Supplementary Information

Competitive Threading of $Ru(bpy)_3$ Stopped "V" Type Pseudo[2]rotaxane-like supramolecules

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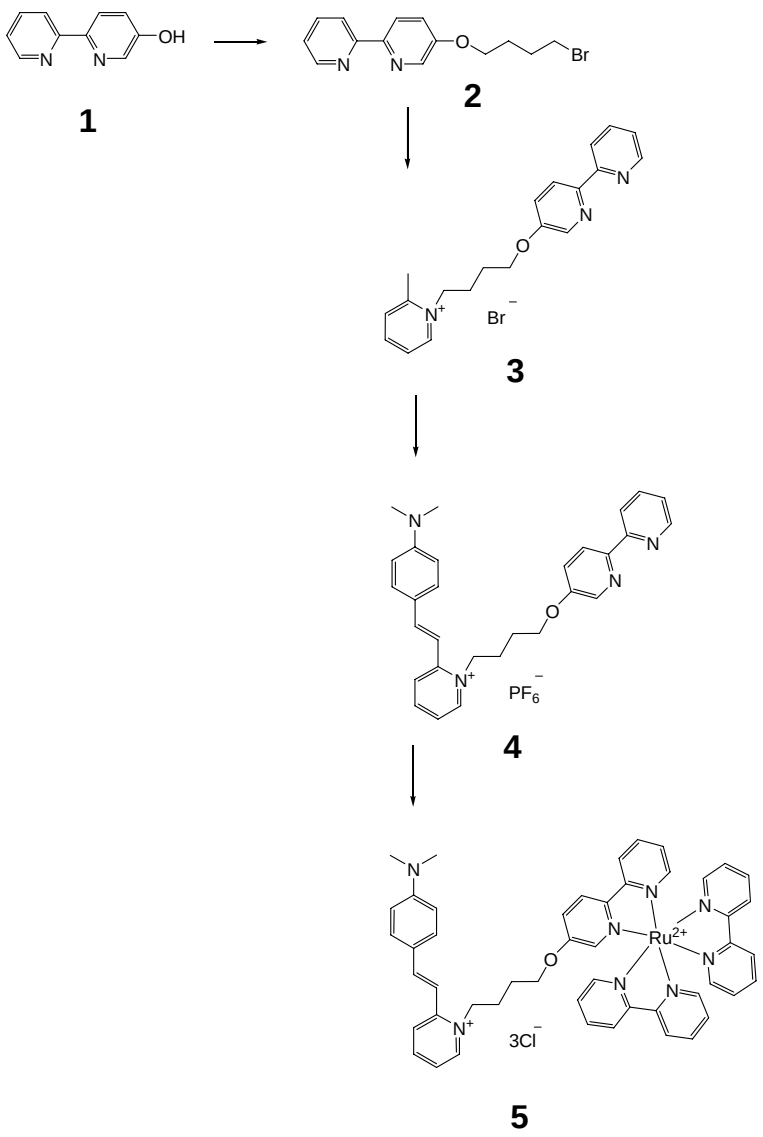
Experimental Details

Instruments: ^{1}H NMR spectra and the ^{13}C NMR were measured on a Brüker AV-400 spectrometer in D_2O. The Chemical shifts of all the samples are calibrated to solvent protons at 4.7ppm. And the concentration of all the samples was ca. 1.0×10^{-2} M. The electronic spray ionization (ESI) mass spectra were tested on a HP5989 mass spectrometer. Absorption spectra were done on a Varian Cary 500 UV/Vis spectrophotometer (1-cm quartz cell used), while the CD spectra were recorded on a Jasco J-815 CD spectrophotometer in a 1 mm quartz cell. Melting points were determined by using an X-6 micro-melting point apparatus.

Materials: 2,2'-bipyridin-5-ol, 1,4-dibromobutane, 2-methylpyridine, 4-(dimethylamino) benzaldehyde, cis-Ru(bpy)Cl_2•$2H_2O$, KNO_3, NH_4PF_6, tetrabutylaminochlorate and β-CD were commercially available and used as received. CB[7] were synthesized according to the early report. Acetone was dried with anhydrous magnesium sulfate. Acetonitrile and DMF were dried by 4A molecular sieve and distilled under reduced pressure before use.



Synthesis of 2

A suspension of 500mg (2.9mmol) 2,2'-bipyridin-5-ol and 803mg (5.8mmol) K_2CO_3 in 30ml acetone was stirred for 30min at 50°C, then 1.9g (8.7mmol) 1,5-dibromopentane was added and refluxed for another 4hours. After the mixture was cooled to room temperature, precipitate was removed by filtration, the filtrate was concentrated under reduced pressure, 50ml hexane was added and the product was collected by filtration to afford compound **2** 650mg (72.8%). M.p. 68.9～70.3° C. ^{1}H NMR (400MHz, $CDCl_3$), δ ppm=8.64 (d, *J*=4.8Hz, 1H), 8.36-8.29 (m, 3H), 7.78 (dd, *J*=2.0, 8.0 Hz, 1H), 7.30 (dd, *J*=2.8, 8.8 Hz, 1H), 7.27-7.23 (m, 1H), 4.11 (t, *J*=5.6Hz, 2H), 3.51 (t, *J*=6.4Hz, 2H), 2.15-2.07(m, 2H), 2.05-1.97(m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$), δ ppm=156.035, 155.387, 149.055, 137.245, 136.836, 122.925, 121.700, 121.525, 120.401, 67.389, 33.235, 29.298, 27.824. HRMS (ESI, *m/z*): calcd for $C_{14}H_{16}N_2OBr$, 307.0446, found 307.0443.

Synthesis of 3

A mixture of 500mg (1.6mmol) compound **2** and 304mg (3.2mmol) 2-methylpyridine in acetonitrile was refluxed for 2 days. Then the mixture was cooled to room temperature, solvent was removed under reduced pressure, 10ml EA was added, the precipitation was filtrated and washed with 5ml EA to afford compound **3** (440mg, 67%). ^{1}H NMR (400MHz, DMSO-d_6), δ ppm=9.02 (d, *J*=6.4Hz, 1H), 8.63 (d, *J*=4Hz, 1H), 8.50-8.45 (m, 1H), 8.39 (d, *J*=3.2Hz, 1H), 8.34 (d, *J*=8.8Hz, 1H), 8.27 (d, *J*=8Hz, 1H), 8.05 (d, *J*=7.6Hz, 1H), 7.98 (t, *J*=7.6Hz, 1H), 7.92-7.87 (m, 1H), 7.56-7.52 (m, 1H), 7.40-7.36 (m,1H), 4.64 (t, *J*=8Hz, 2H), 4.20 (t, *J*=6.4Hz, 2H), 2.86 (s, 3H), 2.05 (br t, 2H), 1.88 (br t, 2H). HRMS (ESI, *m/z*): $[M\text{-}Br^-]^+$ calcd for $C_{20}H_{22}N_3O$, 320.1763, found 320.1760.

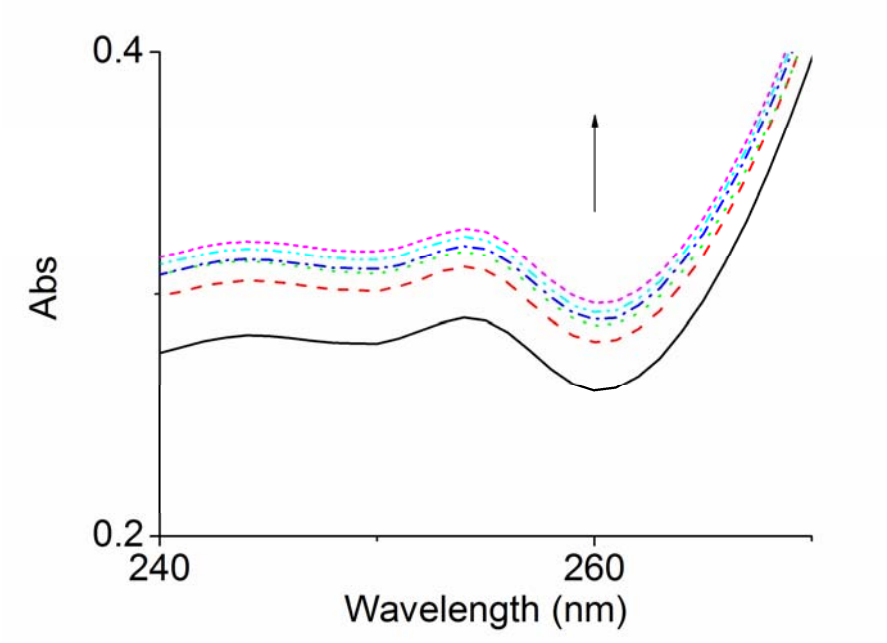
Synthesis of 4

A mixture of 400mg (1.0mmol) compound **3** and 149mg (1.0mmol) 4-(dimethylamino) benzaldehyde in ethanol was heated to 60°C, a drop of piperidine was added, the mixture was refluxed for 4h. After cooled, solvent was removed under reduced pressure, solid was recrystallized by ethanol to afford **4·Br**. The counter anion of **4·Br** was exchanged with NH_4PF_6 to provide **4·PF$_6$** (423mg, 71%). ^{1}H NMR (400MHz, DMSO-d6), δ ppm=8.82 (d, *J*=6.0Hz, 1H), 8.63 (d, *J*=4.4Hz, 1H), 8.47 (d, *J*=8.0Hz, 1H), 8.39-8.31 (m, 3H), 8.27 (d, *J*=8.0Hz, 1H), 7.96-7.86 (m, 2H), 7.76 (t, *J*=6.8Hz, 1H), 7.63 (d, *J*=8.8Hz, 2H), 7.53-7.48 (m, 1H), 7.41-7.35 (m, 1H), 7.24 (d, *J*=15.6Hz, 1H), 6.67 (d, *J*=8.8Hz, 2H), 4.82 (t, *J*=7.6Hz, 2H), 4.22 (t, *J*=6.0Hz, 2H), 2.94 (s, 6H), 2.09-1.98 (m, 2H), 1.95-1.85 (m, 2H). HRMS (ESI, *m/z*): $[M\text{-}PF_6^-]^+$ calcd for $C_{29}H_{31}N_4O$, 451.2942, found 451.2945.

Synthesis of 5

A solution of cis-Ru(bpy)Cl_2•$2H_2O$ 196mg (0.376mmol) and $AgPF_6$ 191mg (0.753mmol) in acetone 10ml was stirred at room temperature for 10h. The precipitate was filtered and washed with 5ml acetone. 200mg (0.376mmol) Compound **4** was added to the filtrate. The reaction flask was wrapped with aluminum foil and refluxed under Ar atmosphere for 12hours. After it was cooled to room temperature, solvent was removed under reduced pressure. The crude product was purified by column chromatography, using silica gel and a mixture of CH_3CN/H_2O/sat. KNO_3 10/1/1 as elute. The red band was collected, and the counter anion exchanged with NH_4PF_6 to get compound **5·3PF$_6$** (366mg, 75 %). A solution of 200 mg (0.154mmol) Compound **5·3PF$_6$** and

256mg (0.923mmol) tetrabutylaminochlorate in 5ml acetone was stirred at room temperature to produce a precipitate which was collected by filtration and washed with acetone to provide compound **5·3Cl** (136mg, 91%). ^{1}H NMR (400MHz, D_2O), δ ppm=8.46-8.40 (m, 6H), 8.34 (d, *J*=8Hz, 1H), 8.21 (t, *J*=8Hz, 1H), 8.16-8.09 (m, 3H), 7.99-7.91 (m, 3H), 7.73-7.64 (m, 6H), 7.63-7.55 (m, 3H), 7.47 (d, *J*=15.6Hz, 1H), 7.29-7.21 (m, 4H), 7.18-7.08 (m, 2H), 6.98 (d, *J*=8.8Hz, 2H), 6.49 (d, *J*=15.6Hz, 1H), 6.19 (d, *J*=8.8Hz, 2H), 4.42 (t, *J*=7.6Hz, 2H), 4.17 (t, *J*=6Hz, 2H), 2.74 (s, 6H), 1.97-1.75 (m, 4H). HRMS (ESI, *m/z*): $[M\text{-}2Cl^-]^{2+}$ calcd for $C_{49}H_{47}ClN_8ORu$, 450.1294, found 450.1290.



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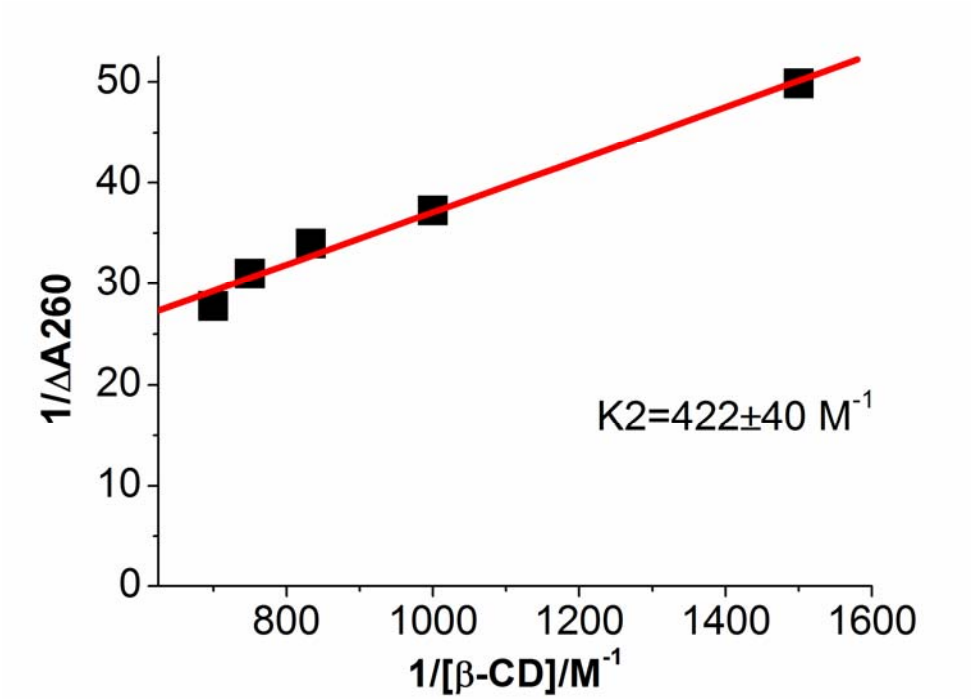

Figure S2 Calculation of the binding constant between **VRu** and *β*-CD in **VRu⊂*β*-CD**.

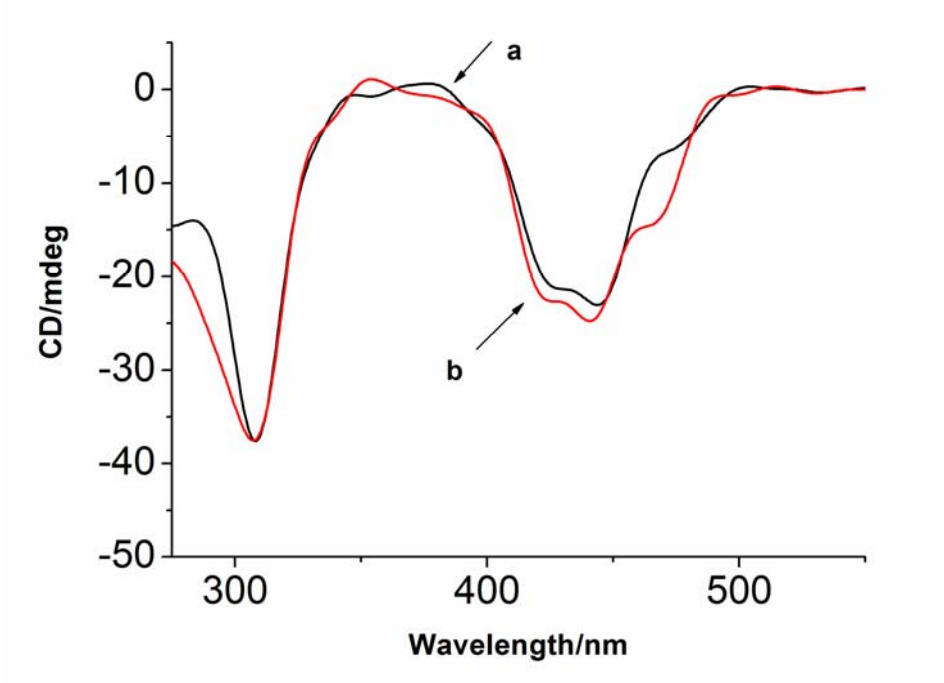

Figure S3 CD spectra of **VRu** (1.5×10^{-4} M, curve **a**) and **VRu⊂*β*-CD** (curve **b**) in H_2O at 298K.

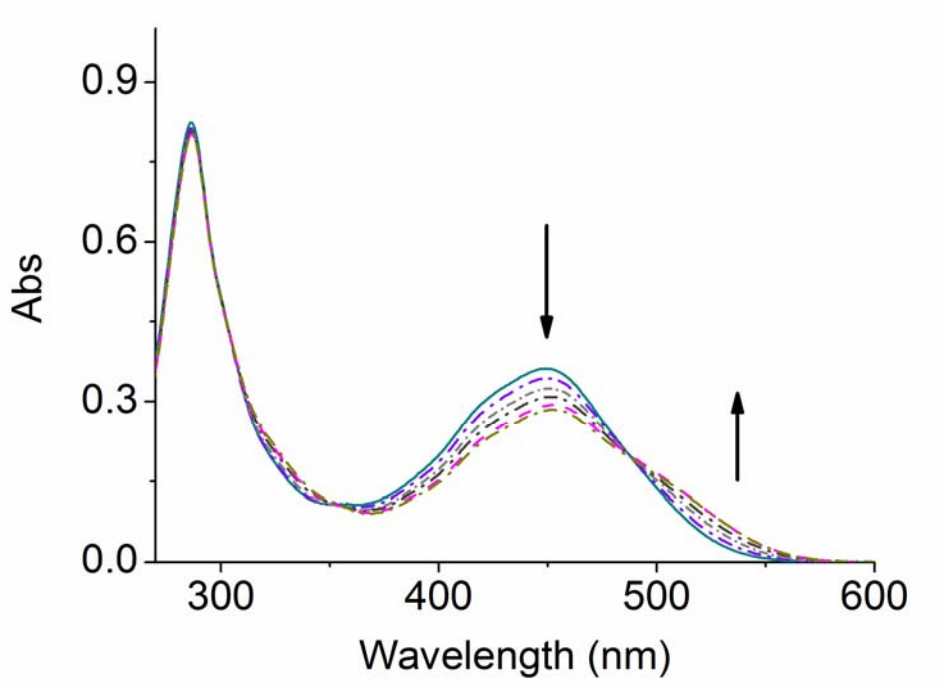

Figure S4 UV-Vis spectra of **VRu** (1×10^{-5} M， H_2O at 298K) and after addition of 0 eq., 0.2 eq., 0.4 eq., 0.6 eq., 0.8 eq. and 1 eq. of CB[7] (along the direction of the arrow).

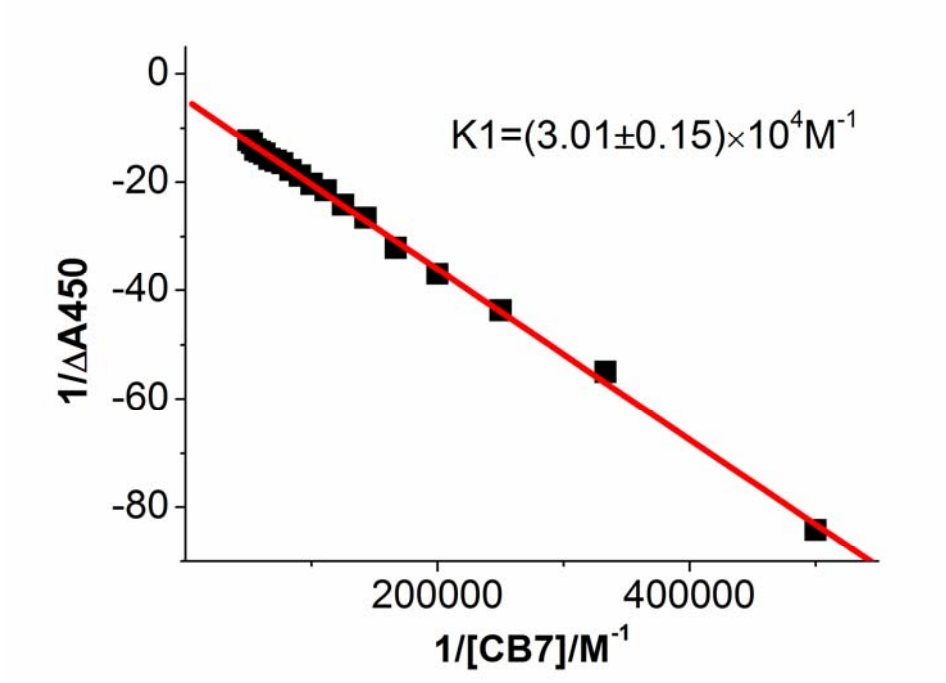

Figure S5 Calculation of the binding constant between **VRu** and CB[7] in **VRu⊂CB[7]**.

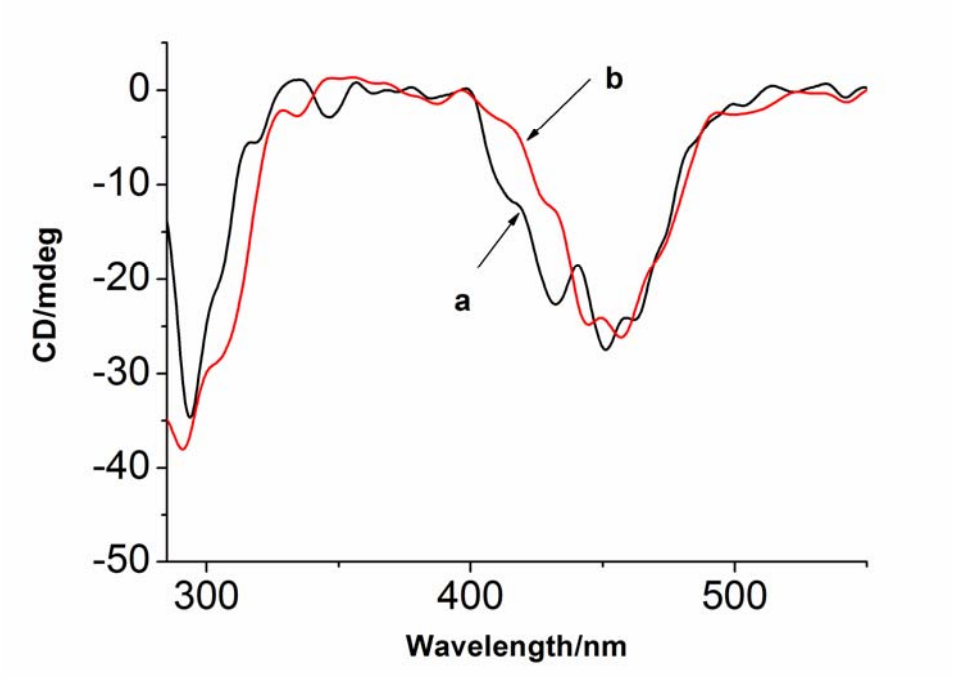

Figure S6 CD spectra of **VRu** (1.5×10^{-4} M, curve **a**) and **VRu⊂CB[7]** (curve **b**) in H_2O at 298K.

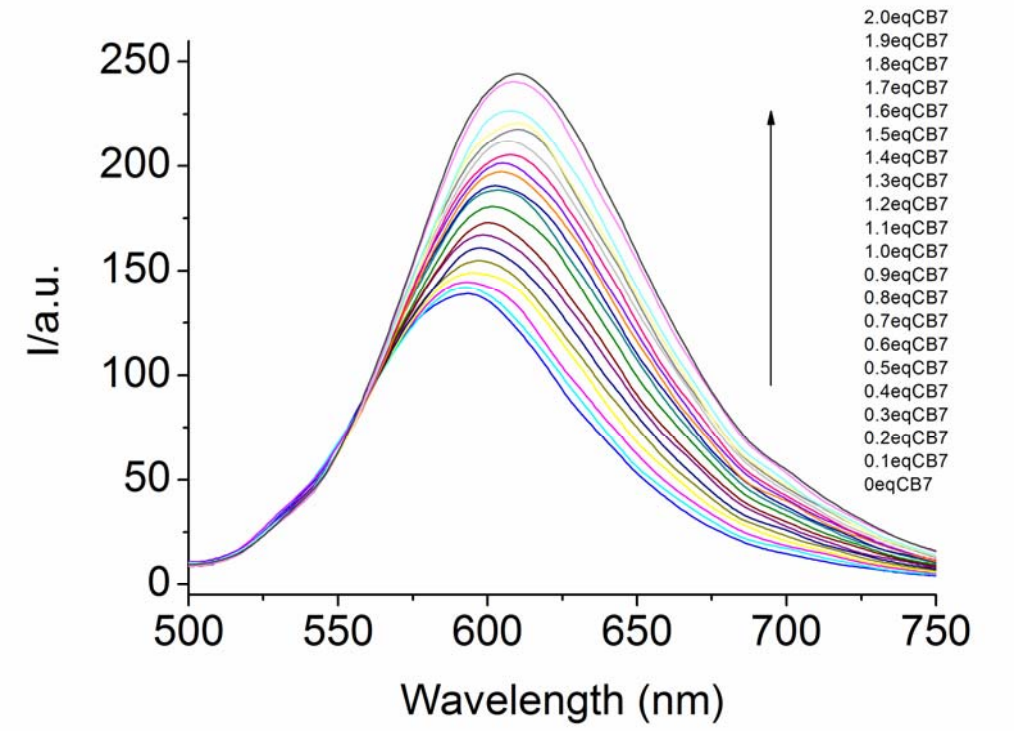

Figure S7 Fluorescence emission spectra of **VRu** (1.0×10^{-5} M, excited at 450nm in H_2O, 298K) and after addition of CB[7]. [S1]

References:

S1 (a) R. L. Halterman, J. L. Moore, L. M. Mannel. *J. Org. Chem.* 2008, **73**, 3266-3269; (b) C. Marquez, R. R. Hudgins, W. M. Nau. *J. Am. Chem. Soc.* 2004, **126**, 5806; (c) J. Mohanty, A. C. Bhasikuttan, W. M. Nau, H. Pal. *J. Phys. Chem. B* 2006, **110**, 5132.