Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Effects of Tuning the Applied Voltage Pulse Periods on the Electroluminescence Spectra of Host-Guest White Light-Emitting Electrochemical Cells

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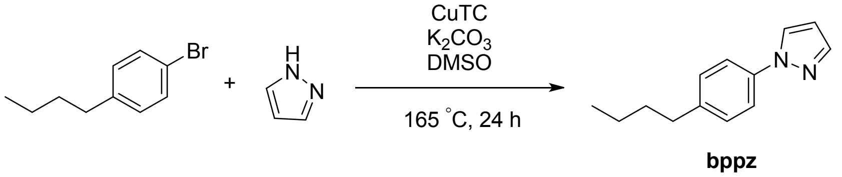
Experimental Section

General Experiments. ^1H and ^{13}C NMR spectra of compounds were collected on a Bruker Ascend 400 MHz spectrometer at room temperature. Photophysical characteristics of complexes in solutions were collected at room temperature using 10^{-5} M acetonitrile (MeCN) solutions of all complexes on spectrofluorometer Edinburgh FS5, which were carefully purged with nitrogen prior to measurements. UV-visible absorption spectra were recorded on Perkin Elmer Lambda 14 spectrophotometer. Oxidation and reduction potentials of all complexes were determined by cyclic voltammetry (CV) at a scan rate of 100 mV/s in MeCN solutions (1.0 mM) on ZIVE SP1. A glassy carbon electrode and a platinum wire were used as the working electrode and the counter electrode, respectively. All potentials were recorded versus the Ag/AgCl (sat'd) reference electrode. For oxidation and reduction CV, 0.1 M tetra-*n*-butylammonium hexafluorophosphate ($TBAPF_6$) in MeCN was used as the supporting electrolyte.

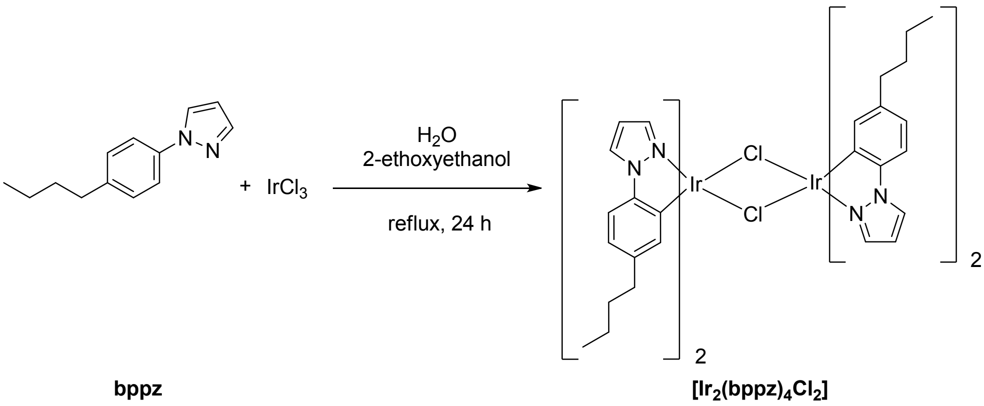
General Procedures for Synthesis. The cyclometalated dimer **[$Ir_2(dfppz)_4Cl_2$]** was prepared according to literature procedures.[1] All experiments involving $IrCl_3 \cdot H_2O$ or any other Ir(III) species were carried out in an inert atmosphere. Cyclometalated Ir(III) dichlorobridged dimers with the general formula $(C^\wedge N)_2Ir(\mu\text{-}Cl)_2Ir(C^\wedge N)_2$ (where C^N represents a cyclometalating ligand) were synthesized following the literature procedure. The series of $(C^\wedge N)_2Ir(N^\wedge N)^+PF_6^-$ complexes were used following the literature procedure.[2]

Synthesis of 1-(4-butylphenyl)-1*H*-pyrazole (bppz). Copper(I) thiophene-2-carboxylate (CuTC) (90 mg, 0.3 mmol), K_2CO_3 (1.30 g, 9.38 mmol), pyrazole (0.64 g, 9.4 mmol), and 1-bromo-4-butylbenzene (1.00 g, 4.69 mmol) under nitrogen atmosphere were placed sequentially in a round-bottom flask, followed by the addition of DMSO (23.45 mL), under nitrogen atmosphere. The reaction flask was then purged with nitrogen, and the reactants were stirred at 135 °C. After completion, the reaction mixture was diluted with water, the product was extracted with ethyl acetate, and the resultant organic layer was dried over anhydrous Na_2SO_4. After removal of the solvent, the crude product was purified by column chromatography on silica gel (hexane/ethyl acetate = 9/1) to give compound **bppz** (0.38 g, 40%) as a clear oil liquid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.88 (s, 1H), 7.70 (s, 1H), 7.58 (d, J = 7.3 Hz, 2H), 7.25 (d, J = 7.3 Hz, 2H), 6.44 (s, 1H), 2.64 (t, J = 7.1 Hz, 2H), 1.61 (d, J = 9.0 Hz, 2H), 1.37 (dd, J = 14.3, 7.1 Hz, 2H), 0.94 (t, J = 6.7 Hz, 3H).



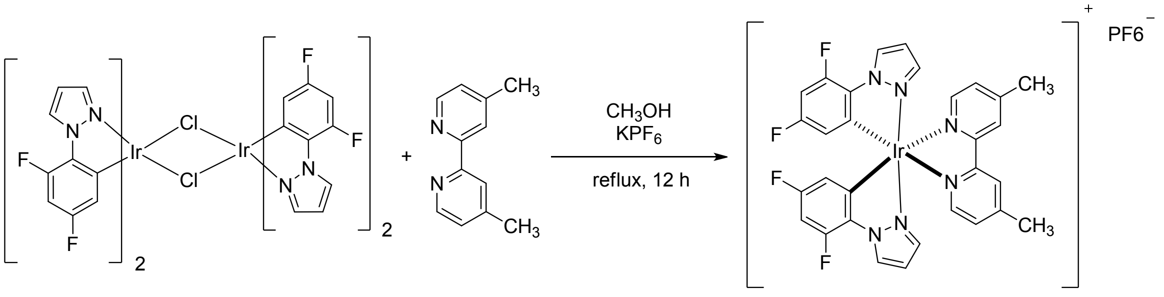
Scheme S1

Synthesis of [$Ir_2(bppz)_4Cl_2$]. bppz (0.36 g, 1.8 mmol) was dissolved in 2-ethoxyethanol (30 mL) in a round-bottom flask. Iridium(III) chloride hydrate (0.27 g, 0.90 mmol) and 9.0 mL of water were then added to the flask. The mixture was stirred under nitrogen at 100 °C for 24 h and then cooled to room temperature. The precipitate was collected, washed with water and dried under vacuum to give cyclometalated dimer **[Ir$_2$(bppz)$_4$Cl$_2$]** (0.18 g, 32%) as a gray solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, J = 2.1 Hz, 4H), 7.84 (s, 4H), 6.99 (d, J = 8.0 Hz, 4H), 6.62 (s, 4H), 6.56 (d, J = 8.0 Hz, 4H), 5.78 (s, 4H), 2.27 – 2.18 (m, 8H), 1.34 – 1.21 (m, 8H), 1.13 (dd, J = 14.7, 7.4 Hz, 8H), 0.76 (t, J = 7.2 Hz, 12H).



Scheme S2

Synthesis of Complex 1. In a round-bottomed flask, **[Ir$_2$(dfppz)$_4$Cl$_2$]** (0.15 g, 0.13 mmol) and 4,4'-dimethyl-2,2'-bipyridine (50 mg, 0.3 mmol) were mixed together in 38.24 mL of methanol. The solution was then refluxed overnight under an inert atmosphere. After cooling to room temperature, counter ion exchange from Cl$^-$ to PF$_6^-$ was accomplished via a metathesis reaction in which complexes were precipitated from the methanol solution with an excess of NH$_4$PF$_6$, washed with water and methanol, and dried under vacuum. The crude product was purified by column chromatography on silica gel (dichloromethane/acetone = 95/5) to give complex **1** (0.19 g, 83%) as a green solid. ^{1}H NMR (400 MHz, CDCl$_3$) δ 8.39 (s, 2H), 8.33 (d, J = 2.8 Hz, 2H), 7.94 (d, J = 5.8 Hz, 2H), 7.45 (d, J = 5.8 Hz, 2H), 7.01 (d, J = 2.4 Hz, 2H), 6.66 (s, 2H), 6.59 (t, J = 2.6 Hz, 2H), 5.72 (d, J = 5.4 Hz, 2H), 1.45 (s, 18H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 160.8, 158.3, 155.5, 152.2, 150.4, 149.4, 147.3, 139.2, 137.7, 132.4, 129.1, 127.0, 125.4, 114.5, 109.6, 100.8, 100.4, 99.5, 98.9, 98.7, 21.0. MS (*m/z*, ESI) $[M]^+$ calcd for $C_{30}H_{22}F_4IrN_6$: 735.15, found 735.15. Anal. calcd for $C_{30}H_{22}F_{10}IrN_6P$: C, 40.96; H, 2.52; N, 9.55, found C, 40.75; H, 2.42; N, 9.52.

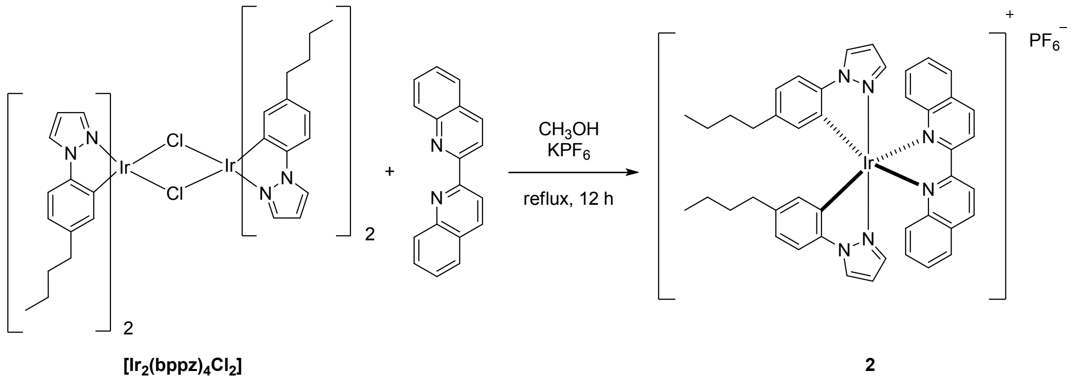


[Ir$_2$(dfppz)$_4$Cl$_2$]

1

Scheme S3

Synthesis of Complex 2. Following the procedure for compound **1**, **[Ir$_2$(bppz)$_4$Cl$_2$]** (0.24 g, 0.19 mmol), 2,2'-biquinoline (0.10 mg, 0.38 mmol), and 55.88 mL of methanol gave complex **2** (0.24 g, 63%) as a red solid. ^1H NMR (400 MHz, $CDCl_3$) δ 8.90 (d, J = 8.3 Hz, 2H), 8.74 (d, J = 8.7 Hz, 2H), 8.03 (d, J = 9.7 Hz, 4H), 7.94 (d, J = 8.3 Hz, 2H), 7.53 (t, J = 7.3 Hz, 2H), 7.24 – 7.17 (m, 2H), 7.11 (d, J = 8.3 Hz, 2H), 6.75 (d, J = 8.0 Hz, 4H), 6.52 (s, 2H), 5.77 (s, 2H), 2.32 (dd, J = 12.7, 6.5 Hz, 4H), 1.33 (dd, J = 14.8, 7.4 Hz, 4H), 1.06 (dt, J = 14.1, 7.0 Hz, 4H), 0.79 (t, J = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.7, 147.9, 141.3, 139.9, 139.5, 132.4, 131.3, 130.9, 129.3, 128.9, 128.5, 127.7, 122.9, 121.7, 111.9, 108.6, 34.4, 33.0, 20.9, 13.7. MS (*m/z*, ESI) $[M]^+$ calcd for $C_{44}H_{42}IrN_6$: 847.31, found 847.31. Anal. calcd for $C_{44}H_{42}F_6IrN_6P$: C, 53.27; H, 4.27; N, 8.47, found C, 53.31; H, 4.48; N, 8.29.



Scheme S4

Table S1. Summary of physical properties of complexes **1** and **2**

Compound	Absorption λ_{max} (nm)[ab]	Emission λ_{max} (nm)[ab]	$E^{ox}_{1/2}$ (V)[cd]	HOMO (eV)	LUMO (eV)	Φ_{PL} (%)[g]
1	282, 310	504	+1.66	-6.02	-3.14[e]	65
2	368, 487	624	+1.47	-5.83	-3.65[f]	59

[a] At room temperature. [b] Measured in MeCN (10^{-5} M).

[c] Potential vs ferrocene/ferrocenium redox couple. [d] $TBAPF_6$ (0.1 M) in MeCN.

[e] The potential was derived from the onset of emission wavelength at 430 nm.

[f] The potential was derived from the onset of emission wavelength at 570 nm.

[g] Measured in 10^{-5} M CH_2Cl_2 solution relative to L-Tyrosine (Φ_{PL} = 14%) with 275 nm excitation.

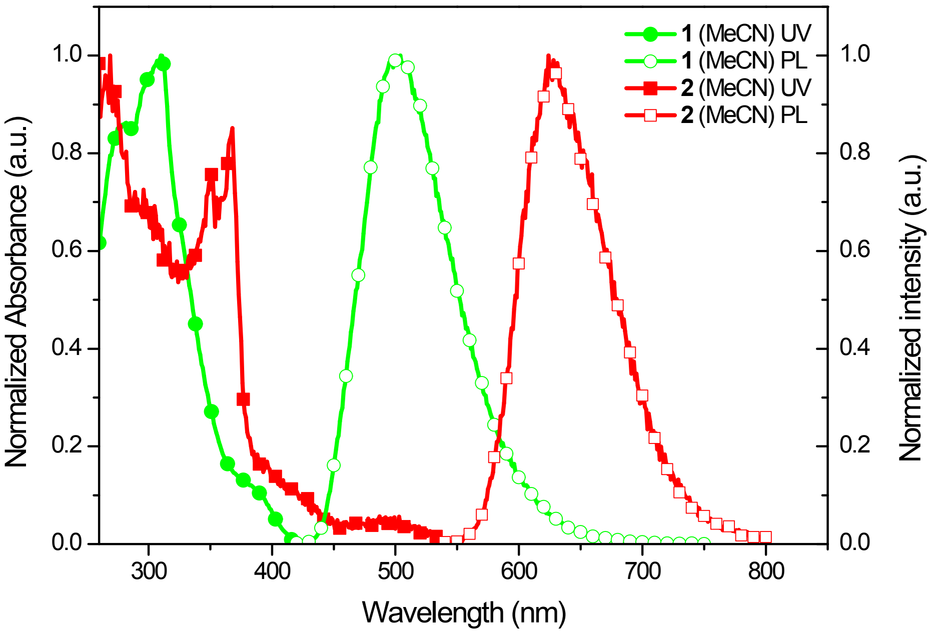


Figure S1. Absorption (left axis) and PL spectra (right axis) of complexes **1** and **2** in MeCN solutions (10^{-5} M)

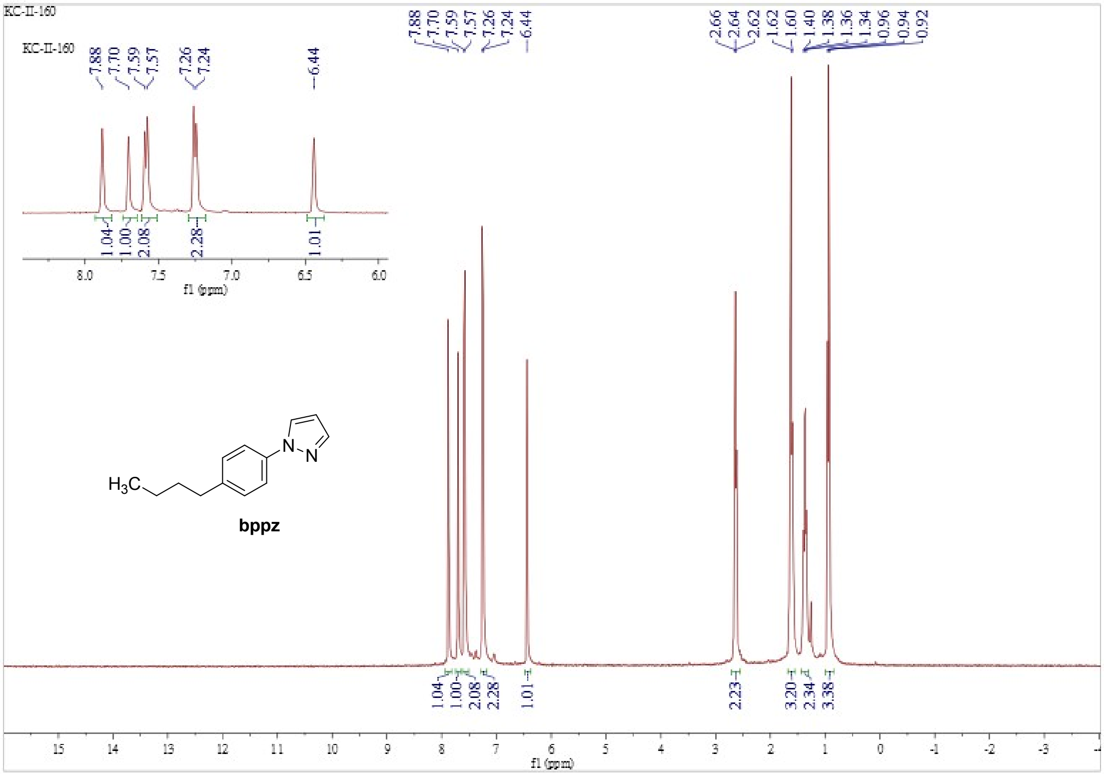


Figure S2. The ^{1}H NMR spectrum for **bppz**

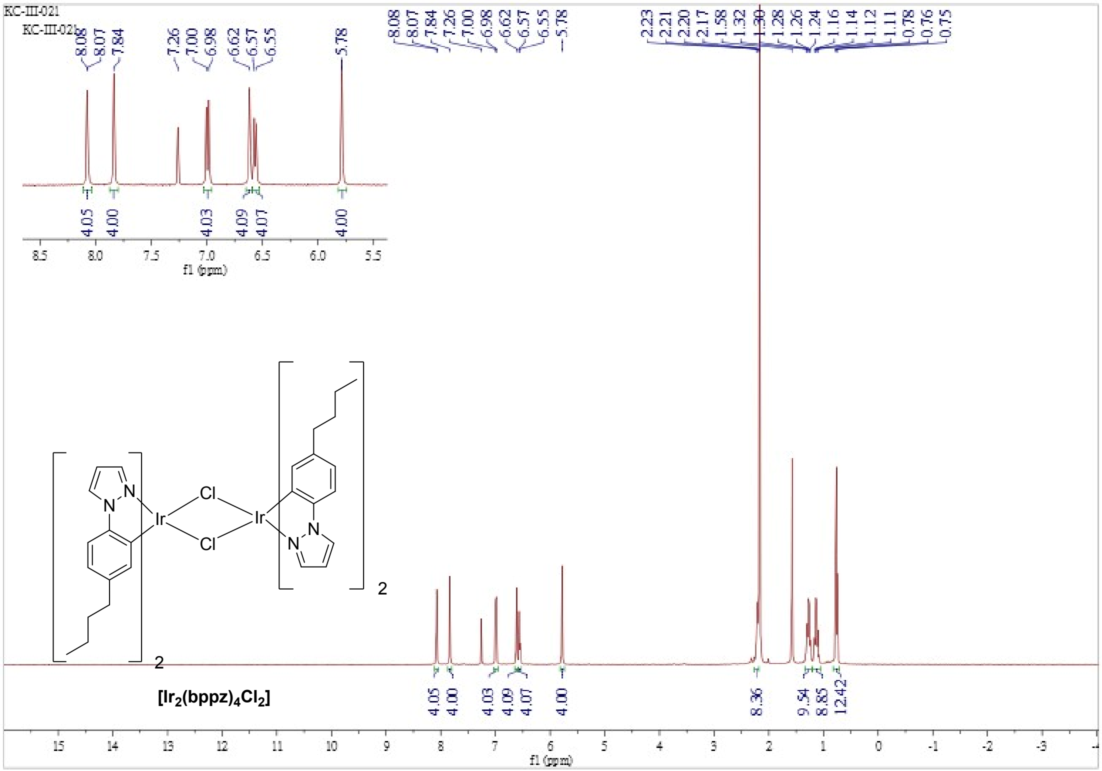


Figure S3. The ^{1}H NMR spectrum for **[Ir$_2$(bppz)$_4$Cl$_2$]**

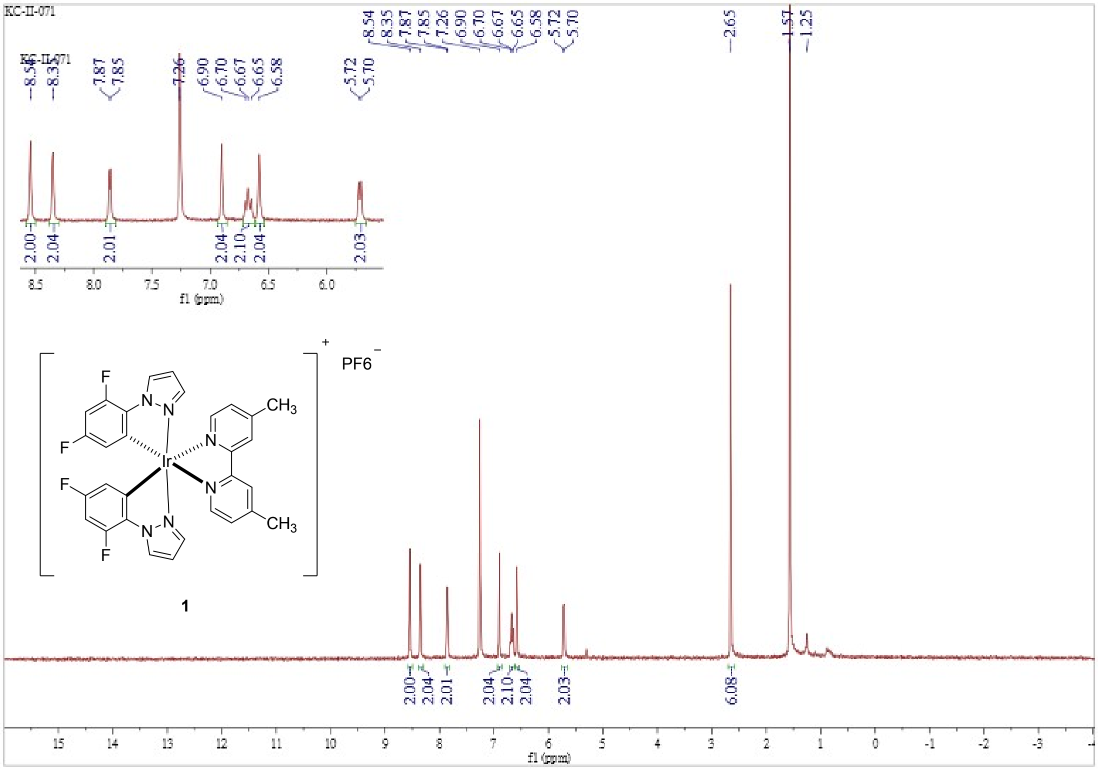


Figure S4. The ^{1}H NMR spectrum for complex **1**

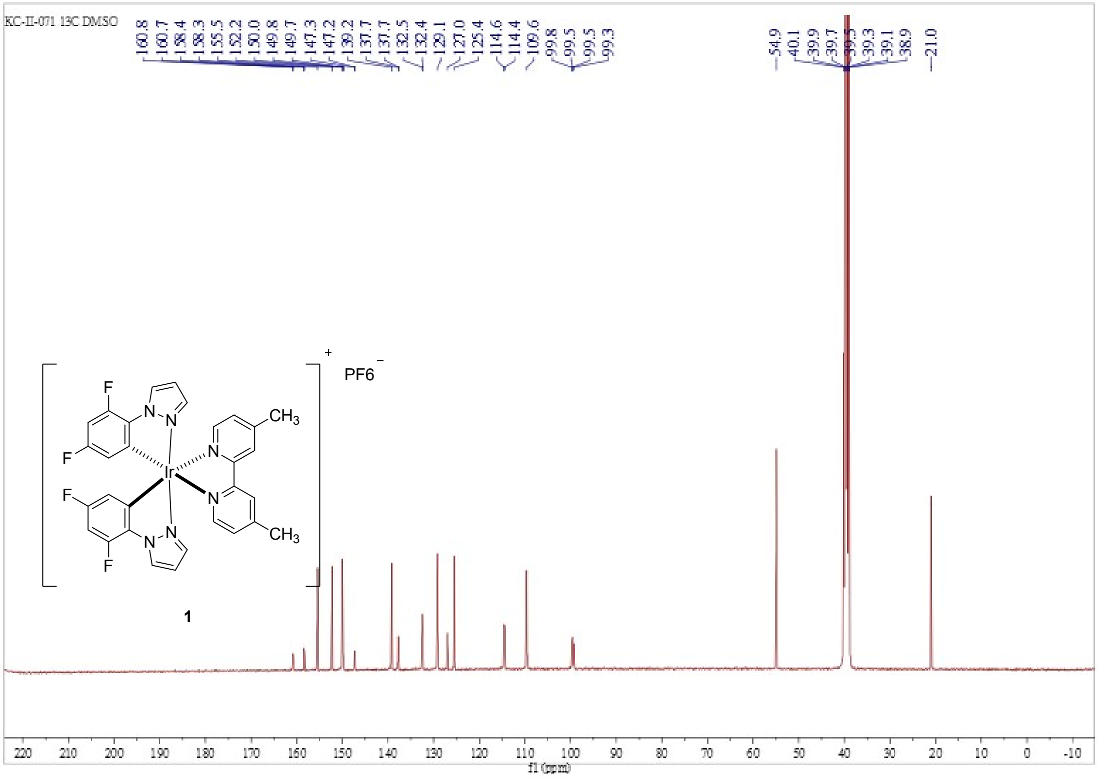


Figure S5. The ^{13}C NMR spectrum for complex **1**

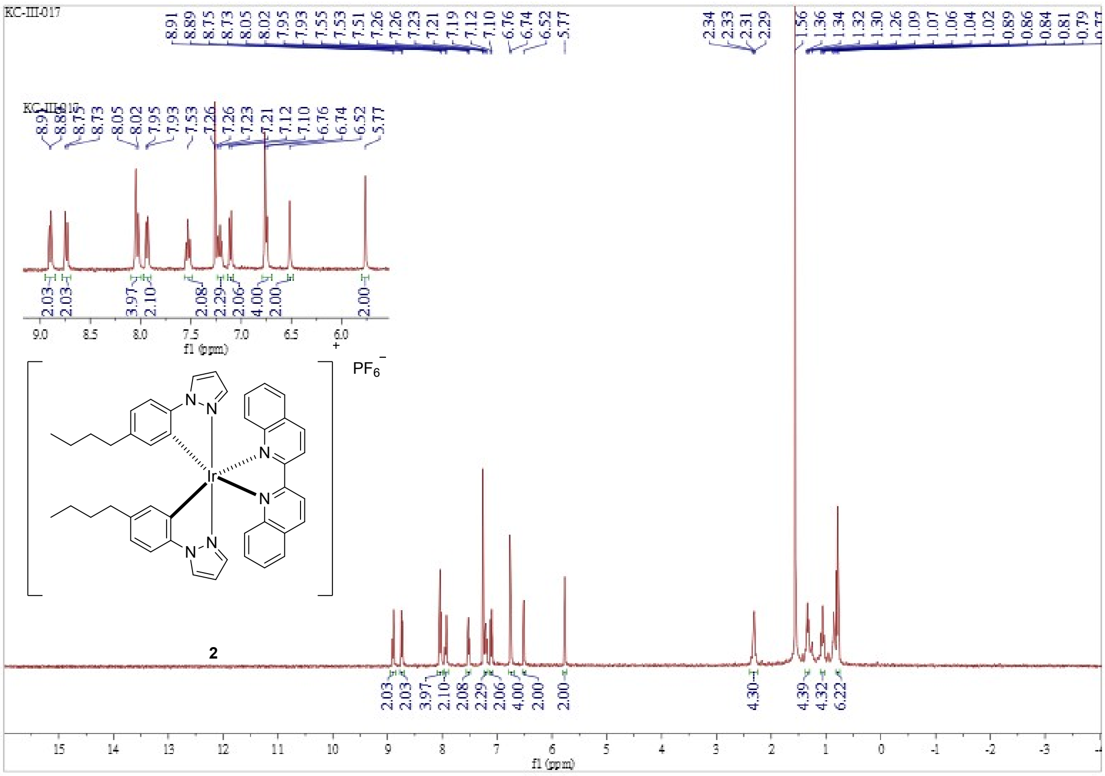


Figure S6. The ^{1}H NMR spectrum for complex **2**

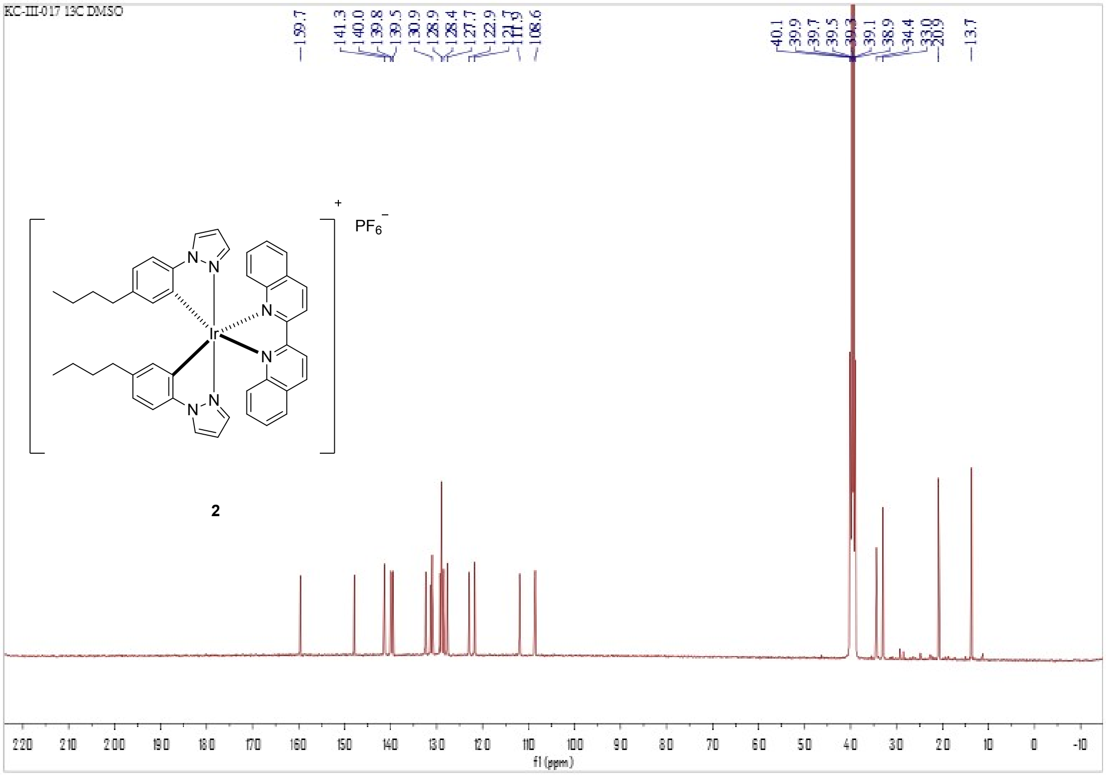


Figure S7. The ^{13}C NMR spectrum for complex **2**

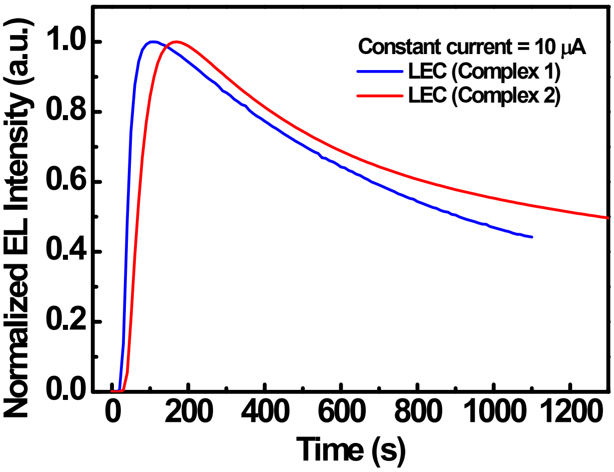


Figure S8 Time-dependent normalized EL intensity of LECs based on complexes **1** and **2** under constant current of 10 μA.

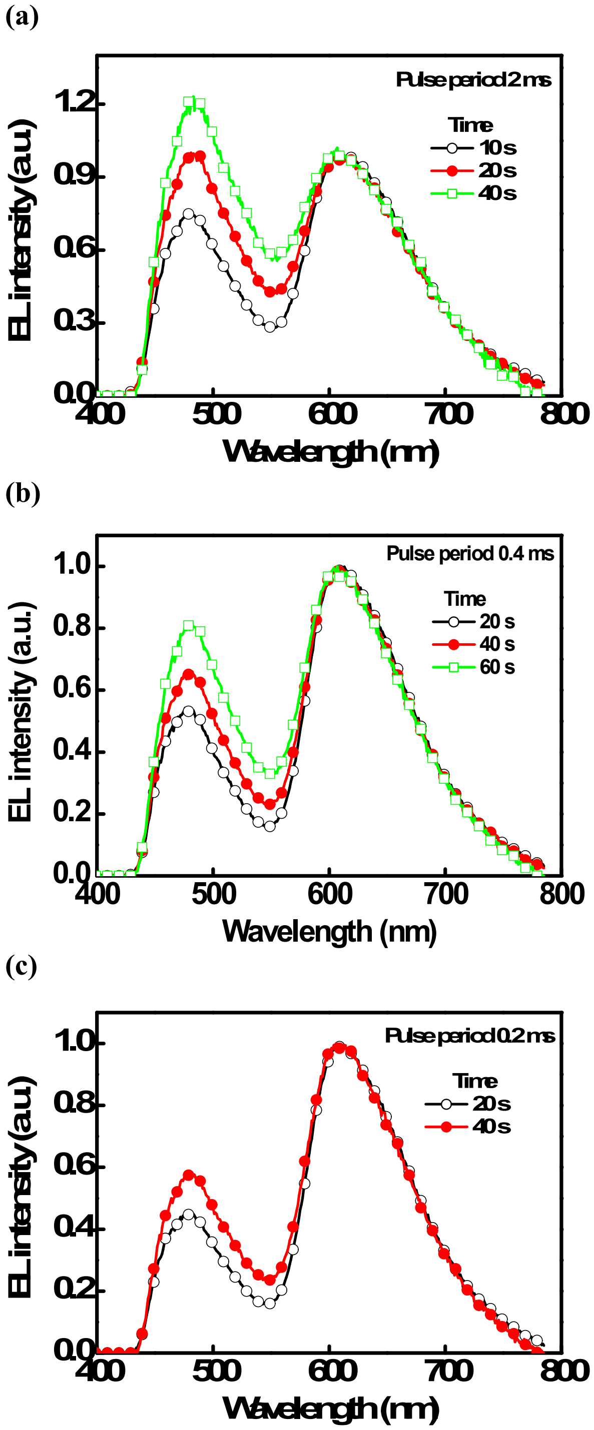


Figure S9. Temporal evolution in EL spectrum of host-guest white LECs driven by pulsed voltages with periods of (a) 2, (b) 0.4 and (c) 0.2 ms.

Reference

(1) Ma, D.-L.; He, H.-Z.; Chan, D. S.-H.; Wong, C.-Y.; Leung, C.-H. *PLoS One* **2014**, *9*.

(2) Tamayo, A. B.; Garon, S.; Sajoto, T.; Djurovich, P. I.; Tsyba, I. M.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2005**, *44*, 8723