Angewandte Chemie
Eine Zeitschrift der Gesellschaft Deutscher Chemiker

# Supporting Information

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# Molecular Loop Lock: a Molecular Machine Based on a Host-Stabilized Charge-Transfer Complex

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**Materials and methods.** All the reagents and solvents employed were commercially available and used as supplied without further purification. All the NMR data were recorded on a Bruker DRX500 spectrometer. UV-visible absorption spectra were recorded on a Hewlett-Packard 8453 diode array spectrophotometer.

**Electrochemical experiments.** The electrochemical experiments were performed with a Princeton Applied Research Model 273 multipurpose instrument interfaced to a personal computer. A glassy carbon working electrode (0.07 $cm^2$), a Pt counter electrode, and a saturated calomel electrode (SCE) as a reference electrode separated with a fine glass frit were utilized in a single-compartment cell. The surface of the working electrode was polished with 0.05 $\mu$m alumina/water slurry on a felt surface and rinsed with purified water prior to electrochemical experiments. All solutions were deoxygenated by purging with argon gas and maintained under an inert atmosphere during the electrochemical experiments.

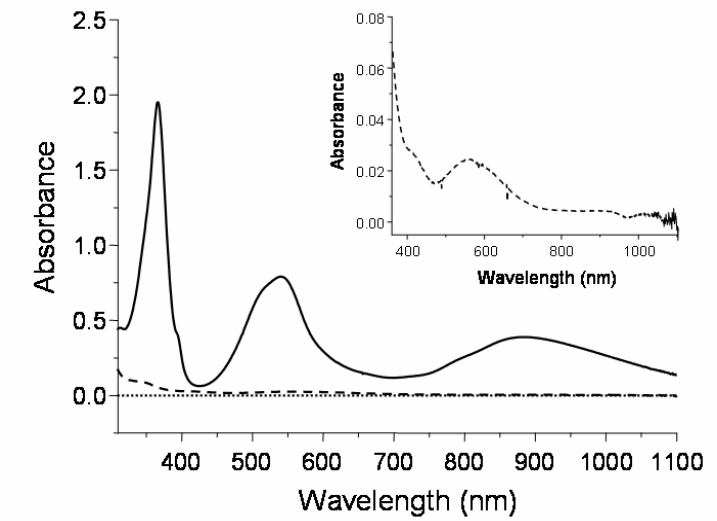



**Figure S1.** Absorption spectra of $\mathbf{1}^{2+}$ (dashed line and inset) and $\mathbf{2}^{2+}$ (solid line); the latter was generated by 1-electron reduction of the former with $Na_2S_2O_4$ in pH 10.0 carbonate buffer.

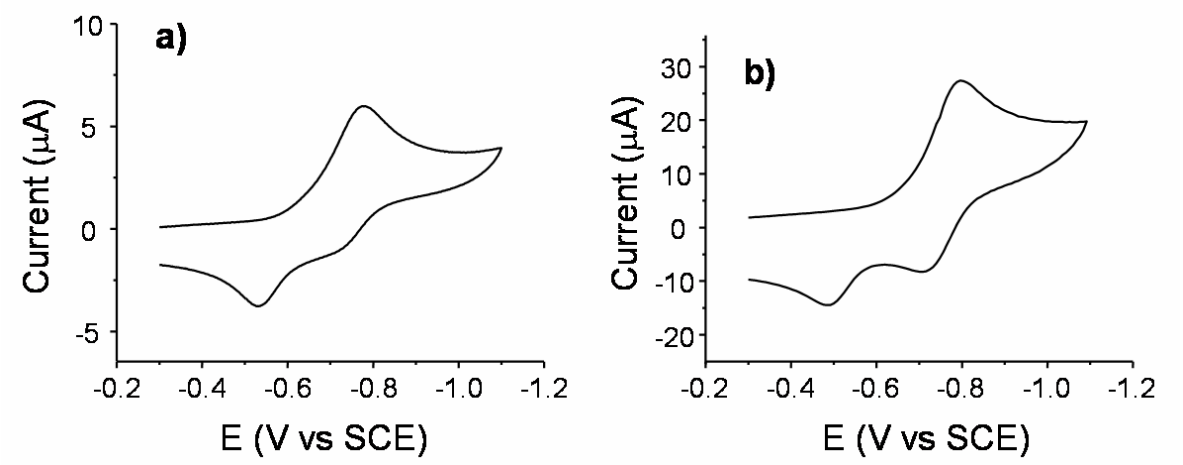



**Figure S2.** Cyclic voltammograms of a 0.6 mM solution of the CT-complex $\mathbf{1}^{2+}$ in 0.1 M phosphate buffer solution (pH 7.0). a) Scan rate = 100 mV $s^{-1}$ and b) Scan rate = 3 V $s^{-1}$.

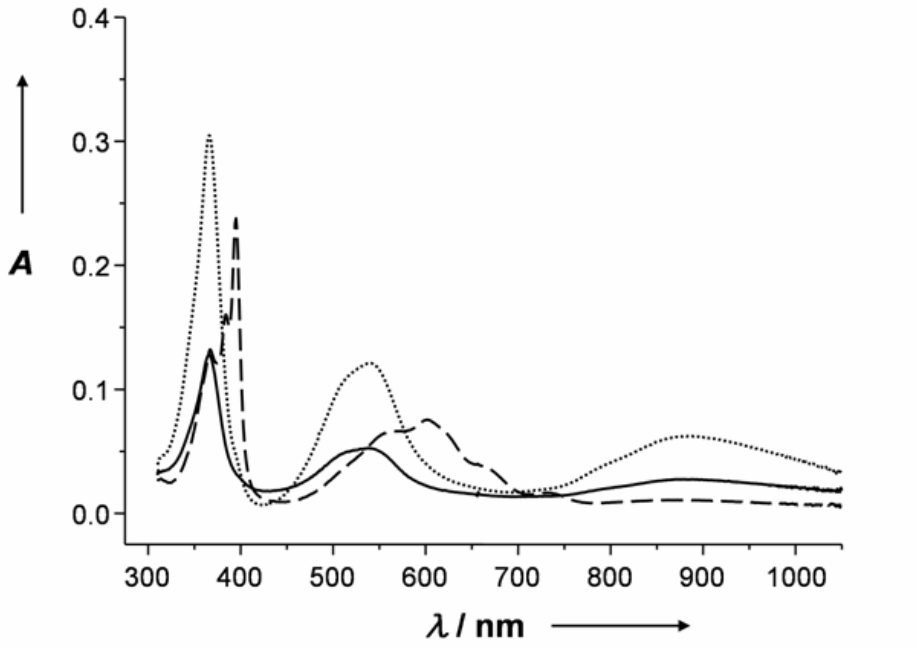
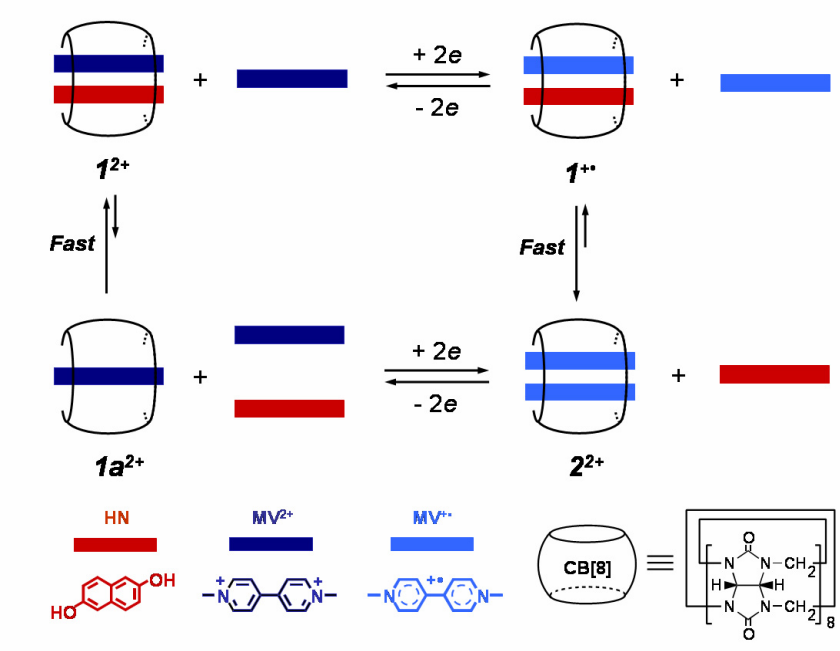
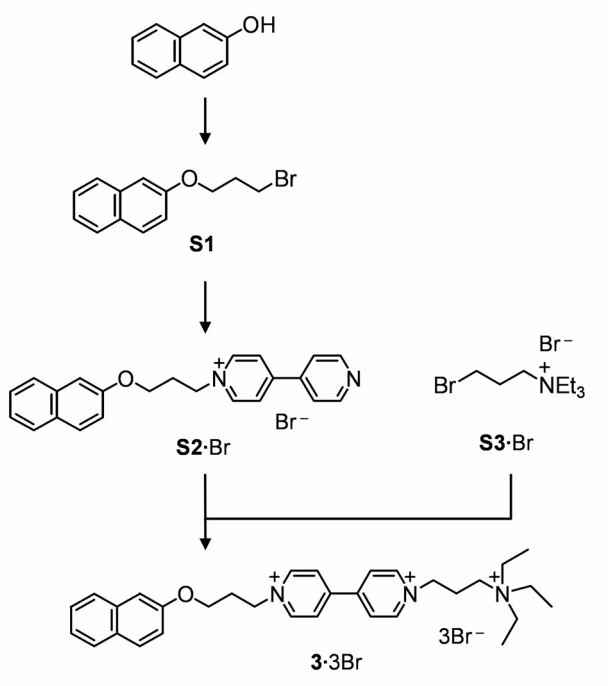



**Figure S3**. Absorption spectra of $\mathbf{MV}^{2+}$ (dashed line), $\mathbf{1}^{2+}$ (solid line), and in the presence of additional 1 equiv of free $\mathbf{MV}^{2+}$ (dotted line) in 0.1 M phosphate buffer solution (pH 7.0). (Applied potential, –0.85 V vs SCE).




**Scheme S1.** Proposed mechanism of the redox-controlled reversible transformation between hetero-guest pair ($\mathbf{1}^{2+}$) and homo-guest pair ($\mathbf{2}^{2+}$) inclusion in CB[8] triggered by electrochemical stimuli.




**Scheme S2.** Synthetic scheme for **3**·3Br.

**2-(3-Bromopropoxy)naphthalnene (S1):** A solution of naphthalene-2-ol (0.50 g, 3.50 mmol) and 1,3-dibromopropane (14.0 g, 69.3 mmol) in DMF (0.4 mL) in the presence of $K_2CO_3$ (4.79 g, 35.0 mmol) was stirred for 27 h at 50 °C. Usual aqueous workup followed by purification using column chromatography gave **S1** (0.65 g, 71 %). $^1$H NMR (500 MHz, [$D_6$]DMSO, 25 °C, TMS): $\delta$ = 7.84 – 7.80 (m, 3H; Np), 7.46 (t, *J* (H,H) = 7.5 Hz, 1H; Np), 7.36 – 7.33 (m, 2H; Np), 7.18 (dd, *J* (H,H) = 2.3, 9.0 Hz, 1H; Np), 4.21 (t, *J* (H,H) = 6.0 Hz, 2H; $OCH_2$), 3.72 (t, *J* (H,H) = 6.5 Hz, 2H; $CH_2Br$), 2.32 (m, 2H; $CH_2$); $^{13}$C NMR (125 MHz, [$D_6$]DMSO): $\delta$ = 157.13, 135.13, 130.21, 129.41, 128.38, 127.58, 127.28, 124.50, 119.53, 107.66, 66.23, 32.71, 32.21.

**1-[3-(Naphthalen-2-yloxy)propyl]-4,4'-bipyridinyl (S2·Br):** A solution of **S1** (0.43 g, 1.53 mmol) and 4,4'-dipyridyl (1.19 g, 7.63 mmol) in DMF (2 mL) was stirred for 22 h at 80 °C. After cooling to room temperature, ethyl acetate was added to the solution to produce a precipitate which was collected by filtration and washed with ethyl acetate to provide the desired product (0.60 g, 93 %). $^1$H NMR (500 MHz, [$D_6$]DMSO, 25 °C, TMS): $\delta$ = 9.29 (d, *J* (H,H) = 6.6 Hz, 2H; Py), 8.88 (d, *J* (H,H) = 5.9 Hz, 2H; Py), 8.62 (d, *J* (H,H) = 6.6 Hz, 2H; Py), 8.02 (d, *J* (H,H) = 5.9 Hz, 2H; Py), 7.81 – 7.76 (m, 3H;

Np), 7.45 (t, *J* (H,H) = 7.0 Hz, 1H; Np), 7.34 (t, *J* (H,H) = 7.1 Hz, 1H; Np), 7.26 (d, *J* (H,H) = 2.0 Hz, 1H; Np), 6.92 (dd, *J* (H,H) = 2.2, 8.9 Hz, 1H; Np), 4.89 (t, *J* (H,H) = 6.8 Hz, 2H; $NCH_2$), 4.26 (t, *J* (H,H) = 5.6 Hz, 2H; $OCH_2$), 2.56 (m, 2H; $CH_2$); $^{13}C$ NMR (125 MHz, [$D_6$]DMSO): $\delta$ = 156.66, 151.91, 146.54, 141.75, 135.00, 130.18, 129.43, 128.40, 127.51, 127.37, 126.13, 124.61, 122.78, 119.13, 107.62, 65.79, 59.50, 30.69; FAB-MS *m/z* 341.20 $[M\text{-}Br]^+$; Elemental analysis calcd for $C_{23}H_{21}BrN_2O{\cdot}0.25H_2O$: C 64.87, H 5.09, N 6.58; found: C 64.87, H 5.03, N 6.76.

**(3-Bromopropyl)triethylammonium bromide (S3·Br):** Stirring of a solution of triethylamine (0.60g, 5.93 mmol) and 1,3-dibromopropane (23.9 g, 118.6 mmol) in THF (3 mL) for 10 h at room temperature. Diethylether was added to make a precipitate which was collected by filtration to provide the desired product (0.60 g, 34 %). $^1H$ NMR (500 MHz, $D_2O$, 25 °C, TMS): $\delta$ = 3.57 (t, *J* (H,H) = 6.0 Hz, 2H; $NCH_2$), 3.40 - 3.32 (m, 8H; $BrCH_2$, $NCH_2$), 1.31(t, *J* (H,H) = 7.2 Hz, 9H; $CH_3$); $^{13}C$ NMR (125 MHz, $D_2O$): $\delta$ = 55.73, 53.23, 29.66, 24.60, 7.05; HRMS (ESI) calcd for $C_9H_{21}BrN$ $[M\text{-}Br]^+$ *m/z* 222.0857; found: 222.0852.

**Synthesis of 3·3Br:** A solution of **S2** (0.10 g, 0.23 mmol) and **S3** (0.21 g, 0.71 mmol) in $CH_3CN$ (10 mL) was refluxed for 7 d and then cooled to room temperature. The resulting precipitate was collected and washed with $CH_3CN$ to yield the desired product as a bromide salt (0.065 g, 38 %). $^1H$ NMR (500 MHz, $D_2O$, 25 °C, TMS): $\delta$ = 9.19 (t, *J* (H,H) = 6.1 Hz, 4H; Py), 8.44 (m, 4H; Py), 7.85 (d, *J* (H,H) = 8.1 Hz, 1H; Np), 7.79 (t, *J* (H,H) = 8.4 Hz, 2H; Np), 7.52 (t, *J* (H,H) = 7.5 Hz, 1H; Np), 7.44 (t, *J* (H,H) = 7.5 Hz, 1H; Np), 7.24 (d, *J* (H,H) = 2.0 Hz, 1H; Np), 6.96 (dd, *J* (H,H) = 2.4, 8.9 Hz, 1H; Np), 5.04 (t, *J* (H,H) = 6.3 Hz, 2H; Py-$CH_2$), 4.87 (t, *J* (H,H) = 7.9 Hz, 2H; Py-$CH_2$), 4.43 (t, *J* (H,H) = 5.3 Hz, 2H; $OCH_2$), 3.46 (t, *J* (H,H) = 8.4 Hz, 2H; $NCH_2$), 3.39 (q, *J* (H,H) = 7.2 Hz, 6H; $NCH_2$), 2.74 (m, *J* (H,H) = 5.6 Hz, 2H; $CH_2$), 2.63 - 2.56 (m, 2H; $CH_2$), 1.34 (t, *J* (H,H) = 7.2 Hz, 9H; $CH_3$); $^{13}C$ NMR (125 MHz, $D_2O$): $\delta$ = 155.57, 150.77, 149.93, 146.25, 145.98, 134.41, 130.04, 129.13, 128.05, 127.57, 127.38, 127.17, 127.11, 124.77, 118.33, 107.53, 65.33, 60.66, 58.62, 53.56, 53.06, 29.68, 23.86, 7.14; HRMS (ESI) calcd for $C_{32}H_{42}BrN_3O$ $[M\text{-}2Br]^{2+}$ *m/z* 281.6250; found: 281.6255.

**Synthesis 4·3Br:** To a solution of **3**·3Br (7.0 mg, 9.7 $\mu$mol) in $D_2O$ (4 mL) was added CB[8]·$H_2SO_4$·$16H_2O$ (20.0 mg, 11.6 $\mu$mol) and the resulting mixture was sonicated for 1

min. Undissolved solid was filtered off and the filtrate was slowly evaporated under a reduce pressure to yield the product as a bromide salt (18.2 mg, 92 %). $^1$H NMR (500 MHz, $D_2O$, 25 $^oC$, TMS): $\delta$ = 8.84 (d, *J* (H,H) = 6.3 Hz, 1H; Py), 8.79 (d, *J* (H,H) = 6.6 Hz, 2H; Py), 8.76 (d, *J* (H,H) = 6.3 Hz, 1H; Py), 6.85 - 6.78 (m, 2H; Py, Np), 6.74 (d, *J* (H,H) = 6.5 Hz, 3H; Py, Np), 6.65 (d, *J* (H,H) = 8.9 Hz, 1H; Np), 6.62 (d, *J* (H,H) = 4.8 Hz; Np), 6.56 (d, *J* (H,H) = 8.1 Hz, 1H; Np), 6.51 (d, *J* (H,H) = 3.4 Hz, 2H; Np), 6.06 (d, *J* (H,H) = 1.9 Hz, 1H; Np), 5.72 (dd, *J* (H,H) = 9.2, 15.3 Hz, 16H; CB[8]), 5.47 (s, 16H; CB[8]), 5.08 - 5.02 (m, 2H; Py-$CH_2$), 4.91 - 4.88 (m, 2H; Py-$CH_2$), 4.62 - 4.57 (m, 2H; $OCH_2$), 4.21 - 4.16 (dd, *J* (H,H) = 9.2, 15.3 Hz, 16H; CB[8]), 3.66 (t, *J* (H,H) = 9.1 Hz, 2H; $NCH_2$), 3.57 - 3.56 (m, 6H; $NCH_2$), 2.99 - 2.66 (m, 4H; $CH_2$), 1.46 (t, *J* (H,H) = 7.11 Hz, 9H; $CH_3$); HRMS (ESI) calcd for $C_{80}H_{90}N_{35}O_{17}$ $[M-3Br]^{3+}$ *m/z* 604.2418; found: 604.2411.

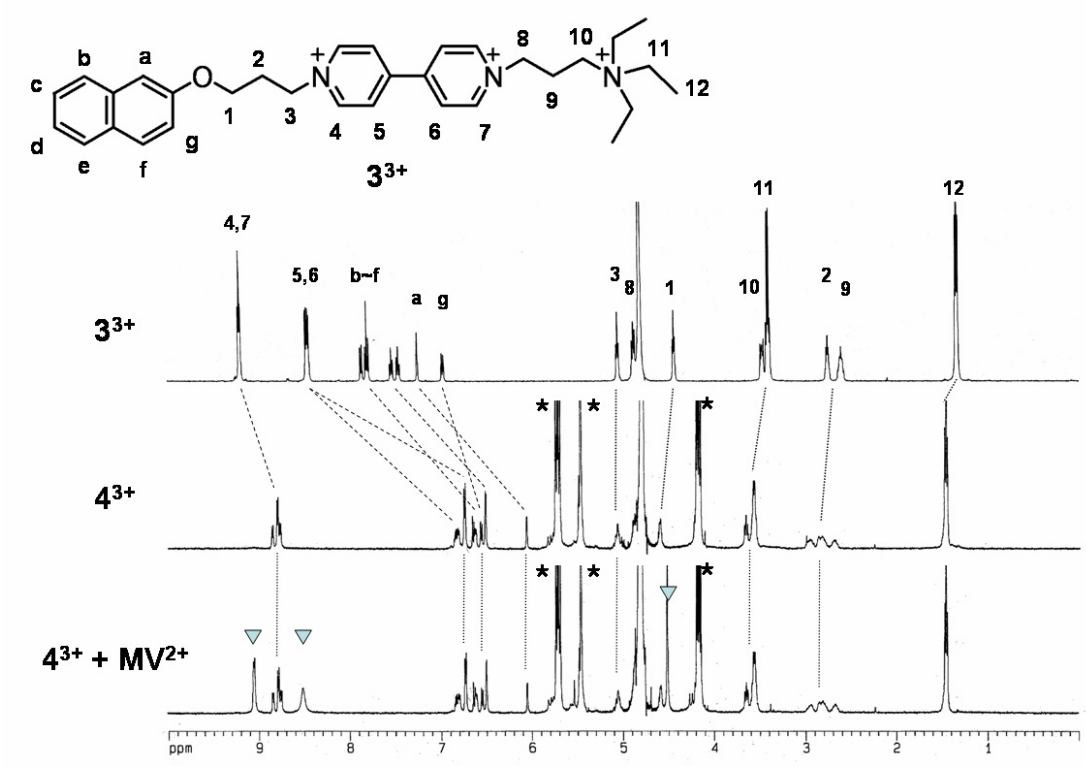



**Figure S4.** $^1$H NMR spectra of $\mathbf{3}^{3+}$, $\mathbf{4}^{3+}$, and $\mathbf{4}^{3+}$ and 1 equiv of $\mathbf{MV}^{2+}$. The signals labeled with asterisks and triangles correspond to the CB[8] host and $\mathbf{MV}^{2+}$, respectively.

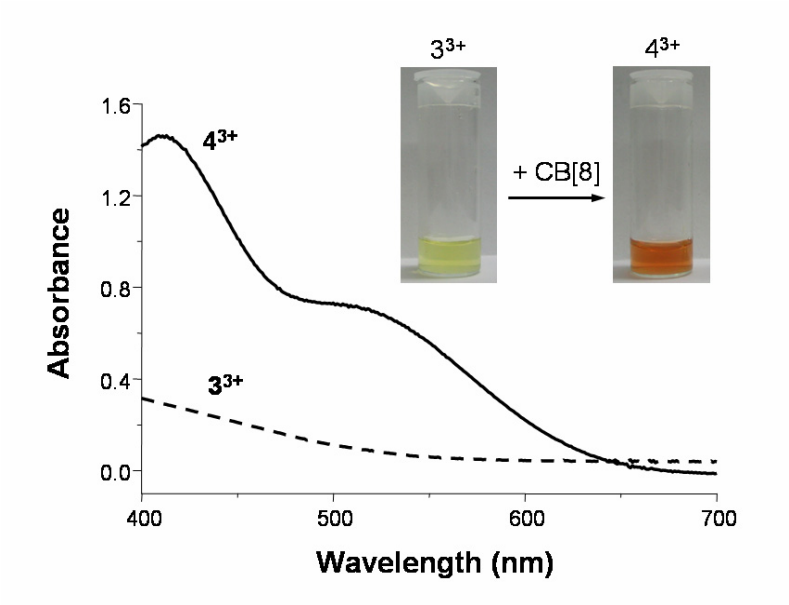
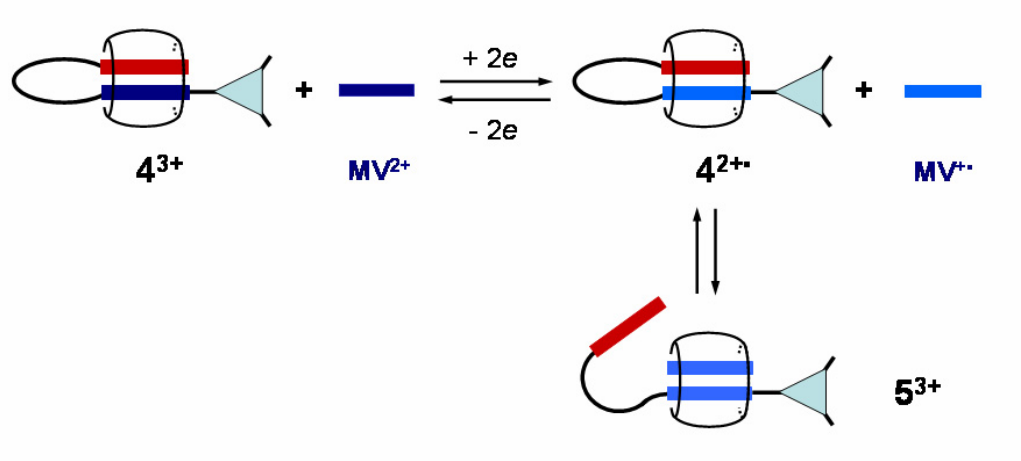



**Figure S5.** Absorption spectra of $\mathbf{3}^{3+}$ (dashed line), and $\mathbf{4}^{3+}$ (solid line) in $H_2O$; the latter shows CT bands at 411 and 530 nm.




**Scheme S3.** Proposed mechanism of the redox-driven reversible transformation between "closed" conformation ($\mathbf{4}^{3+}$) and "open" conformation ($\mathbf{5}^{3+}$) triggered by redox stimuli.

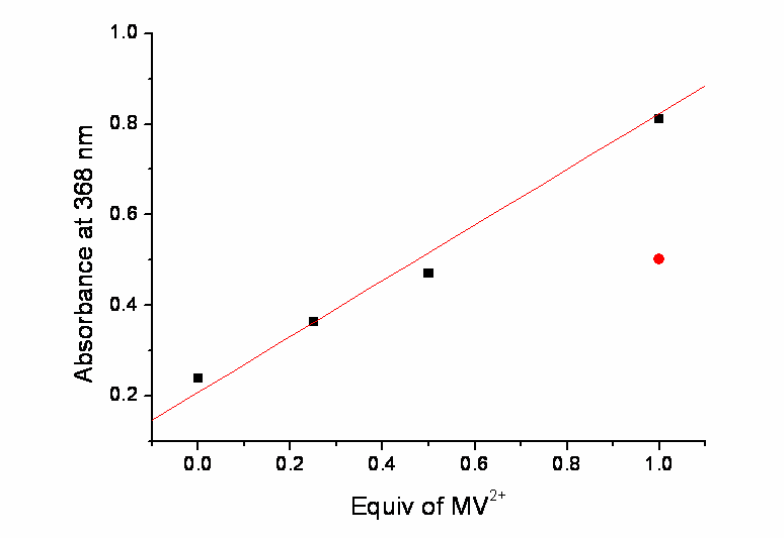



**Figure S6.** The change in the absorbance at 368 nm after the reduction of $\mathbf{4}^{3+}$ (0.25 mM, pH 10.0 carbonate buffer) with $Na_2S_2O_4$ in the presence of increasing amounts of $\mathbf{MV}^{2+}$. The red solid circle represents the absorbance at 368 nm after the reduction of a 1:1 mixture of CB[8] and $\mathbf{MV}^{2+}$ (0.25 mM, pH 10.0 carbonate buffer) with $Na_2S_2O_4$.