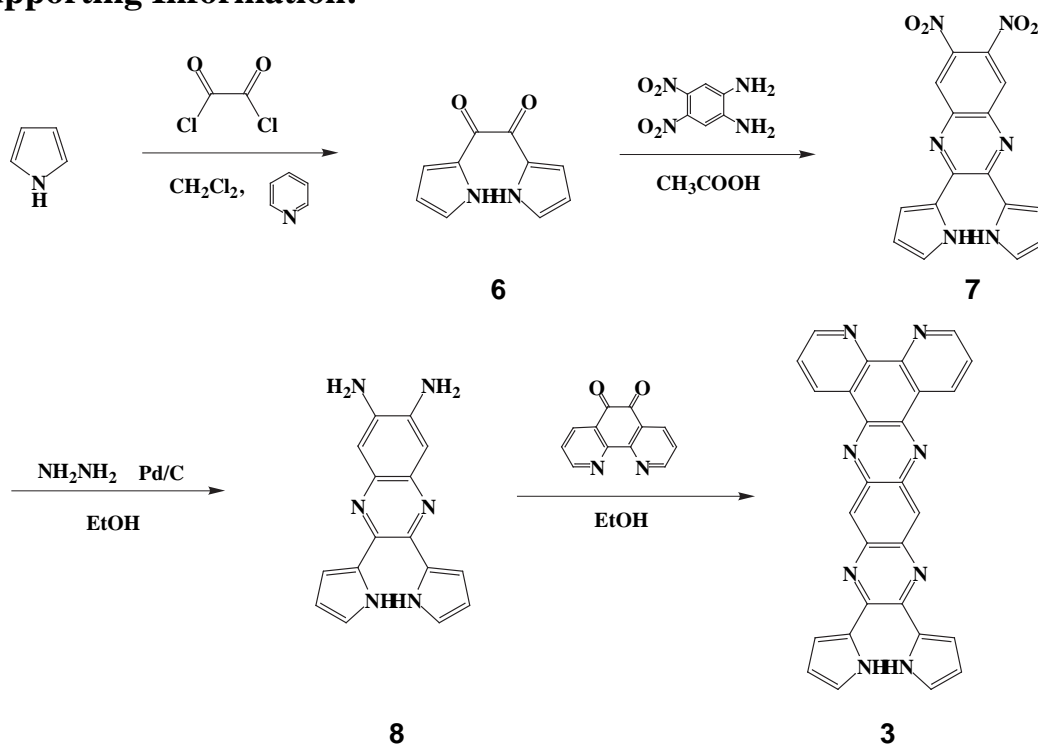


Phenanthroline Complexes Bearing Fused Dipyrrolylquinoxaline Anion Recognition Sites. Efficient Fluoride Anion Receptors

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Supporting Information:



Scheme 1 Synthesis of metal-ligand conjugated with anion binding site

2,3-Dipyrrol-2'-yl-6,7-dinitroquinoxaline (**7**)

The diketone **6** (0.5 g 3.18 mmol) and 1,2-diamino-4,5-dinitrobenzene (0.8 g, 4.04 mmol) were dissolved in glacial acetic acid (80 ml) and the resultant solution was heated at reflux in the dark for 4 h. The solvent was removed under vacuum and the residue was taken up in CH_2Cl_2 and washed with water and brine. The organic phase was dried over Na_2SO_4 , filtered and evaporated to dryness. The resulting powder was redissolved in mixed solvent ($\text{CH}_2\text{Cl}_2/\text{hexane} = 2/1$) and purified by silica gel chromatography (eluent; $\text{CH}_2\text{Cl}_2/\text{hexane} = 2/1$ then CH_2Cl_2) to give **7** as orange powder (0.80 g, 72%); m.p. 215 – 217 °C; $^1\text{H-NMR}$ (250 MHz, $\text{DMSO}-d_6$, TMS, 27°C) δ 6.20-6.28 (2H, m pyrrole-4H), 6.68-6.77 (2H, m, pyrrole-3H), 7.15-7.22 (2H, m, pyrrole-2H), 8.50 (2H, s, Ar-H), 11.94 (2H, brs, pyrrole-NH); $^{13}\text{C-NMR}$ (57.5 MHz, $\text{DMSO}-d_6$, TMS, 27°C) δ 109.9, 114.9, 124.6, 125.7, 127.9, 140.0, 140.7, 147.7; FAB-MS (M-H^+)

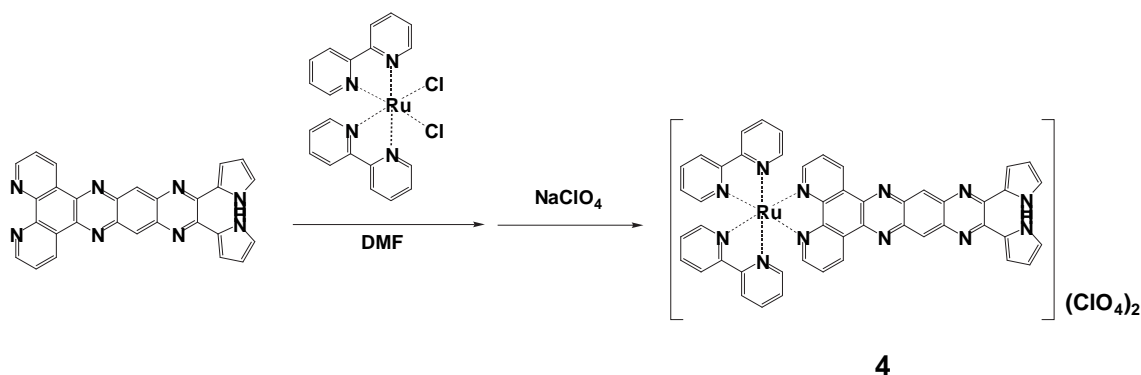
m/z 351 ; Anal. Calcd for $C_{16}H_{10}N_6O_4$: C, 54.86; H, 2.88; N, 23.99. Found C, 54.98; H, 2.94; N, 23.78.

2,3-Dipyrrol-2'-yl-6,7-diaminoquinoxaline (8)

To the suspension of 2,3-dipyrrol-2'-yl-6,7-dinitroquinoxaline **7** (400 mg, 1.14 mmol) and Pd/C (100 mg) in EtOH (70 ml) was added $NH_2NH_2 \cdot H_2O$ (2.0 ml) prior to heating at reflux for 3 h. After cooling, the reaction mixture was filtered to remove Pd/C. The filtrate was evaporated *in vacuo*. This gave **8** as a yellow powder (250 mg, 80%); m.p. > 220 °C (dec.); 1H -NMR (230 MHz, $DMSO-d_6$, TMS, 27°C) δ 6.00 (d, 2H, pyrrole-4H), 6.12 (t, 2H, pyrrole-3H), 6.86 (br, 2H, pyrrole-2H), 7.01 (s, 2H, Ar-H); ^{13}C -NMR (57.5 MHz, $DMSO-d_6$, TMS, 27°C) δ 105.3, 108.3, 108.8, 118.9, 129.9, 136.4, 139.8, 140.9; HRMS (CI+) m/z calcd for $C_{16}H_{15}N_6$: 291.135820, found 291.135978; Anal. Calcd for $C_{16}H_{14}N_6 + 0.7H_2O$: C 63.38; H, 5.12; N, 27.73. Found C, 63.87; H, 5.12; N, 26.06.

Phenanthroline –quinoxaline conjugate (3)

2,3-Dipyrrol-2'-yl-6,7-diaminoquinoxaline **8** (100 mg, 3.44 mmol) and 1,10-phenanthroline-5,6-dione (72.4 mg, 3.44 mmol) were heated at reflux in EtOH (10 ml) for 3 h. After cooling, the suspension was filtered giving **3** as a tan powder (80 mg, 80%); m.p. > 220 °C (dec.); 1H -NMR (230MHz, $DMSO-d_6$, TMS, 27°C) 6.21 (2H, br, pyrrole-4H), 6.62 (2H, br, pyrrole-3H), 7.15 (2H, br, pyrrole-2H), 7.95 (2H, dd, phen-3H), 8.80 (2H, s, Ar-H), 9.21 (2H, d, phen-4H), 9.60 (2H, d, phen-2H), 11.98 (2H, brs, pyrrole-NH); HRMS (CI+) m/z calcd for $C_{28}H_{17}N_8$: 465.157618, found: 465.157360; UV-vis ($DMSO$) λ_{max} [nm] (log ϵ) 323 (4.79), 531 (4.50); Anal. Calcd for $C_{28}H_{16}N_8 + 0.4H_2O$: C, 71.23; H, 3.50; N, 23.74. Found C, 71.28; H, 3.53; N, 23.64.



Scheme 2 Synthesis of metal complex **4**.

Ru(II) complex (4)

Ligand **3** (30.0mg, 64.6 μ mol) and bis-bipyridine ruthenium dichloride monohydrate (31.3 mg, 64.6 μ mol) were suspended in DMF (10 ml) and the resultant solution was heated at 140 °C for 3 h. After cooling, most of solvent was removed *in vacuo*. The residue was solubilized by adding a small amount of DMF (0.5 ml) and this solution was then diluted by adding water (40 ml). $NaClO_4$ (500 mg) was added to this

solution to precipitate the crude metal complex **4** in the form of its ClO_4^- salt. After collecting this complex by filtration, it was reprecipitated from $\text{MeCN}/\text{Et}_2\text{O}$ to give a purple solid (55 mg, 90 %); m.p. > 220 °C (dec.); $^1\text{H-NMR}$ (500 MHz, $\text{DMSO}-d_6$, TMS, 27 °C) 6.24, 6.25 (2H, t, pyrrole-4H), 6.66 - 6.68 (2H, m, pyrrole-3H), 7.18-7.21 (2H, m, pyrrole-2H), 7.40 (2H, *peude*-t, bpy-4H), 7.60 (2H, dd, bpy-4'H), 7.79 (2H, d, bpy-3H), 7.82 (2H, d, bpy-3'H), 8.01 (2H, dd, phen-3,8H), 8.14 (2H, t, bpy-5H), 8.21 (2H, d, phen-4,7H), 8.22 (2H, t, bpy-5'H), 8.86 (2H, s, Ar-H), 8.86 (2H, d, bpy-6'H), 8.89 (2H, d, bpy-6H), 9.64 (2H, d, phen-2,9-H), 11.97 (2H, s, pyrrole-NH); ESI-MS ($[\text{Ru}(\text{bpy})_2(\text{L})](\text{ClO}_4)^+$) m/z 977.0; UV-vis (DMSO) λ_{max} [nm] (log ϵ) 291 (4.58), 532 (4.16); Anal. Calcd for $\text{C}_{48}\text{H}_{32}\text{Cl}_2\text{N}_{12}\text{O}_8\text{Ru}+3.8\text{NaClO}_4+\text{H}_2\text{O}$: C, 36.92; H, 2.20; N, 10.77. Found C, 37.17; H, 2.66; N, 10.86.

Co(III) complex (**5**)

Ligand **3** (30.0mg, 64.6 μmol) and bis-phenanthroline cobalt trichloride (26.4 mg, 64.6 μmol) were suspended in DMF (10 ml) and the resultant solution was heated at 140 °C for 3 h. After cooling, most of solvent was removed *in vacuo*. The residue was solubilized by adding a small amount of DMF (0.5 ml) and this solution was then diluted by adding water (40 ml). NaClO_4 (500 mg) was added to this solution to precipitate the crude metal complex **4** in the form of its ClO_4^- salt. After collecting this complex by filtration, it was reprecipitated from $\text{MeCN}/\text{Et}_2\text{O}$ to give a purple solid (54 mg, 80 %); m.p. > 220 °C (dec.); $^1\text{H-NMR}$ (500 MHz, $\text{DMSO}-d_6$, TMS, 27 °C) 6.24 (2H, br, pyrrole-3H), 6.70 (2H, br, pyrrole-4H), 7.19 (2H, br, pyrrole-2H), 7.63 (2H, d, phen-4H), 7.67 (2H, d, phen-7H), 7.94 (4H, m, phen-4, 8H), 8.04 (2H, dd, phen-2H), 8.10 (2H, dd, phen'-4, 7H), 8.55 (2H, d, phen-5H), 8.58 (2H, d, phen-6H), 8.89 (2H, s, Ar-H), 9.14 (2H, d, phen-2H), 9.19 (2H, d, phen'-9H), 9.86 (2H, br, phen'-2, 9H), 11.98 (2H, br, pyrrole-NH); FAB-MS ($[\text{Co}(\text{phen})_2(\text{L})]$) m/z 883.2; UV-vis (DMSO) λ_{max} [nm] (log ϵ) 291 (4.58), 532 (4.16); Anal. Calcd for $\text{C}_{52}\text{H}_{32}\text{Cl}_3\text{CoN}_{12}\text{O}_{12}+0.35\text{NaClO}_4+3.0\text{H}_2\text{O}$: C, 48.78; H, 2.99; N, 13.13. Found C, 48.22; H, 3.31; N, 13.68.

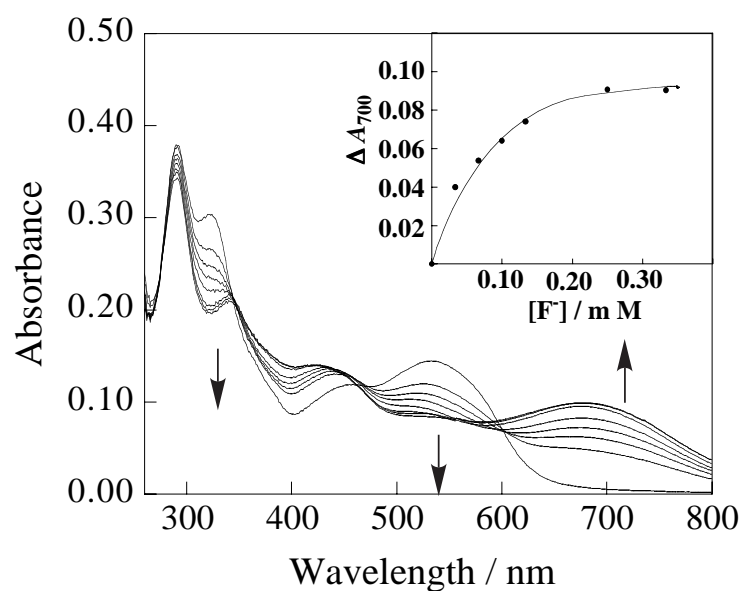


Fig.1 UV-vis spectral changes of Ru(II) complex **4** upon the addition of fluoride anion; $[\mathbf{4}] = 1.0 \times 10^{-5} \text{ M}$, $[\text{TBAF}] = 0 - 5 \times 10^{-4} \text{ M}$, DMSO, 25°C . The inset shows the fit of the experimental data to a 1:1 binding profile.

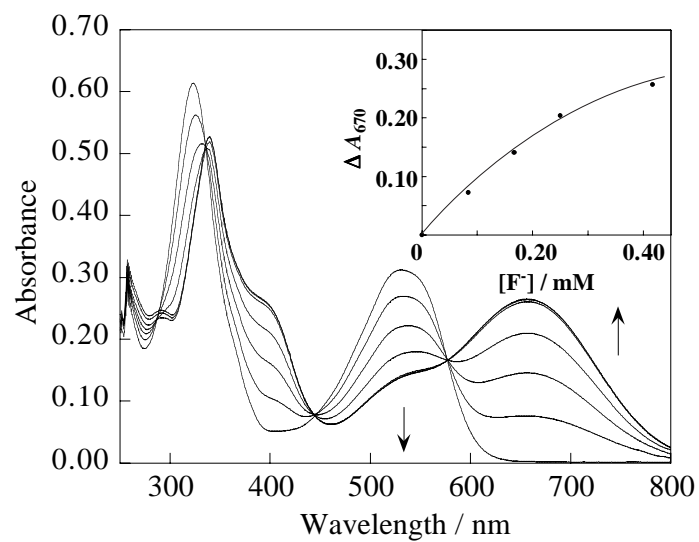


Fig.1 UV-vis spectral changes of Ligand **3** upon the addition of fluoride anion; $[\mathbf{3}] = 1.0 \times 10^{-5} \text{ M}$, $[\text{TBAF}] = 0 - 5 \times 10^{-4} \text{ M}$, DMSO, 25°C . The inset shows the fit of the experimental data to a 1:1 binding profile.

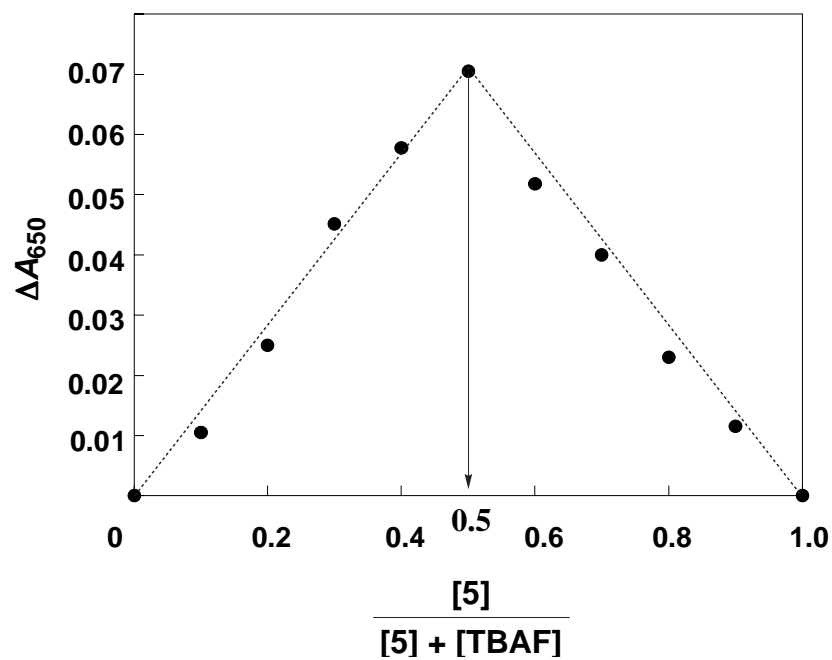


Fig. 3 The stoichiometry analysis of fluoride complex **5**•F⁻ by Job plot analysis;
 $[5] + [TBAF] = 1.5 \times 10^{-5}$ M, DMSO, r.t.