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A ruthenium biimidazole-like anion receptor with two chelating N – H···O intramolecular hydrogen bonds

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ABSTRACT

A new ruthenium biimidazole-like anion receptor featuring two "chelating" N – H···O intramolecular hydrogen bonds, $[Ru(bpy)_2(DNBbimH_2)](PF_6)_2$ (**2**·$(PF_6)_2$) (bpy = 2,2′-bipyridine; $DNBbimH_2$ = 5,5′,6,6′-tetramethyl-7,7′-dinitro-2,2′-bibenzimidazole), has been synthesized. Its anion-binding ability towards different anions in acetonitrile has been studied.

The field of anion recognition has attracted much attention in recent years, due to the important roles of anions in various chemical, biological and environmental processes [1]. Artificial anion receptors with different recognition units, such as urea [2], thiourea [2a], amide [3], and pyrrole [4], have been developed. Most of these receptors can bind strong basic anions such as F^-, OAc^-, and $H_2PO_4^-$, but only a few of them show binding affinity towards weak basic anions like Cl^-, Br^-, and I^-. In our recent study, we reported a ruthenium receptor $[Ru(bpy)_2(DMBbimH_2)](PF_6)_2$ (**1**·$(PF_6)_2$) (bpy = 2,2′-bipyridine; $DMBbimH_2$ = 7,7′-dimethyl-2,2′-bibenzimidazole) that showed strong binding affinity towards weak basic anions like Cl^-, Br^-, I^-, NO_3^-, and HSO_4^-, due to the strong acidity of N – H protons and pocket effect of methyl groups at the 7 and 7′ positions of biimidazole-like ligand [5]. However, this "open pocket" seemed to be a little big, and receptor **1**·$(PF_6)_2$ displayed similar binding strength towards those five anions, regardless of their sizes and shapes. In this work, a new ruthenium compound $[Ru(bpy)_2(DNBbimH_2)](PF_6)_2$ (**2**·$(PF_6)_2$) ($DNBbimH_2$ = 5,5′,6,6′-tetramethyl-7,7′-dinitro-2,2′-bibenzimidazole) has been synthesized, and two nitro groups are introduced to the 7 and 7′ positions of biimidazole-like ligand (Scheme 1). Due to the short distance between imidazole N – H fragments and nitro groups, two intramolecular N – H···O hydrogen bonds could be formed, and a "chelating mode" is displayed, creating an open pocket smaller than that in receptor **1**·$(PF_6)_2$. The strong electron withdrawing nature of nitro groups would render the imidazole N – H fragments highly acidic. Thus, combining the small pocket and high N – H acidity, **2**·$(PF_6)_2$ would have the controllable binding ability towards various anions (F^-, OAc^-, Cl^-, Br^-, I^-, NO_3^- and HSO_4^-).

Compound **2**·$(PF_6)_2$ was prepared by the reaction of $Ru(bpy)_2Cl_2$ with $DNBbimH_2$ ligand in refluxing ethylene glycol (see Supplementary material). Compound **2**·$(PF_6)_2$ was characterized by ^1H NMR as well as ESI-MS and gave satisfactory elemental analysis. The ^1H NMR spectra of **2**·$(PF_6)_2$ in CD_3CN showed the resonance of N – H protons at 13.0 ppm (Fig. S1, Supplementary material). The multiple peaks in 7.45−8.83 ppm were assigned as the resonances of protons on bipyridine ligands. The 5.70 and 3.95 ppm shifts were attributed to H4 and methyl group on the $DNBbimH_2$ ligand, respectively.

The electronic absorption spectrum of compound **2**·$(PF_6)_2$ in acetonitrile displays three bands at 290, 378 and 462 nm (Fig. S2, Supplementary material). The 290 and 378 nm bands are assigned as the intraligand transition of bipy and $DNBbimH_2$, respectively, while the 462 nm band is attributed to the Ru(d) → bpy(π^*) transition [6]. Compound **2**·$(PF_6)_2$ exhibits a quasi-reversible oxidation potential (Fig. S3, Supplementary material) at 0.84 V for the $Ru^{2+/3+}$ couple. Using the UV–vis method, the pKa_1 value of **2**·$(PF_6)_2$ in the acetonitrile–water mixture (V/V = 2/3) is determined to be 3.62 ± 0.05 (Fig. S4, Supplementary material) [7,8], which is much smaller than that of **1**·$(PF_6)_2$ (6.21 ± 0.05) [5]. This can be rationalized by the stronger electron withdrawing ability of nitro groups on **2**·$(PF_6)_2$. The much higher N – H acidity of **2**·$(PF_6)_2$ makes it non-emissive in acetonitrile, while **1**·$(PF_6)_2$ displays a low quantum yield of 2.8×10^{-3} in acetonitrile, due to a non-radiative deactivation pathway to the spin-forbidden ^3MLCT state provided by the acidic N – H proton [9].

To investigate the binding ability of **2**·$(PF_6)_2$ towards different anions, UV–vis titration experiments were performed. The electronic absorption spectra of **2**·$(PF_6)_2$ in acetonitrile showed no change upon addition of five equiv. of Cl^-, Br^-, I^-, NO_3^-, or HSO_4^-, while a 69 nm

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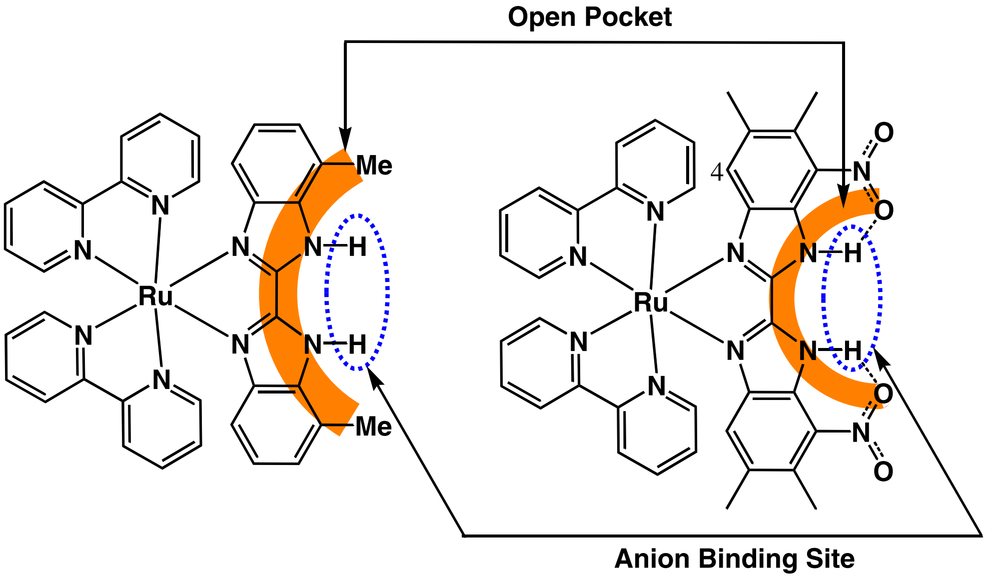

1^{2+} 2^{2+}

Scheme 1. Structures of receptors $\mathbf{1}^{2+}$ and $\mathbf{2}^{2+}$.

red-shift of the MLCT band was observed upon addition of five equiv. of F^- or OAc^- (Fig. S5, Supplementary material). The MLCT band of $\mathbf{2}\cdot(PF_6)_2$ was red-shifted from 462 to 492 nm upon adding 1 equiv. of F^- or OAc^- (Figs. 1 and S6 (Supplementary material), respectively), attributed to mono-deprotonation of $\mathbf{2}\cdot(PF_6)_2$ [5,10,11]. Meanwhile, the high energy band at 378 nm was blue-shifted to 364 nm, which was ascribed to the destruction of the first N–H···O intramolecular hydrogen bond on the $DNBbimH_2$ ligand [11]. The MLCT band further red-shifted to 531 nm when 2 equiv. of F^- or OAc^- were added, which is due to the second deprotonation process [5]. At the same

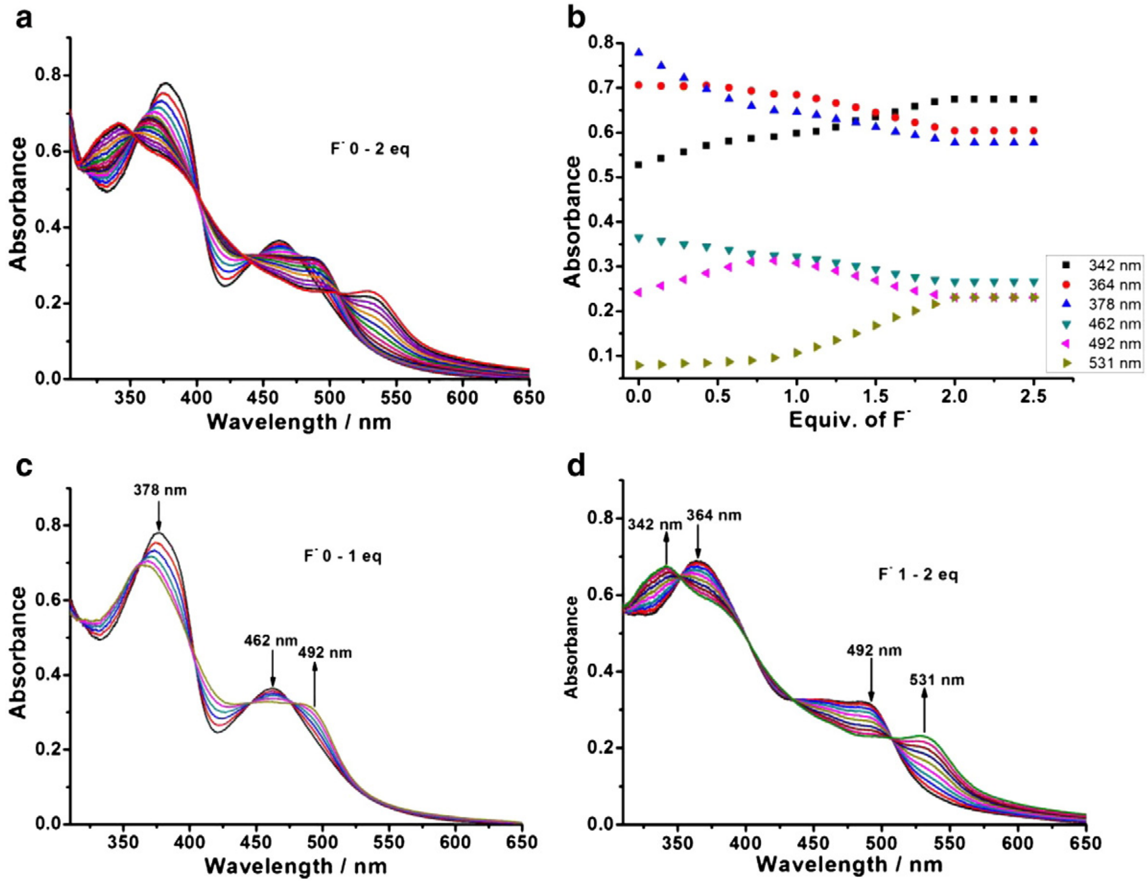

Fig. 1. UV–vis titration of $\mathbf{2}\cdot(PF_6)_2$ in acetonitrile upon addition of F^- (a) 0–2 equiv., (c) 0–1 equiv., and (d) 1–2 equiv. (b) Absorbance at 342, 364, 378, 462, 492, and 531 nm vs. equiv. of F^-.