

Supporting Information

Syntheses and Remarkable Photophysical Properties of 2-(2-Pyridyl) Pyrazolate Boron Complexes; Photoinduced Electron Transfer

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General Experiments: All reactions were performed under nitrogen. Solvents were distilled from appropriate drying agent prior to use. Commercially available reagents were used without further purification unless otherwise stated. All reactions were monitored by TLC with Macherey-Nagel pre-coated glass plates (0.20 mm with fluorescent indicator UV₂₅₄). Compounds were visualized with UV light at 254 nm and 365 nm. Flash column chromatography was carried out using silica gel from Merck (230-400 mesh). Mass spectra were obtained on a JEOL SX-102A instrument operating in electron impact (EI) mode or fast atom bombardment (FAB) mode. ¹H and ¹³C NMR spectra were recorded on Varian Mercury-400 or INOVA-500 instruments; chemical shifts are quoted with respect to the internal standard tetramethylsilane for ¹H and ¹³C NMR data.

Spectroscopic and Dynamic Measurements: Steady-state absorption and emission

spectra were recorded by a Hitachi (U-3310) spectrophotometer and an Edinburgh (FS920) fluorimeter, respectively. The excitation light source of the fluorimeter has been corrected by the Rodamine B spectrum. In addition, the wavelength-dependent characteristics of the monochromator and photomultiplier have been calibrated by recording the scattered light spectrum of the corrected excitation light from a diffused cell in the 220-700 nm ranges. Fluorescence quantum yields were measured using quinine sulfate/1.0 N H₂SO₄ ($\Phi = 0.546$) as a standard. A liquid nitrogen cryostat (Graseby Specac Limited, Model P/N21525) coupled with an automatic temperature controller (P/N 20120) was used for the temperature-dependent study in the range of 298-150 K.

The setup of picosecond dynamical measurements consists of a femtosecond Ti-Sapphire oscillator (82 MHz, Spectra Physics). The fundamental train of pulses was pulse-selected (Neos, model N17389) to reduce its repetition rate down to typically 0.8-8 MHz, and then used to produce second harmonics (380-400 nm) as an excitation light source. A polarizer was placed in the emission path to ensure that the polarization of the fluorescence was set at the magic angle (54.7°) with respect to that of the pump laser to eliminate the fluorescence anisotropy. An Edinburgh OB 900-L time-correlated single photon counting system was used as a detecting system. The time-dependent fluorescence data were analyzed by the sum of exponential functions incorporating the excitation-pulse profile with an iterative convolution method, which allows partial removal of the instrument time broadening and consequently renders a temporal resolution of ~ 15 ps. The data were analyzed using a nonlinear least squares fitting program with a deconvolution method. For dynamical measurements sample solution was degassed via three freeze-pump-thaw cycles to avoid the oxygen quenching interference.

Electrochemical Studies: Cyclic voltammetry (CV) was performed in 1.0 mM of substrate on a BAS 100B Potentiostat, Bioanalytical System Inc. All oxidation and reduction reactions were measured in anhydrous CH₃CN with 0.1 M of *n*-Bu₄NPF₆ as

supporting electrolyte. The solution was purging with argon prior to each measurement. Platinum electrode was used as working electrode, platinum wire as counter electrode, and Ag/AgNO₃ (sat'd) as reference electrode. Ferrocenium/ferrocene redox couple was used as external reference, which occurs at $E^\circ = +0.37$ V vs. Ag/AgNO₃ (sat'd) in CH₃CN.

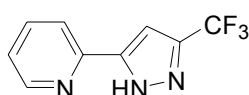
Synthetic Procedures: The methyl and t-butyl derivatives were synthesized following the procedures described in the literature,ⁱ using ethyl picolinate and 3,3-dimethyl-2-butanone (or acetone) as reactants; on the other hand, the CF₃ substituted compound was obtained by a Claisen condensation using approximately equal amount of ethyl trifluoroacetate and 2-acetylpyridine, followed by treatment with hydrazine hydrate in boiling ethanol solution.ⁱⁱ

3-Trifluoromethyl-5-(2-pyridyl) pyrazole (1a)

2-Acetylpyridine (5.6 mL, 50 mmol) was added dropwise to a stirred suspension of sodium ethoxide (5.1 g, 75 mmol) in dry THF solution (80 mL), which was cooled in an ice bath. Five minutes later, ethyl trifluoroacetate (6.5 mL, 55 mmol) was added slowly and the content was gradually warmed up to ambient temperature over a period of one hour. After then, the resulting mixture was brought to reflux for 20 hr and then slowly cooled to room temperature. The solvent was removed under vacuum and the yellowish brown solid was dissolved in water (30 mL). The aqueous solution was neutralized with minimal amount of conc. HCl solution and extracted with diethyl ether (3 × 30 mL). The organic phase was dried over Na₂SO₄ and the solvent was removed *in vacuo* to yield the crude 1,3-dione intermediate. This 1,3-dione was then dissolved in ethanol (60 mL) and the ethanol solution was treated with an excess of hydrazine (98%, 1.5 mL) and refluxed for 12 hr. After then, the ethanol solvent was removed *in vacuo*, the residue dissolved in CH₂Cl₂ (30 mL), and the organic phase was washed with water to remove hydrazine hydrate, dried over Na₂SO₄ and concentrated *in vacuo*, for which the resulting oily material would

contain a mixture of desired 2-pyridyl-pyrazole and hydroxy-dihydropyrazole intermediate, the latter was produced by the in-completed dehydration. This oily mixture was then re-dissolved in 50 mL of ethanol along with 1 mL of conc. HCl. The solution was brought to reflux for additional 5 hr to ensure the total conversion to 5-(2-pyridyl) pyrazole. The ethanol was evaporated again under vacuum and the resulting solid was dissolved in ethyl ether (50 mL). The ether phase was then washed with water twice, dried over Na₂SO₄ and re-concentrated *in vacuo*. The desired product was purified by sublimation (400 mtorr/70°C), followed by recrystallization in CH₂Cl₂ and hexane mixture to give the colorless solid (4.8 g, 22.9 mmol); yield: 45%.

Selected spectral data of **1a**. ¹H NMR (400 MHz, CDCl₃): δ 12.64 (br, 1H, NH), 8.66 (dd, *J*_{HH} = 4.8 Hz, 1.6 Hz, 1H, CH_{py}), 7.80 (ddd, *J*_{HH} = 7.6 Hz, 7.6 Hz, 1.4 Hz, 1H, CH_{py}), 7.64 (dd, *J*_{HH} = 7.6 Hz, 1.2 Hz, 1H, CH_{py}), 7.32 (ddd, *J*_{HH} = 7.6 Hz, 4.8 Hz, 1.2 Hz, 1H, CH_{py}), 6.94 (s, 1H, CH_{pz}). ¹³C NMR (125 MHz, CDCl₃): δ 149.5 (s, 1C, CH_{py}), 146.7 (s, 1C, C_{py}), 144.2 (q, *J*_{CF} = 37.8 Hz, 1C, C_{pz}), 142.9 (s, 1C, C_{pz}), 137.8 (s, 1C, CH_{py}), 123.9 (s, 1C, CH_{py}), 121.2 (q, *J*_{CF} = 267.3 Hz, 1C, CF₃), 120.7 (s, 1C, CH_{py}), 101.7 (s, 1C, CH_{pz}). ¹⁹F NMR (470.3 MHz, CDCl₃): δ -62.4 (s).



1a

Selected spectral data of **1b**. ¹H NMR (400 MHz, CDCl₃): δ 12.95 (br, 1H, NH), 8.54 (d, *J*_{HH} = 5.0 Hz, 1H, CH_{py}), 7.48 (s, 1H, CH_{py}), 7.14 (d, *J*_{HH} = 5.0 Hz, 1H, CH_{py}), 6.93 (s, 1H, CH_{pz}), 2.42 (s, 3H, CH₃). ¹³C NMR (125 MHz, CDCl₃): δ 149.4 (s, 1C, C_{py}), 149.1 (s, 1C, CN_{py}), 146.4 (s, 1C, C_{py}), 144.1 (q, *J*_{CF} = 37.7 Hz, 1C, C_{pz}), 142.9 (s, 1C, C_{pz}), 124.9 (s, 1C, CH_{py}), 121.5 (s, 1C, CH_{py}), 121.2 (q, *J*_{CF} = 267.2 Hz, 1C, CF₃), 101.4 (s, 1C, CH_{pz}), 21.2 (s, 1C, CH₃). ¹⁹F NMR (470 MHz, CDCl₃): δ -113.2 (s, CF₂), -84.7 (s, CF₃).

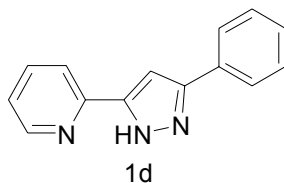
Selected spectral data of **1c**. ^1H NMR (500 MHz, d_6 -acetone): δ 13.52 (br, 1H, NH), 8.64 (ddd, $J_{\text{HH}} = 5.0$ Hz, 1.5 Hz, 1.0 Hz, 1H, CH_{py}), 7.95 (ddd, $J_{\text{HH}} = 8.0$ Hz, 8.0 Hz, 1.5 Hz, 1H, CH_{py}), 7.91 (ddd, $J_{\text{HH}} = 8.0$ Hz, 1.5 Hz, 1.0 Hz, 1H, CH_{py}), 7.39 (ddd, $J_{\text{HH}} = 8.0$ Hz, 5.0 Hz, 1.5 Hz, 1H, CH_{py}), 7.30 (s, 1H, CH_{pz}). ^{13}C NMR (125 MHz, d_6 -acetone): δ 150.5 (s, 1C, CN_{py}), 147.9 (s, 1C, C_{py}), 144.9 (s, 1C, C_{pz}), 142.4 (t, $J_{\text{CF}} = 28.8$ Hz, 1C, C_{pz}), 138.3 (s, 1C, CH_{py}), 124.7 (s, 1C, CH_{py}), 121.3 (s, 1C, CH_{py}), 119.9 (qt, $J_{\text{CF}} = 283.5$ Hz, 38.0 Hz, 1C, CF_3), 112.1 (tq, $J_{\text{CF}} = 247.5$ Hz, 38.9 Hz, s, 1C, CF_2), 103.6 (s, 1C, CH_{pz}). ^{19}F NMR (470 MHz, d_6 -acetone): δ -84.4 (s, CF_3), -111.9 (s, CF_2).

3-Phenyl-5-(2-pyridyl) pyrazole (**1d**)

Acetophenone (8.3 mL, 70mmol) was added dropwise to a stirred suspension of sodium ethoxide (5.1 g, 75 mmol) in dry THF solution (80 mL) at room temperature. Ethyl picolinate (6.8 mL, 50 mmol) was then added slowly, and the resulting mixture was brought to reflux for 20 hr. After stopping the reaction, the content was neutralized with conc. HCl and extracted with diethyl ether. The resulting solid material was then dissolved in ethanol (60 mL) and treated with 98% hydrazine hydrate (2.8 mL, 57 mmol) in refluxing ethanol (12 hours). The crude product was purified by sublimation at 85°C and 240 mtorr. Recrystallization from a mixture of CH_2Cl_2 and hexane gave colorless solid product (5.9 g, 72%).

Selected spectral data of **1d**. MS (EI), m/z 221, M^+ . ^1H NMR (500 MHz, acetone- d_6 , 294K): δ 12.82 (br, 1H, NH), 8.63 (d, $J_{\text{HH}} = 7.5$ Hz, 1H, H_{py}), 7.98 ~ 7.91 (m, 3H, H_{py} and H_{pz}), 7.85 (dd, $J_{\text{HH}} = 7.5$ Hz, 7.5 Hz, 1H, H_{py}), 7.44 (dd, $J_{\text{HH}} = 7.5$ Hz, 7.5 Hz, 2H, H_{ph}), 7.35 ~ 7.30 (m, 3H, H_{ph}). ^{13}C NMR (125 MHz, d_6 -acetone): δ 153.1 (s, 1C, C_{py}), 150.3 (s, 1C, CH_{py}), 149.2 (s, 1C, C_{pz}), 144.0 (s, 1C, C_{ph}), 137.9 (s, 1C, CH_{py}), 134.9 (s, 1C, C_{pz}), 129.5 (s, 2C, CH_{ph}), 128.4 (s, 1C, CH_{ph}), 126.2 (s, 2C,

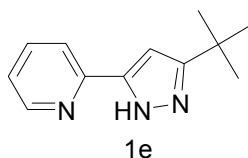
CH_{ph}), 123.7 (s, 1C, CH_{py}), 120.7 (s, 1C, CH_{py}), 101.2 (s, 1C, CH_{pz})



3-tert-Butyl-5-(2-pyridyl) pyrazole (1e)

To a suspension of NaH (1.7 g, 68 mmol) in THF (50mL) at 0°C was added 8.4 mL of 3,3-dimethyl-2-butanone (6.8 g, 68 mmol). The mixture was stirred at room temperature for 30 min and then allowed to warm to 60°C. Ethyl picolinate (8 g, 52 mmol) in 50 mL of THF was slowly added to the mixture. After completing the addition of picolinate, the mixture was further heated to 70°C for 20 min and the solution was slowly cooled to room temperature. Diluted HCl solution was added to the mixture until pH 8 ~ 9 at 0°C, and the aqueous solution was extracted with diethyl ether (4 × 10 mL). The combined organic phase was washed with brine and dried over MgSO₄, the diethyl ether solvent was removed *in vacuo* to yield the crude 1,3-dione. This 1,3-dione was then dissolved in ethanol (60 mL) and the resulting ethanol solution was treated with an excess of hydrazine (98%, 5.3 mL) and then refluxed for 2 hr. The ethanol solvent was removed *in vacuo*, the residue dissolved in CH₂Cl₂ (40 mL), and the organic phase was washed with water to remove unreacted hydrazine, dried over MgSO₄ and concentrated *in vacuo*, giving a yellow oily material. The colorless solid product was obtained by recrystallization in CH₂Cl₂ and hexane at room temperature (5.8 g, 28.8 mmol); yield: 55%.

Selected spectral data of **1e**. ¹H NMR (300 MHz, CDCl₃, 294 K): δ 8.58 (d, *J*_{HH} = 4.4 Hz, 1H, CH_{py}), 7.78 (br, 1H, CH_{py}), 7.69 (t, *J*_{HH} = 7.6 Hz, 1H, CH_{py}), 7.17 (t, *J*_{HH} = 5.7 Hz, 1H, CH_{py}), 6.65(s, 1H, CH_{pz}), 1.36 (s, 9H, CMe₃). ¹³C NMR (75 MHz, CDCl₃, 294 K): δ 159.1 (s, 1C, CN_{py}), 150.3 (s, 1C, CN_{pz}), 149.2 (s, 1C, CN_{py}), 146.7 (s, 1C, CN_{pz}), 136.7 (s, 1C, CH_{py}), 122.5 (s, 1C, CH_{py}), 119.9 (s, 1C, CH_{py}), 99.8 (s, 1C, CH_{pz}), 31.6 (s, 1C, CMe₃), 30.6 (s, 1C, Me).

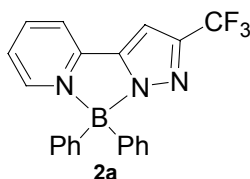


[3-Trifluoromethyl-5-(2-pyridyl) pyrazolate]BPh₂ (**2a**)

To a 50 mL reaction flask, it was charged with 0.1 g of 3-trifluoromethyl-5-(2-pyridyl) pyrazole (**1a**) (0.47 mmol) and 30 mL of anhydrous THF. To this solution was added 2 mL of the 0.25 M solution of BPh₃ in THF (0.5 mmol), and the mixture was stirred at room temperature for 40 min. After then, the solution was concentrated to dryness and crystalline solid of **2a** was obtained from recrystallization in a mixture of CH₂Cl₂ and hexane (0.16 g, 0.42 mmol, 90 %).

Spectral data of **2a**: MS (EI), *m/z* 377, M⁺. ¹H NMR (300 MHz, CDCl₃, 294K): δ 8.54 (d, *J*_{HH} = 4.9 Hz, 1H, CH_{py}), 8.14 (t, *J*_{HH} = 6.5 Hz, 1H, CH_{py}), 7.87 (d, *J*_{HH} = 8.2 Hz, 1H, CH_{py}), 7.49 (t, *J*_{HH} = 7.1 Hz, 1H, CH_{py}), 7.23 (s, 10H, CH_{ph}), 6.99 (s, 1H, CH_{pz}). ¹³C NMR (125 MHz, CDCl₃): δ 147.6 (q, *J*_{CF} = 38.0 Hz, 1C, CCF₃), 146.6 (s, 1C, CN), 144.3 (br, 2C, C), 143.5 (s, 1C, CN), 142.3 (s, 1C, CH), 141.0 (s, 1C, CN), 132.6 (s, 4C, CH), 127.8 (s, 4C, CH), 127.3 (s, 2C, CH), 122.9 (s, 1C, CH), 121.4 (q, *J*_{CF} = 267.3 Hz, 1C, CF₃), 118.9 (s, 1C, CH), 99.4 (s, 1C, CH). ¹⁹F NMR (470 MHz, CDCl₃): δ -61.4 (s). Anal. Calcd. For C₂₁H₁₅BF₃N₃: N, 11.4; C, 66.87; H, 4.01. Found: N, 11.1; C, 66.58; H, 4.37.

Selected crystal data of **2a**: C₂₁H₁₅BF₃N₃, M = 377.17, orthorhombic, space group *P* 2₁2₁2₁, *a* = 9.2385(5), *b* = 11.4876(6), *c* = 17.0928(10) Å, *V* = 1814.0(2) Å³, *Z* = 4, ρ_{calcd} = 1.381 gcm⁻³, *F*(000) = 776, crystal size = 0.30 × 0.30 × 0.20 mm, λ(Mo-K_α) = 0.7107 Å, T = 295 K, μ = 0.104 mm⁻¹, 4153 reflections collected (R_{int} = 0.0226), final wR₂(all data) = 0.1244. R₁[*I* > 2σ(*I*)] = 0.0480.



[3-Trifluoromethyl-5-(4-methyl-2-pyridyl) pyrazolate]BPh₂ (**2b**)

Compound **2b** was obtained in 73% by the similar procedure described for parent complex **2a**.

Selected spectral data of **2b**: MS (EI), m/z 391, M^+ . ^1H NMR (300 MHz, CDCl_3 , 294K): δ 8.36 (d, $J_{\text{HH}} = 5.9$ Hz, 1H, CH_{py}), 7.64 (s, 1H, CH_{py}), 7.27 (d, $J_{\text{HH}} = 5.9$ Hz, 1H, CH_{py}), 7.22 (s, 10H, CH_{ph}), 6.92 (s, 1H, CH_{pz}), 2.58 (s, 3H, Me). ^{13}C NMR (125 MHz, CDCl_3): δ 155.5 (s, 1C, C), 147.3 (q, $J_{\text{CF}} = 37.2$ Hz, 1C, CCF_3), 146.0 (s, 1C, CN), 144.4 (br, 2C, C), 142.5 (s, 1C, CN), 141.0 (s, 1C, CN), 132.6 (s, 4C, CH), 127.7 (s, 4C, CH), 127.2 (s, 2C, CH), 124.0 (s, 1C, CH), 121.5 (q, $J_{\text{CF}} = 269.0$ Hz, 1C, CF_3), 119.2 (s, 1C, CH), 99.0 (s, 1C, CH), 22.0 (s, 1C, CH_3). ^{19}F NMR (470 MHz, CDCl_3): δ -61.3 (s). Anal. Calcd. For $\text{C}_{22}\text{H}_{17}\text{BF}_3\text{N}_3$: N, 10.74; C, 67.55; H, 4.38. Found: N, 10.21; C, 65.77; H, 4.44.

[3-Pentafluoroethyl-5-(2-pyridyl) pyrazolate]BPh₂ (**2c**)

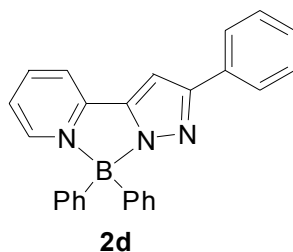
Compound **2c** was obtained in 78% by the similar procedure described for the parent complex **2a**.

Selected spectral data of **2c**: MS (EI), m/z 427, M^+ . ^1H NMR (300 MHz, CDCl_3 , 294K): δ 8.51 (d, $J_{\text{HH}} = 5.6$ Hz, 1H, CH_{py}), 8.09 (t, $J_{\text{HH}} = 8.0$ Hz, 1H, CH_{py}), 7.82 (d, $J_{\text{HH}} = 8.0$ Hz, 1H, CH_{py}), 7.45 (t, $J_{\text{HH}} = 7.2$ Hz, 1H, CH_{py}), 7.23 (s, 10H, CH_{ph}), 6.99 (s, 1H, CH_{pz}). ^{13}C NMR (125 MHz, CDCl_3): δ 146.4 (s, 1C, CN), 145.9 (t, $J_{\text{CF}} = 27.8$ Hz, 1C, CCF_2), 144.0 (br, 2C, C), 143.4 (s, 1C, CN), 142.3 (s, 1C, CH), 141.4 (s, 1C, CN), 132.6 (s, 4C, CH), 127.8 (s, 4C, CH), 127.3 (s, 2C, CH), 123.0 (s, 1C, CH), 119.0 (qt, $J_{\text{CF}} = 283.8$ Hz, 37.6 Hz, 1C, CF_3), 118.9 (s, 1C, CH), 111.0 (tq, $J_{\text{CF}} = 249.4$ Hz, 38.9 Hz, 1C, CF_2), 100.7 (s, 1C, CH). ^{19}F NMR (470 MHz, CDCl_3): δ -84.6 (s, CF_3), -112.3 (s, CF_2). Anal. Calcd. For $\text{C}_{22}\text{H}_{15}\text{BF}_5\text{N}_3$: N, 9.84; C, 61.86; H, 3.54. Found: N, 9.92; C, 61.70; H, 3.93.

[3-Phenyl-5-(2-pyridyl) pyrazolate]BPh₂ (**2d**)

Compound **2d** was obtained in 87% by the similar procedure described for the parent complex **2a**.

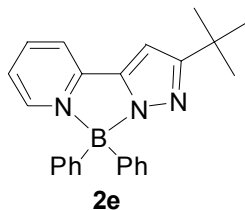
Spectral data of **2d**: MS (EI), m/z 385, M^+ . ^1H NMR (500 MHz, CD_2Cl_2 , 294K): δ 8.48 (d, $J_{\text{HH}} = 6.0$ Hz, 1H, CH), 8.08 (t, $J_{\text{HH}} = 8.0$ Hz, 1H, CH), 7.92 (m, 2H, CH), 7.86 (d, $J_{\text{HH}} = 8.5$ Hz, 1H, CH), 7.42 ~ 7.37 (m, 3H, CH), 7.32 ~ 7.23 (m, 11H, CH), 7.09 (s, 1H, CH). ^{13}C NMR (125 MHz, CD_2Cl_2): δ 157.5 (s, 1C, CN), 147.7 (s, 1C, CN), 145.6 (br, 2C, C), 143.4 (s, 1C, CN), 142.6 (s, 1C, CH), 142.1 (s, 1C, C), 134.5 (s, 1C, CN), 133.1 (s, 4C, CH), 128.9 (s, 2C, CH), 128.0 (s, 4C, CH), 127.8 (s, 1C, CH), 127.4 (s, 2C, CH), 125.9 (s, 2C, CH), 122.6 (s, 1C, CH), 119.1 (s, 1C, CH), 97.6 (s, 1C, CH). Anal. Calcd. For $\text{C}_{26}\text{H}_{20}\text{BN}_3$: N, 10.91; C, 81.05; H, 5.23. Found: N, 10.53; C, 81.12; H, 5.56.



[3-tert-Butyl-5-(2-pyridyl) pyrazolate]BPh₂ (**2e**)

The procedure was identical to that of **2a**, using 3-tert-Butyl-5-(2-pyridyl) pyrazole (**1e**) (0.2 g, 1.0 mmol) and 0.25 M solution of BPh_3 in THF (4 mL, 1.0 mmol) as starting materials. After removal of THF solvent, recrystallization from CH_2Cl_2 and methanol gave a colorless solid of complex **2e** (0.48 g, 1.3 mmol) in 88 % yield.

Spectral data of **2e**: MS (EI), m/z 365, M^+ . ^1H NMR (300 MHz, CDCl_3 , 294K): δ 8.44 (d, $J_{\text{HH}} = 5.9$ Hz, 1H, CH_{py}), 7.97 (t, $J_{\text{HH}} = 7.4$ Hz, 1H, CH_{py}), 7.69 (d, $J_{\text{HH}} = 7.5$ Hz, 1H, CH_{py}), 7.32 ~ 7.16 (m, 11H, CH_{py} and CH_{Ph}), 6.56 (s, 1H, CH_{pz}), 1.38 (s, 9H, CH_3). ^{13}C NMR (125 MHz, CDCl_3): δ 168.1 (s, 1C, CN), 147.7 (s, 1C, CN), 145.4 (br, 2C, C), 142.9 (s, 1C, CN), 141.5 (s, 1C, CH), 140.2 (s, 1C, CN), 132.8 (s, 4C, CH), 127.5 (s, 4C, CH), 126.8 (s, 2C, CH), 121.2 (s, 1C, CH), 118.0 (s, 1C, CH), 96.4 (s, 1C, CH), 32.6 (s, 1C, CMe_3), 30.9 (s, 3C, CH_3). Anal. Calcd. For $\text{C}_{24}\text{H}_{24}\text{BN}_3$: N, 11.50; C, 78.91; H, 6.62. Found: N, 11.53; C, 78.82; H, 6.77.



[3-Trifluoromethyl-5-(2-pyridyl) pyrazolate]B(C₆F₅)₂ (**2f**)

To a 50 mL reaction flask, it was charged with 0.2 g of B(C₆F₅)₃ (0.38 mmol) and 30 mL of anhydrous THF solvent. To this solution was added 70 mg of 3-trifluoromethyl-5-(2-pyridyl) pyrazole (0.34 mmol), and the mixture was stirred at room temperature for 12 hr. After then, the solution was evaporated to dryness and crystalline solid was obtained by recrystallization from a mixture of CH₂Cl₂ and methanol (90 mg, 0.16 mmol, 48 %)

Spectral data of **2f**: MS (EI), m/z 557, M⁺. ¹H NMR (400 MHz, CDCl₃, 294K): δ 8.59 (dd, *J*_{HH} = 6.0 Hz, 1.2 Hz, 1H, CH_{py}), 8.28 (ddd, *J*_{HH} = 8.0 Hz, 7.7 Hz, 1.2 Hz, 1H, CH_{py}), 7.92 (dd, *J*_{HH} = 8.0 Hz, 1.2 Hz, 1H, CH_{py}), 7.60 (ddd, *J*_{HH} = 7.7 Hz, 6.0 Hz, 1.2 Hz, 1H, CH_{py}), 6.99 (s, 1H, CH_{pz}). ¹⁹F NMR (470 MHz, CDCl₃): δ -61.8 (s, 3F, CF₃), -133.7 (s, 4F, CF), -154.1 (s, 2F, CF), -161.9 (s, 4F, CF). Anal. Calcd. For C₂₁H₅BF₁₃N₃: N, 7.54; C, 45.28; H, 0.90. Found: N, 7.41; C, 45.21 ; H, 1.12.

Reference:

- ⁱ Satake, A.; Nakata, T. *J. Am. Chem. Soc.* **1998**, *120*, 10391.
- ⁱⁱ (a) Thiel, W. R.; Eppinger, J. *Chem. Eur. J.* **1997**, *3*, 696. (b) Singh, S. P.; Kumar, D.; Jones, B. G.; Threadgill, M. D. *J. Fluorine Chem.* **1999**, *94*, 199.

Spectroscopic Approaches

The representative solvent dependent spectra for **2a** are shown in Figure A. The difference in dipole moment between ground and excited states can be calculated according to the Lippert equation expressed as follows:

$$\tilde{\nu}_f = \tilde{\nu}_f^{vac} - \frac{2|\vec{\mu}_e - \vec{\mu}_g|^2}{hca_0^3} \Delta f \quad (1)$$

where $\tilde{\nu}_f$ and $\tilde{\nu}_f^{vac}$ in eq. (1) are the spectral position (in terms of wavenumber) of the solvation equilibrated fluorescence maxima and the value extrapolated to the diluted gas-phase, respectively, $\vec{\mu}_g$ and $\vec{\mu}_e$ are the dipole moment vectors of the ground and excited states, a_0 is cavity radius and was calculated to be 4.87 Å via PM3 method, and Δf is the Lippert solvent polarity parameter, which is generally expressed as

$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{1}{2} \frac{n^2 - 1}{2n^2 + 1}$$

where ε and n denote the static dielectric constant and the refractive index of the solvent, respectively. The plot of spectral maxima for the F₂ band as a function of Δf is shown in Figure B. As predicted by eq (1), a linear relationship is found for the F₂ band with a slope of $-3.8 \times 10^3 \text{ cm}^{-1}$. As a result $|\vec{\mu}_e - \vec{\mu}_g|$ was calculated to be 6.6 Debye.

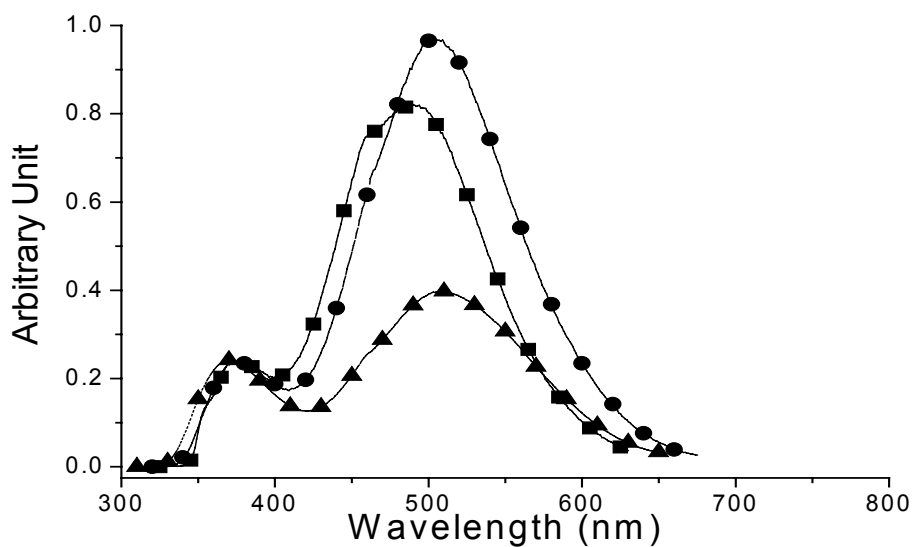


Figure A. Emission spectra of **2a** in CHE (-■-), THF (-●-) and ACN (-▲-). Intensity was normalized at 375 nm.

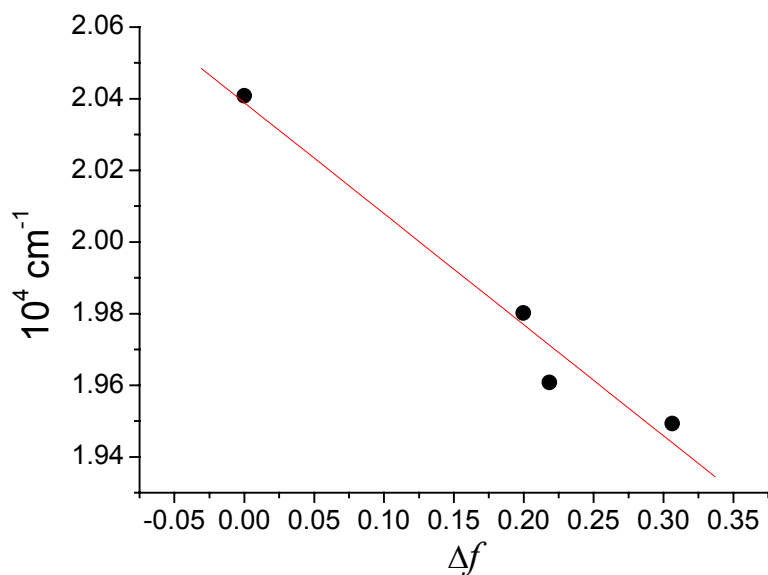


Figure B. The plot of peak frequencies of the CT (F_2) band for **2a** as a function of solvent polarity (Δf)

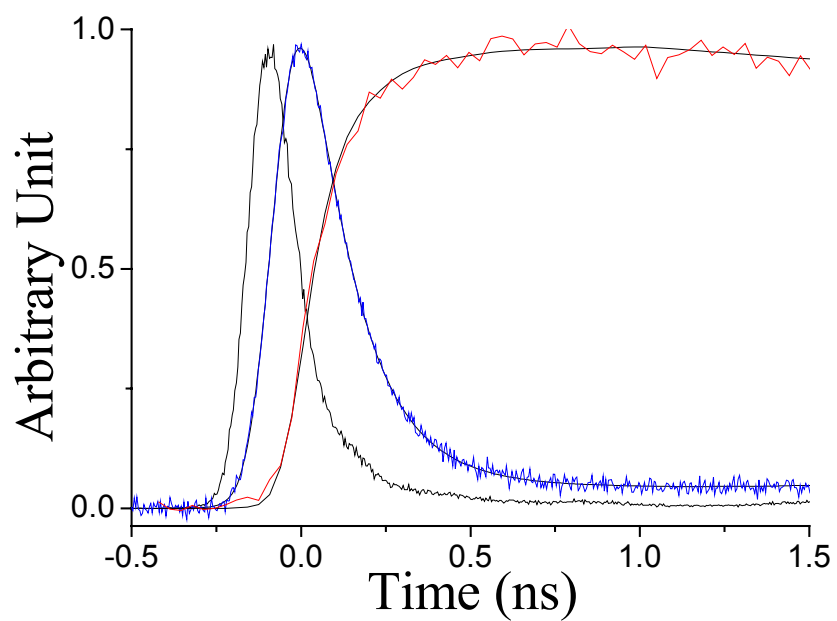


Figure C. The relaxation dynamics of **2a** monitored at 350 nm (—) and 550 nm (—) in aerated THF. (—) System response function. The decay at 350 nm was best fitted to be 530 ps, while the rise dynamics at 550 nm was resolved to be 520 ps. Note trace of long-lived component at 350 nm is due to the interference from the F₂ band.