Supplementary Information

Reversible colour/luminescence colour changes of tetracyanoruthenium(II) complexes by sorption/desorption of water molecules in crystal

Shingo Hattori, Tomoya Nagai, Akiko Sekine, Takuhiro Otuka and Kazuteru Shinozaki*

Graduate School of Nanobioscience, Yokohama City University, 22-2 Seto, Kanazawa-ku, Yokohama 236-0027 JAPAN

School of Science, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8551 JAPAN

Table S1 Selected bond lengths [Å] and angles [º] of $Ca[Ru(bpy)(CN)_4]\cdot 5H_2O$.

Ru1-C23	1.974(2)	Ca2-O3	2.388(1)
C23-N22	1.161(2)	Ca2-O4	2.444(1)
N22-Ca2	2.470(2)	Ca2-O5	2.409(2)
Ru1-C25	1.963(2)	Ca2-O18	2.375(2)
C25-N2	1.170(2)	Ca2-O19	2.451(2)
N24-Ca2$^{\#}$	2.498(2)	Ru1-C23-N22	178.4(2)
Ru1-C21	2.039(2)	C23-N22-Ca2	145.9(1)
C21-N20	1.164(2)	Ru1-C25-N24	176.89(2)
Ru1-C27	2.050(2)	C25-N24-Ca2$^{\#}$	142.9(1)
C27-N26	1.156(2)	Ru1-C21-N20	175.6(2)
Ru1-N12	2.124(2)	Ru1-C27-N26	176.3(2)
Ru1-N6	2.121(2)		

#: x+1 y, z

Table S2 Selected bond lengths[Å] and angles [º] of $Sr[Ru(bpy)(CN)_4]\cdot 6H_2O$.

Ru1-C10	1.993(2)	Sr2-O3	2.68 4 3(2)
C10-N1	1.163(3)	Sr2-O4	2.731(2)
N1-Sr2	2.676(2)	Sr2-O5	2.600(2)
Ru1-C14$^{\#}$	1.991(2)	Sr2-O6	2.603(2)
C14-N13	1.158(3)	Sr2-O7	2.592(2)
N13-Sr2	2.714(2)	Sr2-O8	2.573(2)
Ru1-C12	2.033(2)	Ru1-C10-N1	178.6(2)
C12-N11	1.151(3)	C10-N1-Sr2	139.6(2)
Ru1-C16	2.057(2)	Ru1-C14$^{\#}$-N13$^{\#}$	174.9(2)
C16-N15	1.159(3)	C14-N13-Sr2	118.9(2)
Ru1-N22	2.124(2)	Ru1-C12-N11	176.0(2)
Ru1-N23	2.118(2)	Ru1-C16-N15	179.2(2)

#:x+1, y, z

Table S3 Selected bond lengths [Å] and angles [º] of $Ba[Ru(bpy)(CN)_4]\cdot 6H_2O$.

Ru1-C13	1.955	Ba1-O1	2.782
C13-N5	1.156	Ba1-O2	2.883
N5-Ba1	2.811	Ba1-O3	2.811
Ru1-C12	1.961	Ba1-O4	2.893
C12-N4	1.152	Ba1-O5	2.689
N4-Ba1	2.849	BA1-O6	2.749
Ru1-C11	2.020	Ru1-C13-N5	176.83
C11-N3	1.147	C13-N5-Ba1	129.5
Ru1-C14	2.028	Ru1-C12-N4	178.17
C14-N6	1.149	C12-N4-Ba1	144.49
Ru1-N1	2.110	Ru1-C11-N3	176.19
Ru1-N2	2.088	Ru1-C14-N6	177.19

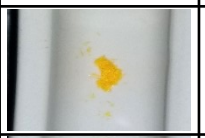
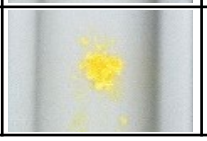
	Ca^{2+}	Sr^{2+}	Ba^{2+}
r.t.			
373 K			
473 K			
r.t.			

Fig. S1 Colour of $M[Ru(bpy)(CN)_4]\cdot nH_2O$ ($M = Ca^{2+}$, Sr^{2+} and Ba^{2+}).

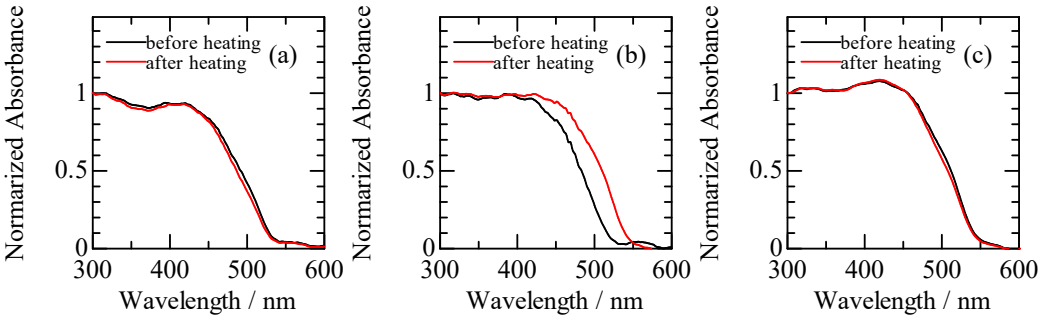


Fig. S2 Absorption spectra of $M[Ru(bpy)(CN)_4]\cdot nH_2O$ (M^{2+} = (a) Ca^{2+}, (b) Sr^{2+} and (c) Ba^{2+}) measured by using a diffuse reflectance mode. The black and red lines are absorption spectra of each complex salts before and after heating, respectively. Since the heat treatment was carried out to use a heat gun, the temperature might be precisely controlled. Fortunately, for Sr^{2+} salt, the absorption band observed in the range of 300-600 nm was red-shifted after heating, which is consistent with the red coloration shown in Fig. S1. For Ca^{2+} and Ba^{2+} salts, however, the heat treatment seems not to contribute to red-shift of absorption band. This reason can be explained by the fact that the heating temperature was slightly low to eliminate water molecules from the crystals of Ca^{2+} and Ba^{2+} salts. The differences in easiness to eliminate water for Ca^{2+}, Sr^{2+} and Ba^{2+} salts are observed in TG results as shown in Fig. 3.

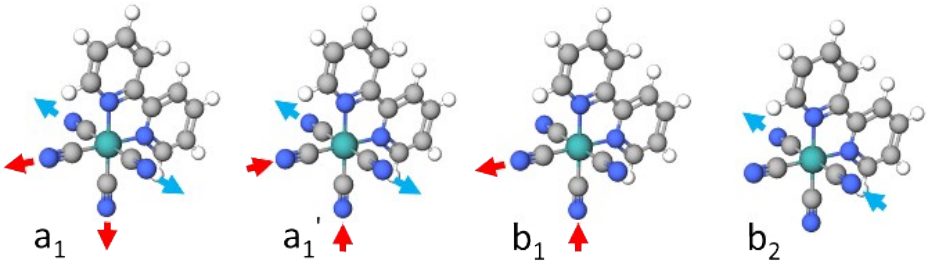


Fig. S3 Normal modes for CN stretching of $[Ru(bpy)(CN)_4]^{2-}$ in C_{2v} symmetry.

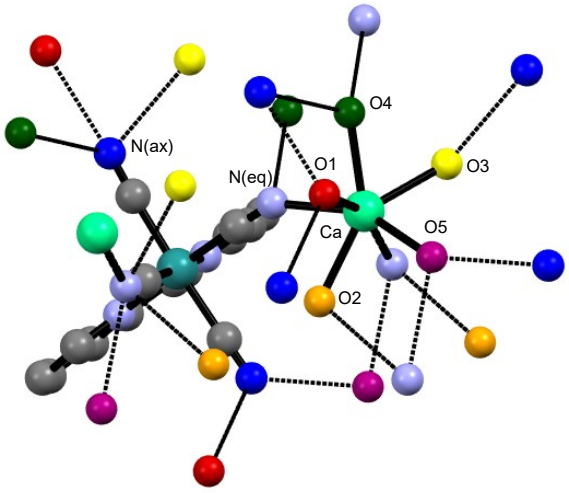


Fig. S4 Hydrogen bonding structure around Ca^{2+} ion (light green) and CN ligands. N(eq) (light purple) and N(ax) (blue) are nitrogen atoms of equatorial and axial CN ligands, respectively. Five oxygen atoms are denoted as O1(red), O2(orange), O3(yellow), O4(green), and O5(purple). The distances of Ca-O are 2.409(2) Å (Ca-O1), 2.451(1) Å (Ca-O2), 2.444(1) Å (Ca-O3), 2.388(1) Å (Ca-O4), and 2.375(2) Å (Ca-O5).

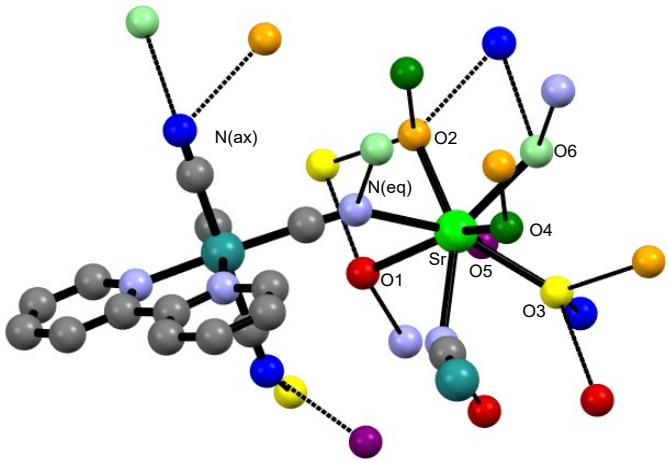


Fig. S5 Hydrogen bonding structure around Sr^{2+} ion (light green) and CN ligands. N(eq) (light purple) and N(ax) (blue) are nitrogen atoms of equatorial and axial CN ligands, respectively. Five oxygen atoms are denoted as O1(red), O2(orange), O3(yellow), O4(green), O5(purple), and O6(light green). The distances of Sr-O are 2.728(2) Å (Sr-O1), 2.6848(2) Å (Sr-O2), 2.600(2) Å (Sr-O3), 2.574(2) Å (Sr-O4), 2.602(2), Å (Sr-O5), and 2.594(2) Å (Sr-O6).

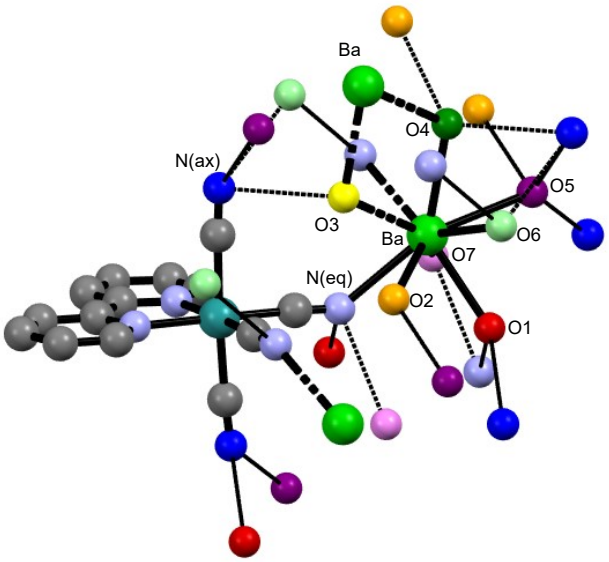


Fig. S6 Hydrogen bonding structure around Ba^{2+} ion (light green) and CN ligands. N(eq) (light purple) and N(ax) (blue) are nitrogen atoms of equatorial and axial CN ligands, respectively. Five oxygen atoms are denoted as O1(red), O2(orange), O3(yellow), O4(green), O5(purple), O6(light green), and O7(violet). The distances of Ba-O are 2.689(2), Å (Ba-O1), 2.862(1) Å (Ba-O2), 2.893(2) Å (Ba-O3), 2.811(2) Å (Ba-O4), 2.833(2) Å (Ba-O5), 2.782(1) Å (Ba-O6), and 2.749(2) Å (Ba-O7). The waters O3 and O4 are shared by adjacent Ba^{2+} ion.