

Sensing behavior of sumanene-functionalized bis(terpyridine) Ruthenium(II) complexes

(¹Grad. Sch. Eng., Osaka Univ., ²ICS-OTRI, Osaka Univ.)

○Junyi Han,¹ Yumi Yakiyama,^{1,2} Yuta Uetake,^{1,2} Hidehiro Sakurai ^{1,2}

Keywords: Sumanene; Terpyridine; Ruthenium complexes; Fluorescence; Ion trapping.

Ru(terpy)_2^{2+} (terpy = 2,2':6',2''-terpyridine) has gained much attention as functional templates in supramolecular chemistry. Addition of the ion sensing units on the terpyridine unit will change the whole physical property and bring the opportunity to be utilized as a photosensor system. In this context, we introduced sumanene, a bowl-shaped π -conjugated molecule,¹ which recently reported to show significant and selective interaction to Cs^+ ,² as an ion trapping site to the ruthenium complex.

Four kinds of terpyridyl ligands **L1-L4** (Fig. 1a) were synthesized by Kröhnke reaction and Suzuki-Miyaura coupling reaction from formylsumanene, bromosumanene and benzaldehyde. Complexation of the ligands with $\text{RuCl}_2(\text{DMSO})_4$ or RuCl_3 in $\text{EtOH}/\text{CHCl}_3$ followed by the counterion exchange with NH_4PF_6 yielded the symmetric disumanenyl complexes (**C1**, **C2**), and unsymmetrical ones (**C3**, **C4**). The absorption spectra of all the complexes showed two intense bands at around 300 nm corresponding to the ligand-centered (LC) state. Their emission spectra were also studied at room temperature to find that all the complexes exhibited one broad emission band at 400–500 nm under the excitation wavelength of 300 nm. Noteworthy is that unsymmetrical complexes showed another emission peak at 530 nm (Fig. 1b). We further focused on their cation recognition property in $\text{MeCN}/\text{H}_2\text{O}$ solution to find their Li^+ sensing ability and the effect of counter anion. (Fig. 1c).

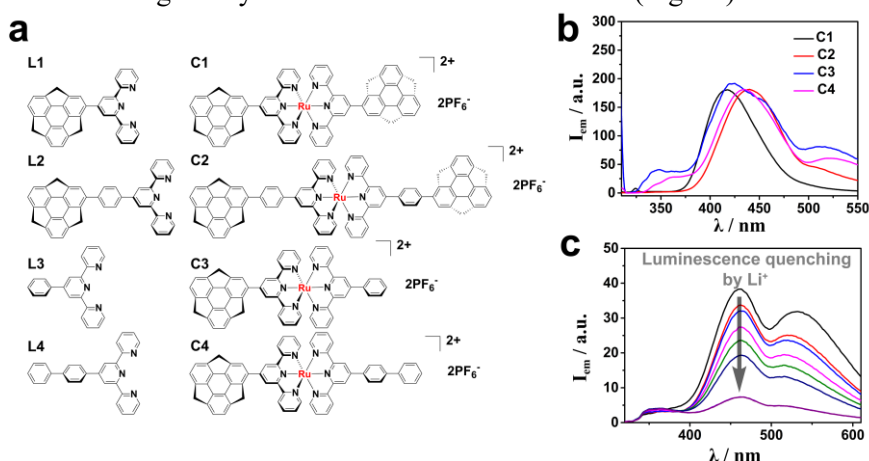


Figure 1. a) Structure of **L1-L4** and **C1-C4**. b) PL spectra of **C1-C4**. c) Li^+ titration study with **C4**.

1) H. Sakurai, T. Daiko, T. Hirao, *Science* **2003**, 301, 1878. 2) a) A. Kasprzak, H. Sakurai, *Dalton Trans.* **2019**, 48, 17147; b) A. Kasprzak, A. Kowalczyk, A. Jagielska, B. Wagner, A. M. Nowicka, H. Sakurai, *Dalton Trans.* **2020**, 49, 9965; c) A. Kasprzak, H. Sakurai, *Chem. Commun.* **2021**, 57, 343.