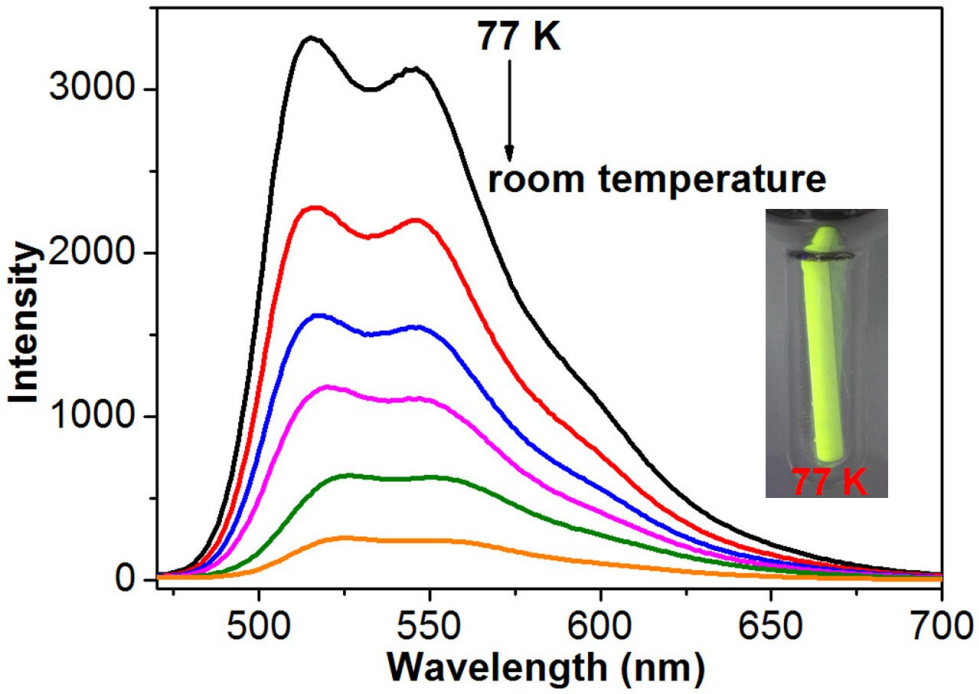


Fig. S16 Luminescence spectral changes of **2** in CH_2Cl_2 upon increasing temperature from 77 K to room temperature (c = 1.0 × 10^{-4} M, λ_{ex} = 377 nm).

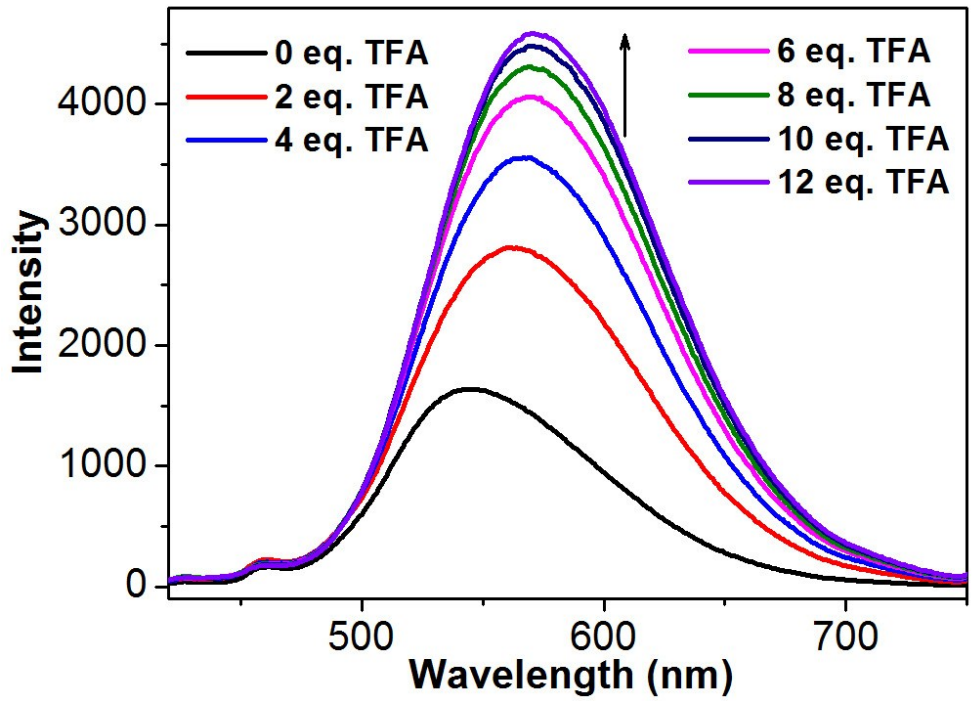


Fig. S17 Luminescence spectral changes of [Ir(dfppy)$_2$(pidpyH$_2$)]2Cl **(1H·2Cl)** in CH_2Cl_2 (c = 1 × 10^{-4} M, λ_{ex} = 377 nm) upon adding TFA.

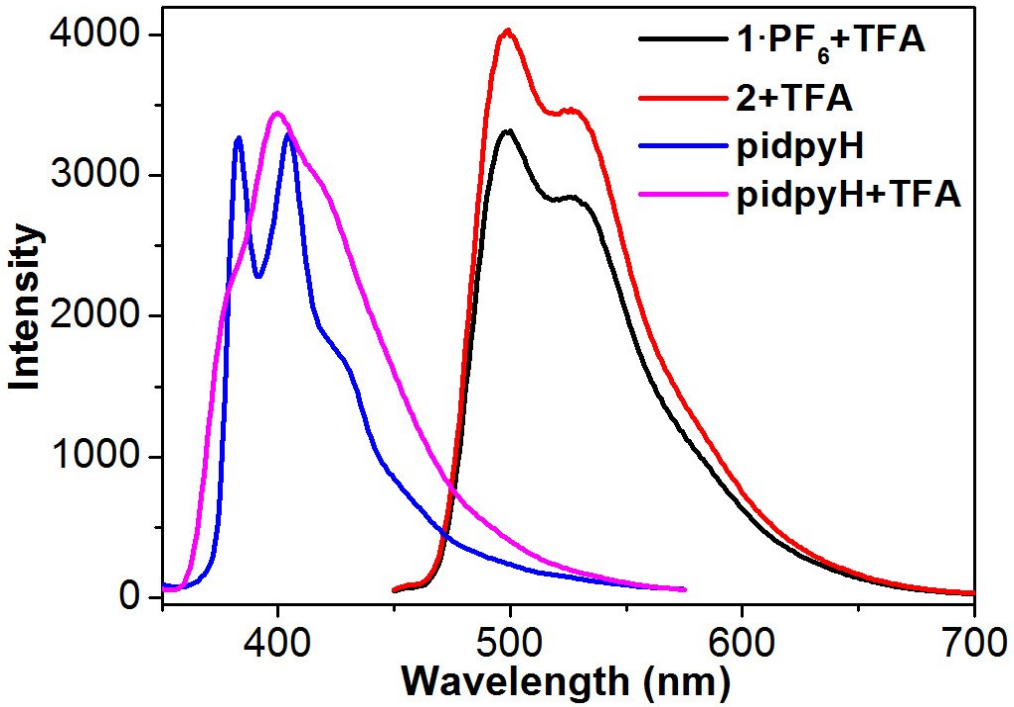


Fig. S18 Luminescence spectra of pidpyH, **1·PF$_6$** and **2** in CH_2Cl_2 at 77 K before and/or after adding TFA (6 eq., 11 eq. and 18 eq., respectively) (c = 1.0 × 10^{-4} M, λ_{ex} = 377 nm).

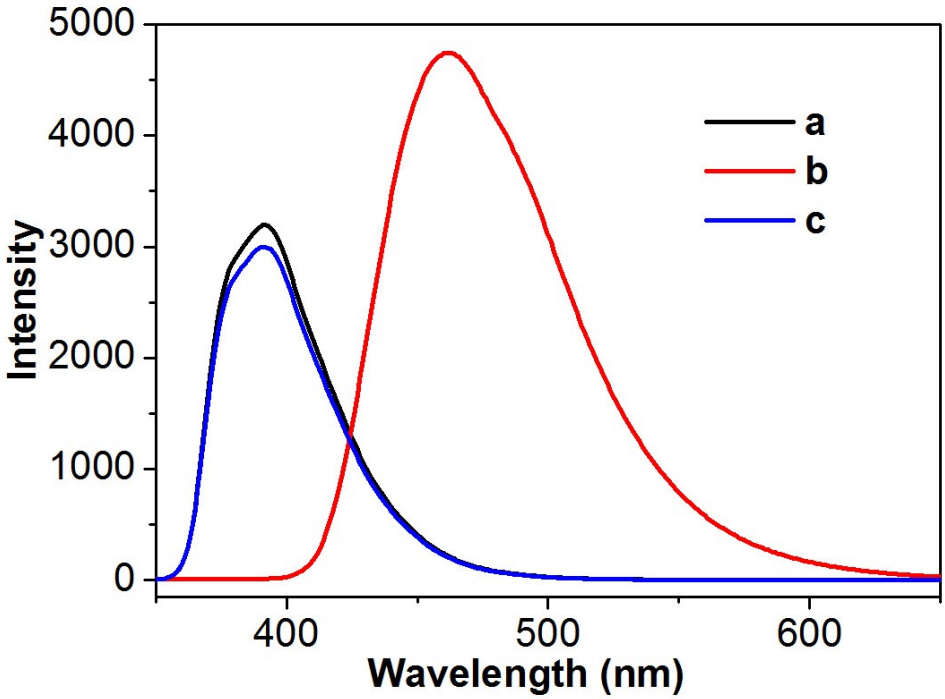


Fig. S19 Luminescence spectra of pidpyH (c = 1 × 10^{-4} M for pidpyH, λ_{ex} = 332 nm) in CH_2Cl_2 (plot a), in CH_2Cl_2 containing 6 eq. TFA (plot b), and in CH_2Cl_2 containing 6.5 eq. TFA and 7 eq. NEt_3 (plot c).

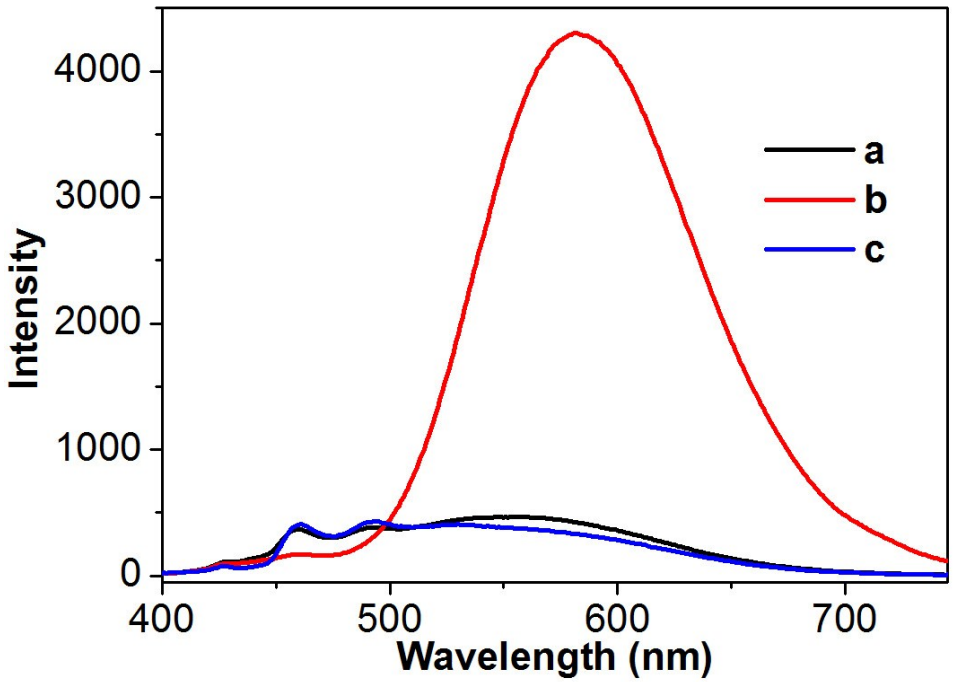


Fig. S20 Luminescence spectra of **1·PF$_6$** (c = 1 × 10^{-4} M, λ_{ex} = 377 nm) in CH_2Cl_2 (plot a), in CH_2Cl_2 containing 11 eq. TFA (plot b), and in CH_2Cl_2 containing 11 eq. TFA and 12 eq. NEt_3 (plot c).

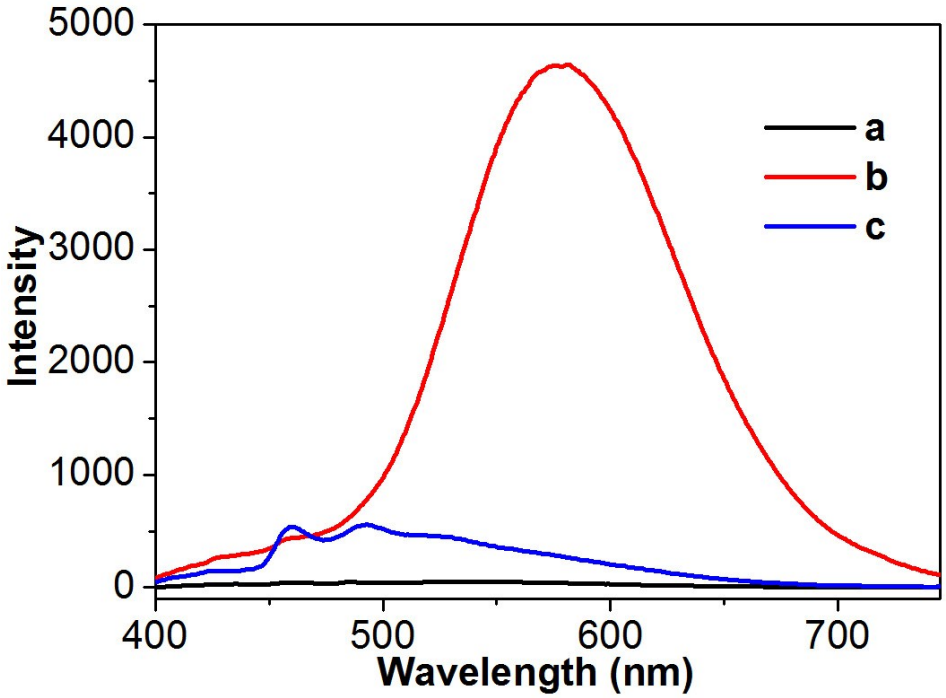


Fig. S21 Luminescence spectra of **2** ($c = 1 \times 10^{-4}$ M, $\lambda_{ex} = 377$ nm) in CH_2Cl_2 (plot a), in CH_2Cl_2 containing 18 eq. TFA (plot b), and in CH_2Cl_2 containing 18 eq. TFA and 19 eq. NEt_3 (plot c).

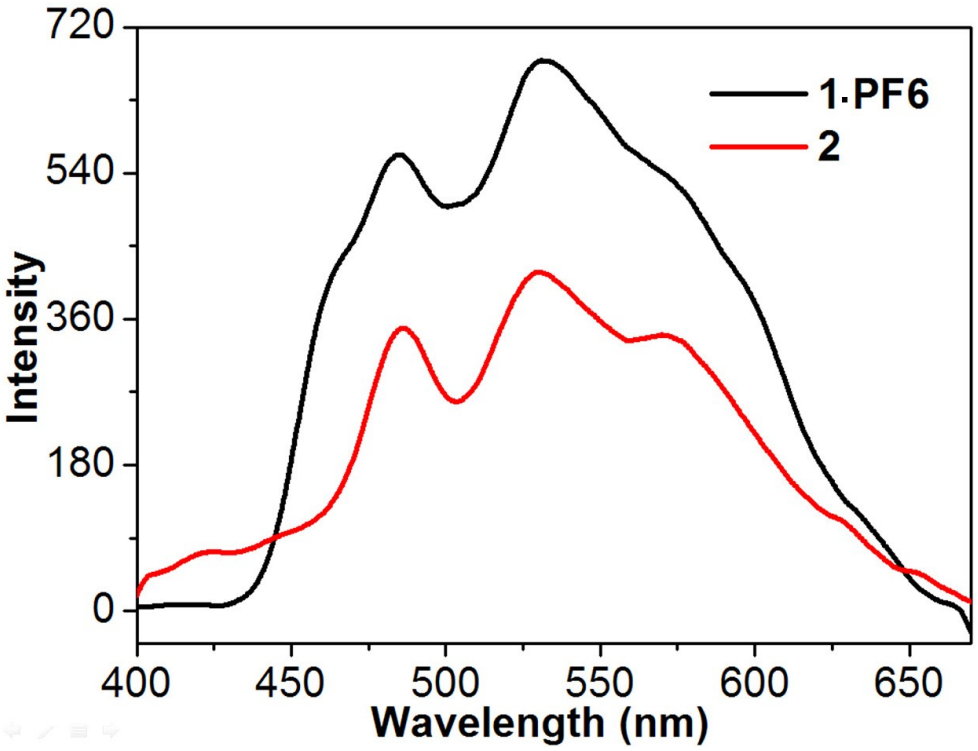


Fig. S22 Solid-state emission spectra of **1·PF$_6$** and **2** at room temperature ($\lambda_{ex} = 375$ nm).