Supporting Information

Phosphorescence switch and logic gate of iridium(III) complexes containing triarylboron moiety triggered by fluoride and electric field

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Experimental section

Materials. Unless otherwise stated, all starting materials and reagents were purchased from commercial suppliers and were used without further purification. CH_3CN was dried under reflux over CaH_2 for several hours at 70-75 ^oC, distilled at these conditions and used freshly.

Measurements. NMR spectra were recorded on a Bruker Ultra Shield Plus 400 MHz NMR instrument. Mass spectra were obtained on a Bruker autoflex matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF/TOF) mass spectrometer. The UV-visible absorption spectra were recorded on a Shimadzu UV-3600 UV-VIS-NIR spectrophotometer. Photo-luminescence spectra were recorded on an Edinburgh FL920 spectrofluorometer system.

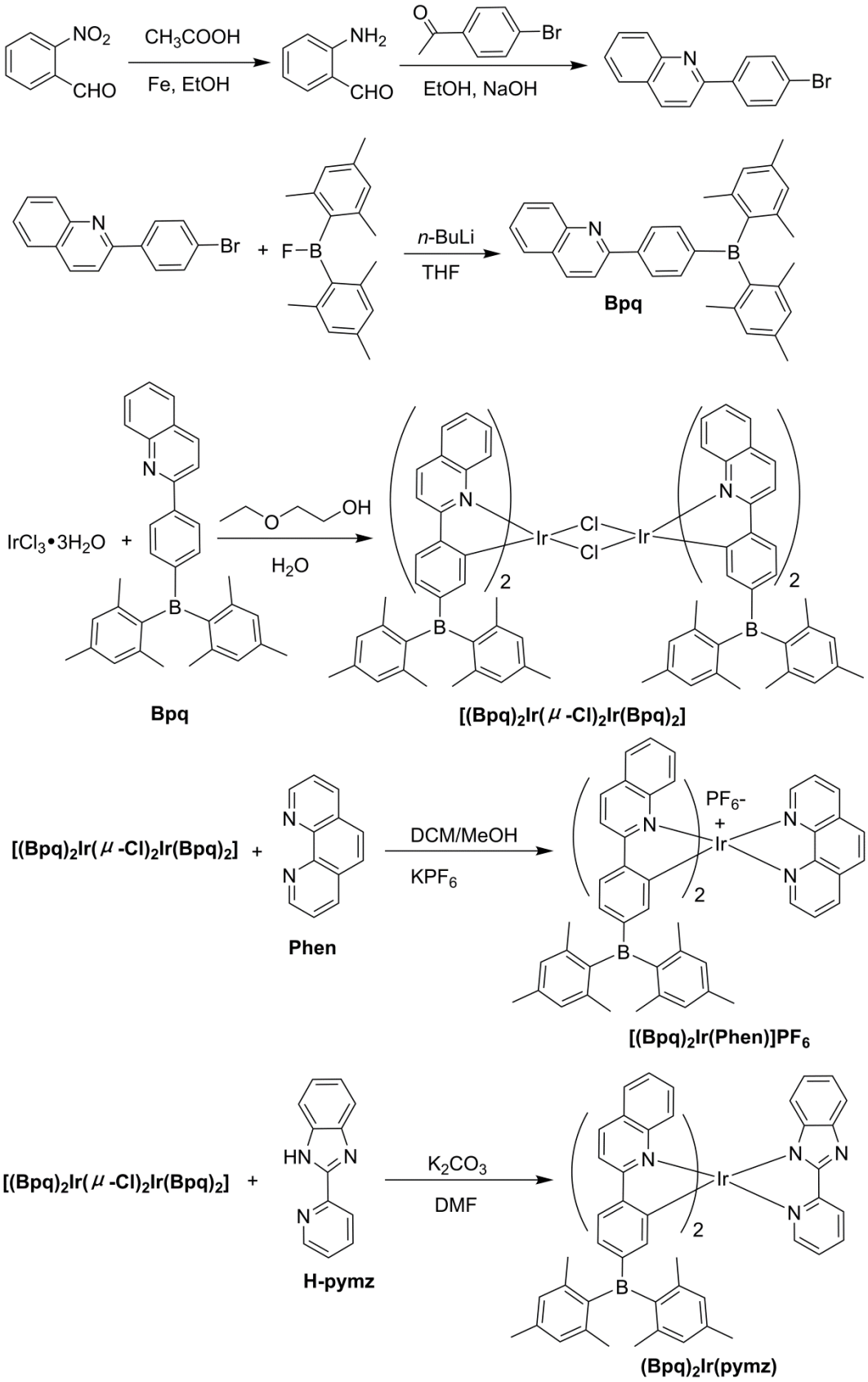
Synthesis.

2-[4-(Dimesitylboryl)phenyl]quinoline (Bpq): This compound was synthesized by using a reported procedure.[1]

$[(Bpq)_2Ir(Phen)]PF_6$: $[(Bpq)_2Ir(Phen)]PF_6$ was synthesized through a standard two-step procedure according a reported method.[2] A mixture of $IrCl_3•3H_2O$ (0.56 mmol) and Bpq (1.12 mmol) in 2-ethoxyethanol/water (8 mL, 3:1 v/v) was heated to reflux under nitrogen atmosphere for 24 h. Next, upon cooling to room temperature, the mixture was added large amounts of water and filtered. Then the residue was dried to give the crude cyclometalated Ir(III) chloro-bridged dimer ($[(Bpq)_2Ir(\mu\text{-}Cl)_2 Ir(Bpq)_2]$). Then a mixture of $[(Bpq)_2Ir(\mu\text{-}Cl)_2Ir(Bpq)_2]$ (0.06 mmol) and ligand 1,10-phenanthroline (Phen) (0.12 mmol) in CH_2Cl_2/MeOH (12 mL, 2:1 v/v) was refluxed under N_2 for 12 h. The solution was then cooled to room temperature and solid KPF_6 (0.60 mmol) was added. The mixture was stirred for 4 h, filtered to remove any insoluble inorganic salts, and evaporated to dryness under reduced pressure. The crude product was purified with column chromatography on silica gel with CH_2Cl_2/acetone (20:1) as the eluent to afford an orange solid in 64% yield. ^1H NMR (400 MHz, $CDCl_3$-d_3) δ ppm 8.53 (dd, J = 8.3, 1.2 Hz, 2H), 8.49 (dd, J = 5.0, 1.2 Hz, 2H), 7.96 (dd, J = 18.5, 8.8 Hz, 4H), 7.91 (s, 2H), 7.89 (d, J = 8.0 Hz, 2H), 7.84 (dd, J

= 8.2, 5.1 Hz, 2H), 7.48 (d, *J* = 7.1 Hz, 2H), 7.29 (dd, *J* = 7.9, 0.8 Hz, 2H), 7.17 (t, *J* = 7.5 Hz, 2H), 6.93 (d, *J* = 8.9 Hz, 2H), 6.68 (ddd, *J* = 8.6, 6.9, 1.3 Hz, 2H), 6.48 (s, 8H), 6.35 (s, 2H), 2.23 (s, 12H), 1.64 (s, 24H). MS (MALDI-TOF): [M-PF_6] m/e: calcd.: 1277.54; found: 1277.61.

$(Bpq)_2Ir(pymz)$: A mixture of [$(Bpq)_2Ir(\mu\text{-}Cl)_2Ir(Bpq)_2$] (0.06 mmol), ligand 2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole (H-pymz) (0.12 mmol) and potassium carbonate (K_2CO_3) (0.24 mmol) in DMF (6 mL) was refluxed under N_2 for 24 h. Next, upon cooling to room temperature, the mixture was added large amounts of water (50 mL) and filtered. The residue was washed with water and extracted with DCM. Then the combined organic phase was dried with anhydrous $MgSO_4$, filtrated and removed in vacuo. The crude product was purified with column chromatography on silica gel to afford an orange solid in 33% yield. ^{1}H NMR (400 MHz, $CDCl_3$-d_3) δ ppm 8.22 (dd, *J* = 8.8, 9.6 Hz, 2H), 8.15-8.04(m, 4H), 8.02(d, *J* = 8.0 Hz, 1H), 7.96-7.86(m, 2H), 7.76-7.65(m, 3H), 7.47-7.31(m, 3H), 7.22(t, *J* = 8.4 Hz, 2H), 7.03(t, *J* = 8.8 Hz, 2H), 6.98-6.85(m, 2H), 6.71-6.62(m, 1H), 6.50-6.39(m, 9H), 6.33(dd, *J* = 8.0, 8.0 Hz, 3H), 2.2(s, 12H), 1.59(s, 24H). MS (MALDI-TOF): [M-PF_6] m/e: calcd.: 1291.54; found: 1291.98.



Scheme S1. Synthesis of ligand Bpq and complexes $[(Bpq)_2Ir(Phen)]PF_6$ and $(Bpq)_2Ir(pymz)$.

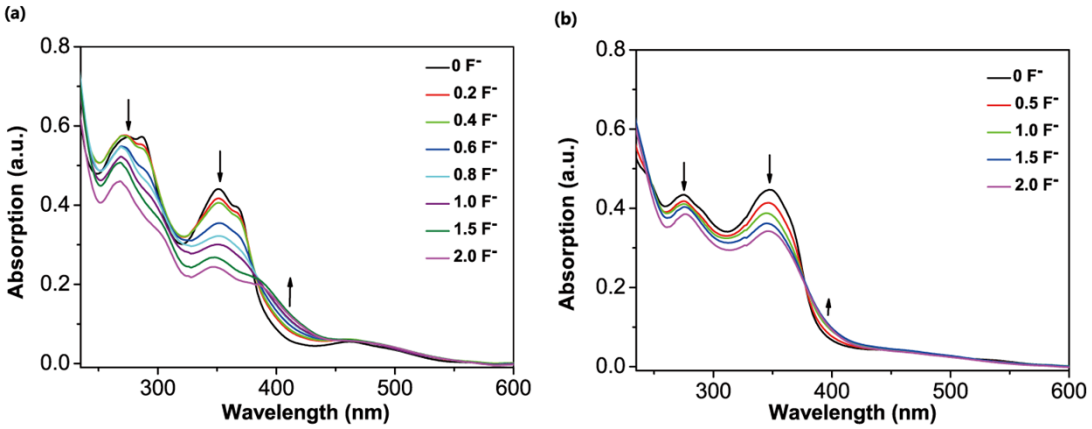


Fig. S1 The UV/vis absorption spectra of complexes (a) $[(Bpq)_2Ir(Phen)]PF_6$ and (b) $(Bpq)_2Ir(pymz)$ (10^{-5} M in CH_3CN) upon titration of TBAF (2 equiv.).

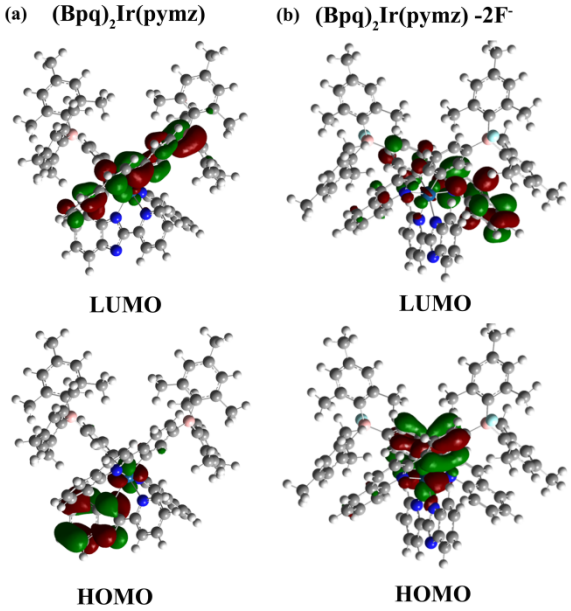


Fig. S2 Orbital distributions of (a) (Bpq)2Ir(pymz) and (b) (Bpq)2Ir(pymz)-2F-.

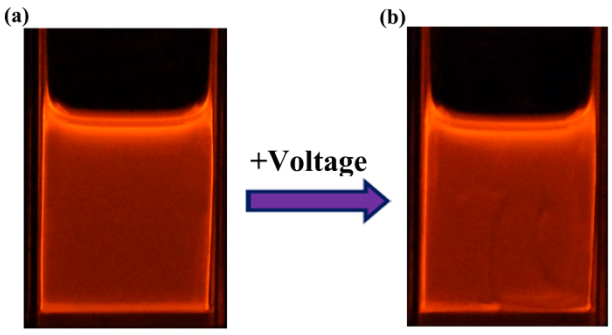


Fig. S3 Photographs of $[(Bpq)_2Ir(Phen)]PF_6$ in CH_3CN (10^{-4} M) without (a) and with (b) electrical stimuli under a UV lamp.

1 (a) R. Stahl, C. Lambert, C. Kaiser, R. Wortmann and R. Jakober, *Chem. Eur. J.*, 2006, **12**, 2358; (b) W. J. Xu, S. J. Liu, X. Y. Zhao, S. Sun, S. Cheng, T. C. Ma, H. B. Sun, Q. Zhao and W. Huang, *Chem. Eur. J.*, 2010, **16**, 7125.

2 Q. Zhao, F. Y. Li, S. J. Liu, M. X. Yu, Z. Q. Liu, T. Yi and C. H. Huang, *Inorg. Chem.*, 2008, **47**, 9256.