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 °C) for one day. This mixture was extracted by benzene (30 mL), and then organic phase was evaporated under vacuum. 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). ^1H NMR (300 MHz, CDCl₃), 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 CH₂Cl₂ (15 mL) and CH₃OH (12 mL) was heated in an oil bath (50 °C) under argon for one day. After evaporation under vacuum, the resultant residue was purified through silica column chromatography using CH₃OH-CH₂Cl₂ (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$_{27}$N$_6$F$_4$ClIr: 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$_3$), $\delta$ (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$_6$F$_4$Cl$_2$: 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$_3$), $\delta$ (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](image1)

**Scheme S1**

![Scheme S2](image2)

**Scheme S2**

![Scheme S3](image3)

**Scheme S3**
Scheme S4

Scheme S5

N, N-chelating mode  N, N’-chelating mode
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\(\cdot\)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-PF$_6$ (400 MHz, CDCl$_3$) after adding a D$_2$O 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·PF₆ and 2 in CH₂Cl₂ (c = 1 × 10⁻⁴ M, λₑₓ = 332 nm for pidpyH, and λₑₓ = 377 nm for 1·PF₆ and 2).
Fig. S15 Luminescence spectral changes of 1-PF$_6$ in CH$_2$Cl$_2$ upon increasing temperature from 77 K to room temperature ($c = 1.0 \times 10^{-4}$ M, $\lambda_{ex} = 377$ nm).

Fig. S16 Luminescence spectral changes of 2 in CH$_2$Cl$_2$ upon increasing temperature from 77 K to room temperature ($c = 1.0 \times 10^{-4}$ M, $\lambda_{ex} = 377$ nm).
Fig. S17 Luminescence spectral changes of [Ir(dfppy)$_2$(pidpy)$_2$]Cl$_2$ (1H-2Cl) in CH$_2$Cl$_2$ ($c = 1 \times 10^{-4}$ M, $\lambda_{ex} = 377$ nm) upon adding TFA.

Fig. S18 Luminescence spectra of pidpyH, 1-PF$_6$ and 2 in CH$_2$Cl$_2$ at 77 K before and/or after adding TFA (6 eq., 11 eq. and 18 eq., respectively) ($c = 1.0 \times 10^{-4}$ M, $\lambda_{ex} = 377$ nm).
Fig. S19 Luminescence spectra of pidpyH ($c = 1 \times 10^{-4}$ M for pidpyH, $\lambda_{ex} = 332$ nm) in CH$_2$Cl$_2$ (plot a), in CH$_2$Cl$_2$ containing 6 eq. TFA (plot b), and in CH$_2$Cl$_2$ containing 6.5 eq. TFA and 7 eq. NEt$_3$ (plot c).

Fig. S20 Luminescence spectra of 1∙PF$_6$ ($c = 1 \times 10^{-4}$ M, $\lambda_{ex} = 377$ nm) in CH$_2$Cl$_2$ (plot a), in CH$_2$Cl$_2$ containing 11 eq. TFA (plot b), and in CH$_2$Cl$_2$ 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$_2$Cl$_2$ (plot a), in CH$_2$Cl$_2$ containing 18 eq. TFA (plot b), and in CH$_2$Cl$_2$ containing 18 eq. TFA and 19 eq. NEt$_3$ (plot c).

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