

Supporting information for

Highly selective fluorescence sensors for the fluoride anion based on carboxylate-bridged dinuclear iron complexes

Yuhan Zhou*, Xiaoliang Dong, Yixin Zhang, Peng Tong, and Jingping Qu*

*State Key Laboratory of Fine Chemicals, School of Pharmaceutical Science and Technology, Dalian
University of Technology, Dalian, 116024, P.R. China*

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Synthesis of $[\text{Cp}^*\text{Ru}(\mu\text{-SEt})_2(\text{MeCN})_2\text{RuCp}^*][\text{PF}_6]_2$ (**4c**)

To a solution of $[\text{Cp}^*\text{Ru}(\mu\text{-SEt})_2\text{Cl}_2\text{RuCp}^*]^1$ (69.4 mg, 0.104 mmol) in MeCN (3 mL) was added NH_4PF_6 (67.9 mg, 0.416 mmol) and then the resulting solution was stirred at room temperature under Ar for 1 h. The solution was removed *in vacuum*. Then, the residue was extracted with CH_2Cl_2 (3 mL). After filtration, the solution was removed *in vacuum*. The residue was washed with Et_2O (2 mL \times 2) to give brown solid $[\text{Cp}^*\text{Ru}(\mu\text{-SEt})_2(\text{MeCN})_2\text{RuCp}^*][\text{PF}_6]_2$ (**4c**, 80.6 mg, 80%). ^1H NMR (400 MHz, CD_2Cl_2): δ 2.92 (q, $J_{\text{H-H}} = 8.0$ Hz, 4H), 2.27 (s, 6H), 1.72 (s, 30H), 1.61 (t, $J_{\text{H-H}} = 8.0$ Hz, 6H).

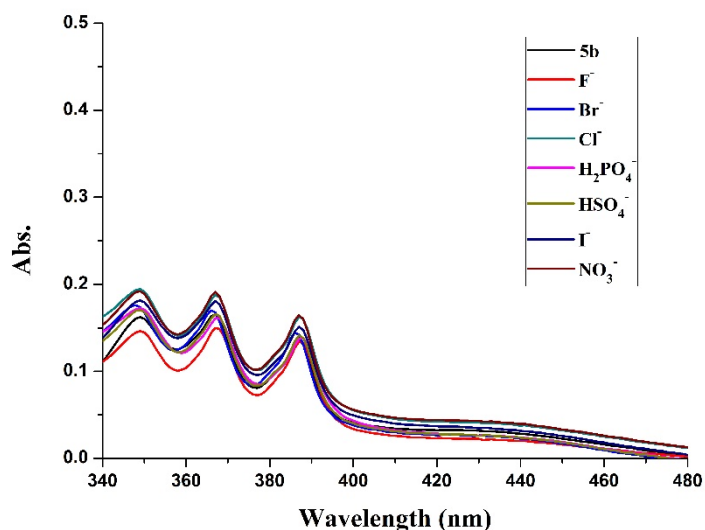


Fig. S1 Absorption spectra of chemosensor **5b** (1×10^{-5} M) upon addition of various anions (3 equiv) in THF solution.

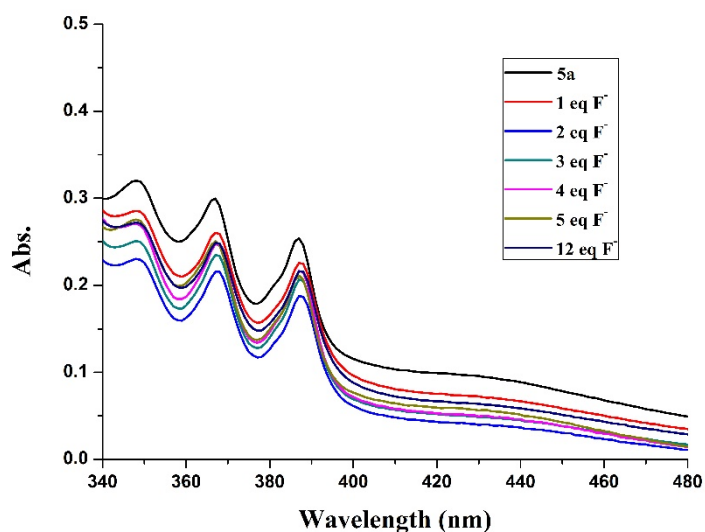


Fig. S2 Absorption spectra of chemosensor **5a** (1×10^{-5} M) upon addition of F⁻ (as its TBA salts) in THF.

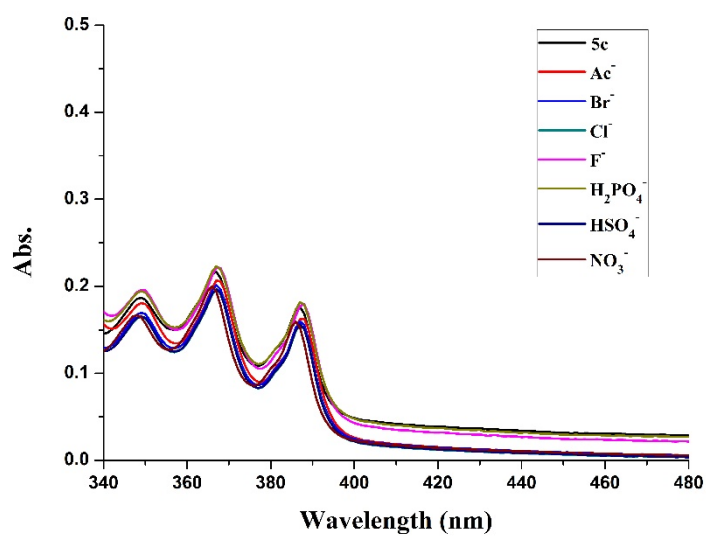


Fig. S3 Absorption spectra of chemosensor **5c** (1×10^{-5} M) upon addition of various anions (as their TBA salts) in THF.

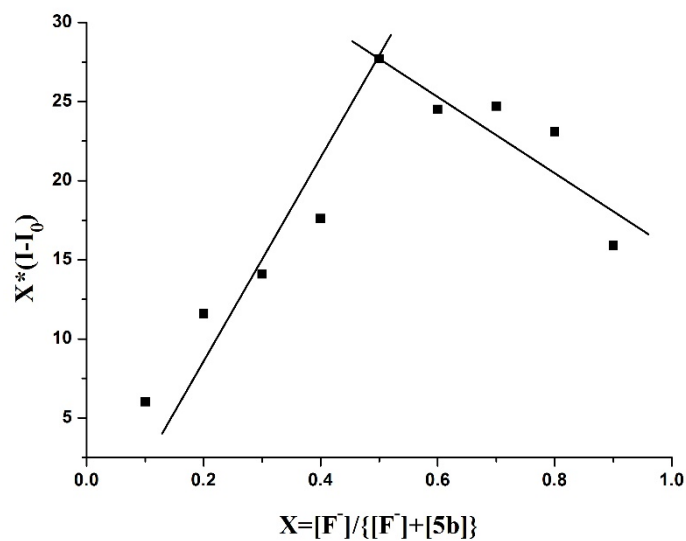


Fig. S4 Job's plot for determining the stoichiometry for chemosensor **5b** and F^- in THF excited with 370 nm. Total concentration of **5b** + Fe^{3+} = 2.5×10^{-5} M. I represents the intensity of **5b** upon addition of F^- and I_0 represents the **5b** original emission intensity at 414 nm excited with 370 nm.

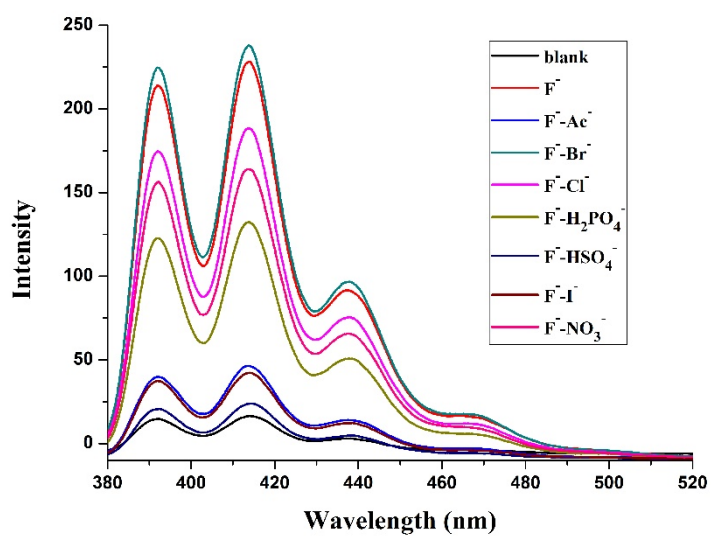


Fig. S5 Fluorescence emission spectra of chemosensor **5b** (1×10^{-5} M in THF) upon addition of anions in the presence of F⁻

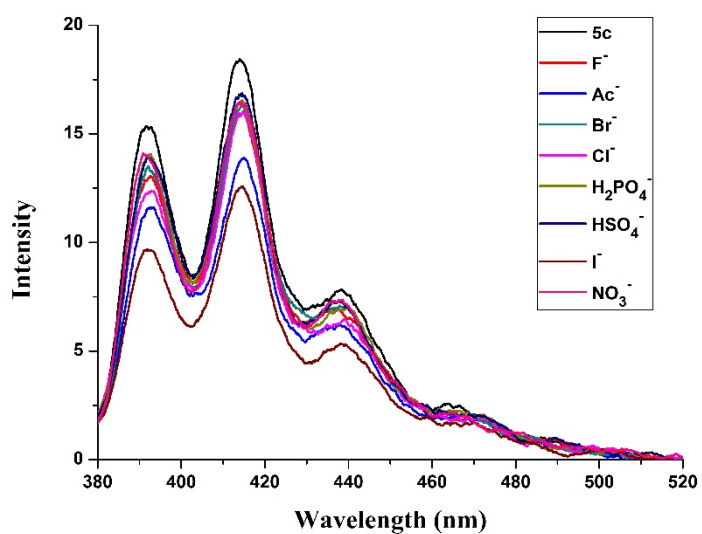


Fig. S6 Fluorescence spectrum of **5c** (1×10^{-5} M in THF) upon addition of different anions (as their TBA salts) excited with 370 nm.

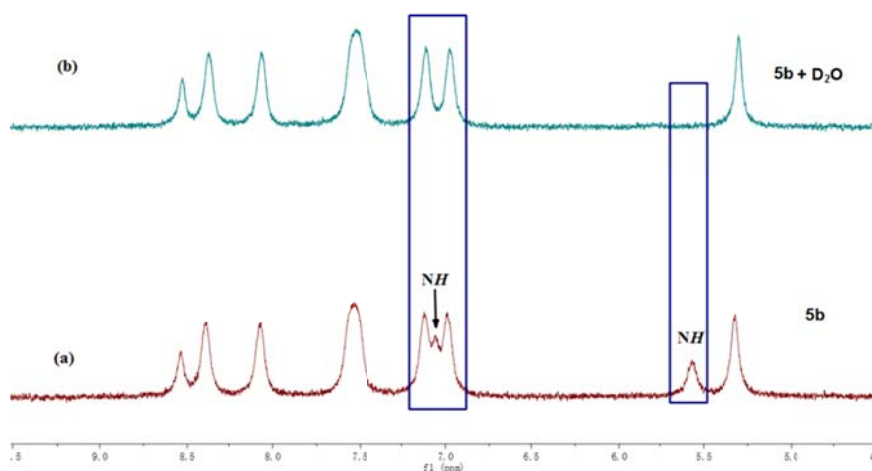


Fig. S7 Partial ^1H NMR (CD_3CN , 400 MHz) spectrum of **5b** before (a) and after (b) adding D_2O .

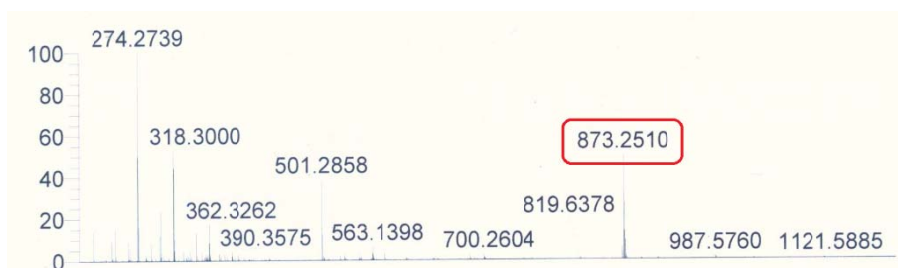


Fig. S8 The ESI-HRMS of chemosensor **5b** upon addition of 2 equiv of F^- .

References

- [1] Y. Nishibayashi, H. Imajima, G. Onodera, Y. Inada, M. Hidai and S. Uemura, *Organometallics* 2004, **23**, 5100-5103.