Electronic Supplementary Information (ESI)

Synthesis of cationic molybdenum-cobalt heterometallic clusters protected against hydrolysis by macrocyclic triazacyclononane complexes

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Table S1. Precedent for capping groups to isolate polyoxomolybdates

Formula	Capping group	Ref.
$[NBu^n_4]_2[\{(\eta^5\text{-}C_5Me_5)Rh\}_2Mo_6O_{20}(OMe)_2]$	$(\eta^5\text{-}C_5Me_5)Rh$	(S1)
$[(\eta^5\text{-}C_5Me_5)MMoO_4]_4$ (M = Rh and Ir)	$(\eta^5\text{-}C_5Me_5)M$	
	(M = Rh and Ir)	(S2)
$[\{(\eta^5\text{-}C_5Me_5)Rh\}_2Mo_3O_9(OMe)_4]$	$(\eta^5\text{-}C_5Me_5)Rh$	(S3)
$[\{(\eta^5\text{-}C_5Me_5)Rh\}_4Mo_6O_{22}]$	$(\eta^5\text{-}C_5Me_5)Rh$	(S3)
$[\{(\eta^6\text{-}C_6Me_6)Ru\}_2Mo_5O_{18}\{(\eta^6\text{-}C_6Me_6)Ru(H_2O)\}]$	$(\eta^6\text{-}C_6Me_6)Ru$	(S4)
$[\{Ru(\eta^6\text{-}C_6Me_6)\}_4Mo_4O_{16}]$	$(\eta^6\text{-}C_6Me_6)Ru$	(S4)
$(NMe_4)[Mo_5O_{13}(OCH_3)_4(NO)\{(\eta^5\text{-}C_5Me_5)Rh(H_2O)\}]$	$(\eta^5\text{-}C_5Me_5)Rh$	(S5)
$[Mo_5O_{13}(OCH_3)_4(NO)\{\{\eta^5\text{-}C_5Me_5\}Rh\}_2(\eta\text{-}Cl)]]$	$(\eta^5\text{-}C_5Me_5)Rh$	(S5)
$[\{(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)Ru\}_4Mo_4O_{16}]$	$(\eta^6\text{-}p\text{-}MeC_6H_4Pr^i)Ru$	(S6)
$(NBu^n_4)_2[\{(\eta^6\text{-}C_6Me_6)Ru\}_2Mo_6O_{20}(OMe)_2]$	$(\eta^6\text{-}C_6Me_6)Ru$	(S7)

(S1) S. Takara, T. Nishioka, I. Kinoshita and K. Isobe, *Chem. Commun.*, 1997, **20**, 891–892.

(S2) Y. Hayashi, K. Toriumi and K. Isobe, *J. Am. Chem. Soc.*, 1988, **110**, 3666–3668.

(S3) Y. Do, X. Z. You, C. Zhang, Y. Ozawa and K. Isobe, *J. Am. Chem. Soc.*, 1991, **113**, 5892–5893.

(S4) V. Artero, A. Proust, P. Herson and P. Gouzerh, *Chem. - A Eur. J.*, 2001, **7**, 3901–3910.

(S5) A. Proust, P. Gouzerh and F. Robert, *Angew. Chemie Int. Ed. English*, 1993, **32**, 115–116.

(S6) V. Artero, A. Proust, P. Herson, R. Thouvenot and P. Gouzerh, *Chem. Commun.*, 2000, 883–884.

(S7) R. Villanneau, V. Artero, D. Laurencin, P. Herson, A. Proust and P. Gouzerh, *J. Mol. Struct.*, 2003, **656**, 67–77.

Abbreviations and molecular weight for $[Co(tacn)(H_2O)_3](CF_3SO_3)_3$ and complexes **1−4**

	Abbreviations	Molecular weight
$[Co(tacn)(H_2O)_3](CF_3SO_3)_3 \cdot H_2O$	----	707.41
$[\{Co(C_6H_{15}N_3)\}_2Mo_3O_{12}] \cdot 2NaCF_3SO_3 \cdot 7H_2O$	**1**	1326.42
$[\{Co(C_6H_{15}N_3)\}_4H_2Mo_7O_{27}](CF_3SO_3)_2 \cdot 13H_2O$	**2**	2372.66
$[\{Co(C_6H_{15}N_3)\}_4H_3Mo_4O_{17}](CF_3SO_3)_5 \cdot 6H_2O$	**3**	2264.94
$[Co_2(C_6H_{15}N_3)_2(C_5H_5N)Mo_5O_{18}] \cdot 4.5H_2O$	**4**	1304.24

Synthetic procedures from **1**

Transformation of 1 into 2. Crystals of **1** (8.75×10^{-3} mmol, 11.6 mg) was dissolved in water (86 mg), and then $[Co(tacn)(H_2O)_3]$ $(CF_3SO_3)_3 \cdot H_2O$ (2.26×10^{-3} mmol, 1.6 mg) was added. The solution was kept at 5ºC. After few days, a few amount crystals of **2** were formed together with unidentified solids. From the IR spectrum, the product was identified to **2** (Figure S2). FT-IR (KBr pellet, 1000-500 cm^{-1}): 912 (s, sh), 893 (s, br), 862 (s, br), 846 (s, br), 673 (m, sh), 640 (s, sh), 575 (m, sh), 544 (m, sh).

Transformation of 1 into 3. Crystals of **1** (4.15×10^{-3} mmol, 5.5 mg) was dissolved in water (55 mg), and then $[Co(tacn)(H_2O)_3](CF_3SO_3)_3 \cdot H_2O$ (1.98×10^{-3} mmol, 1.4 mg) was added. The solution pH value was around 3 as measured using pH meter. After 3 days, purple crystals were formed (Yield: 1.8 mg, 38.17% based on Mo). From the IR spectrum, the product was identified to **3** (Figure S2). FT-IR (KBr pellet, 1000-500 cm^{-1}): 987 (w, sh), 918 (s, sh), 877 (s, sh), 851 (s, sh), 642 (s, sh), 554 (w, br), 518 (w, sh).

Transformation of 1 into 4. Crystals of **1** (4.37×10^{-3} mmol, 5.8 mg) was dissolved in water (91 mg), and then pyridine (0.05 mL) was added. The solution color turned red from purple after standing overnight. Red crystals of **4** were harvested after standing for 12 days (Yield: 0.4 mg, 7.36% based on Mo). From the IR spectrum, the product was identified to **4** (Figure S2). FT-IR (KBr pellet, 1000−500 cm^{-1}): 892 (s, br), 867 (s, br), 850 (s, br), 834 (s, br), 804 (s, sh), 768 (s, sh), 723 (s, sh), 703 (s, sh), 641 (m, sh), 602 (m, sh), 546 (m, sh), 520 (m, sh).

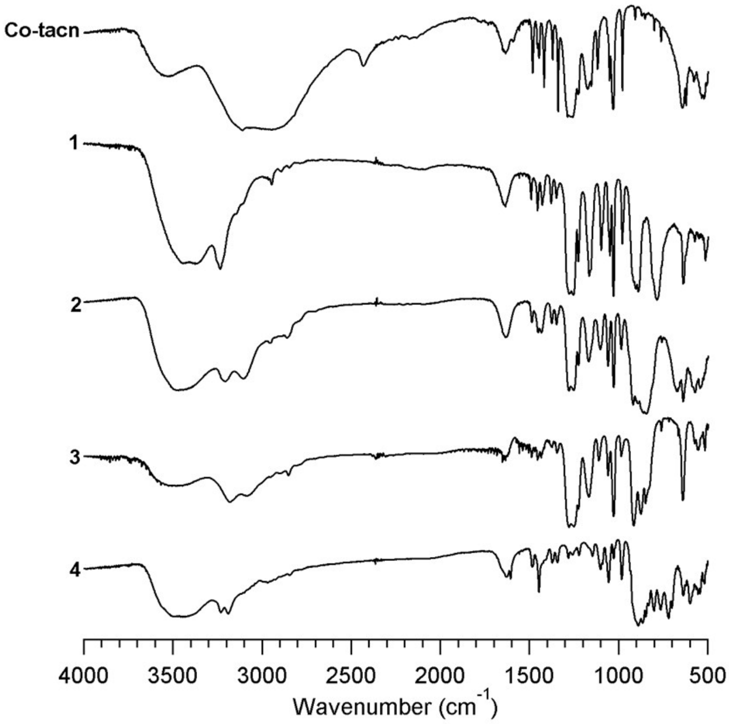

Figure S1. IR spectra of $[Co(tacn)(H_2O)_3](CF_3SO_3)_3$ and clusters **1−4** (KBr disk).

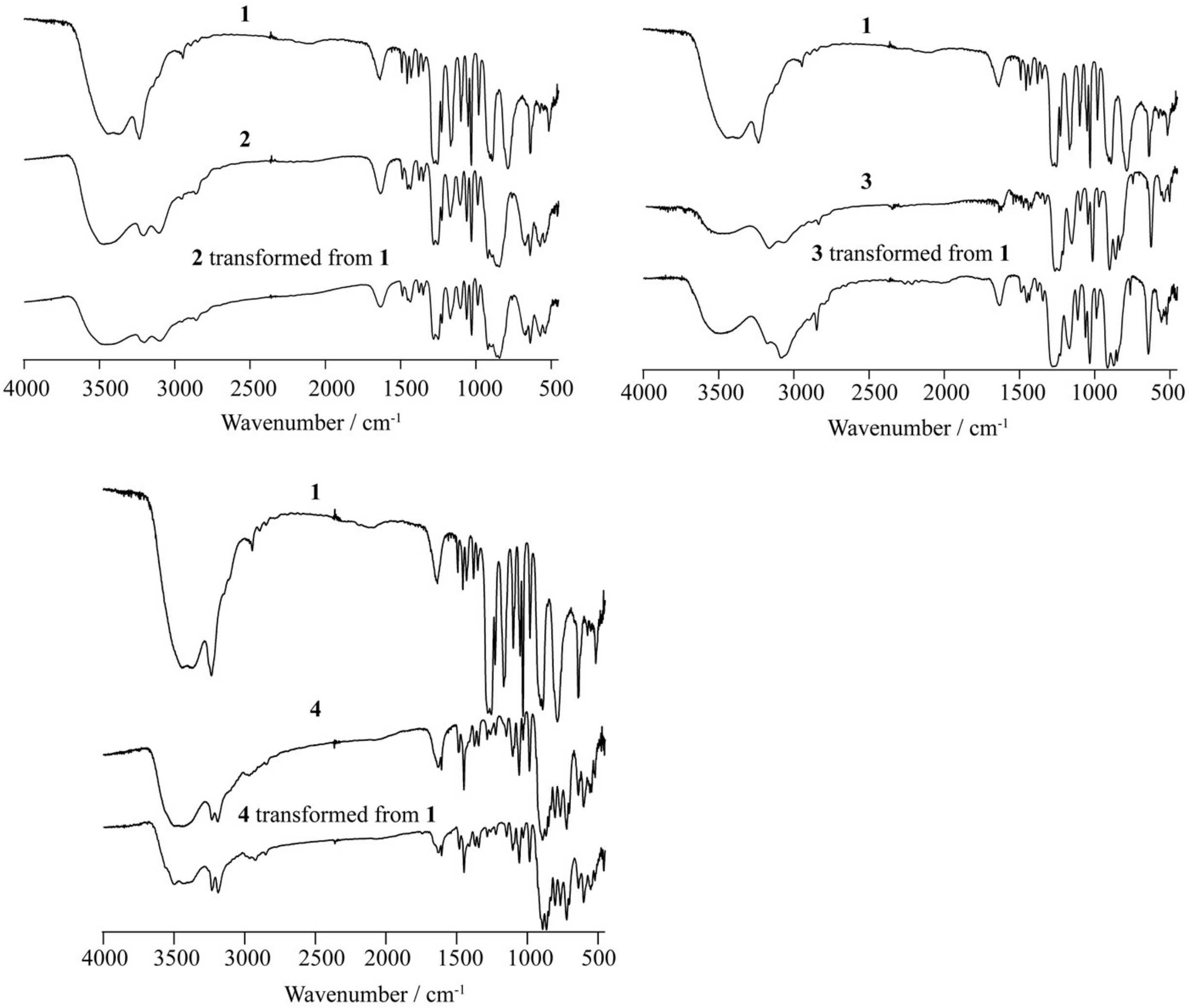

Figure S2. Identification of complexes **2**–**4** synthesized from complex **1**.

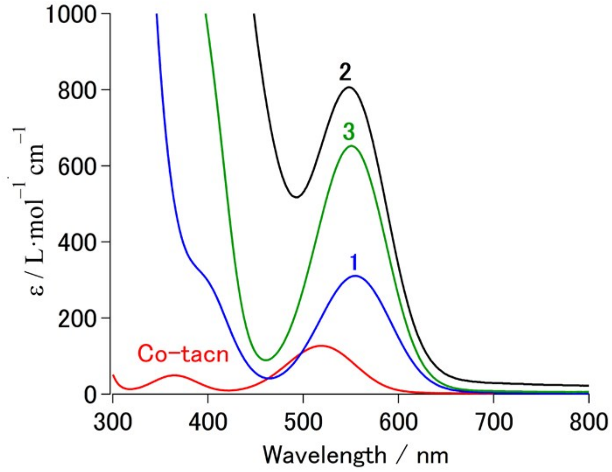

Figure S3. UV−Vis absorption spectra of $[Co(tacn)(H_2O)_3](CF_3SO_3)$ and clusters **1−3** in water.

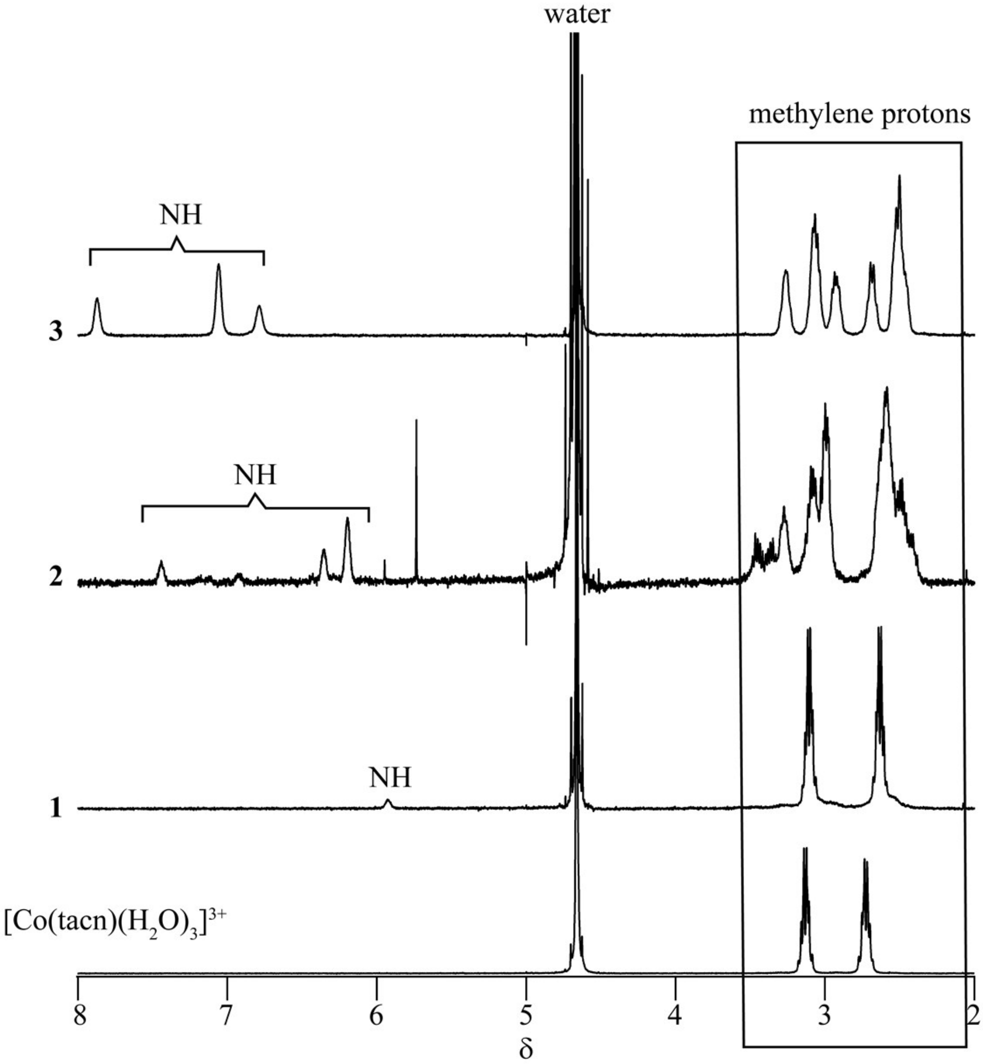

Figure S4. ^{1}H NMR spectra of [Co(tacn)(H$_2$O)$_3$]$^{3+}$, **1**, **2**, and **3** in D$_2$O. The signal intensities of NH protons depend on the chemical environments. The NH protons on [Co(tacn)(H$_2$O)$_3$]$^{3+}$ were unobservable because the exposed NH protons are easily H/D exchange in D$_2$O. In the case of clusters **1**, **2**, and **3**, NH protons on tacn ligands interact with terminal oxygen atoms of molybdate core to form hydrogen bonds, and some of the NH protons interact with solvent water molecules. Therefore, the rates of H/D exchange are different depending on the chemical environment and the rates depend on how strong the NH protons are hydrogen bonded in the cluster core.

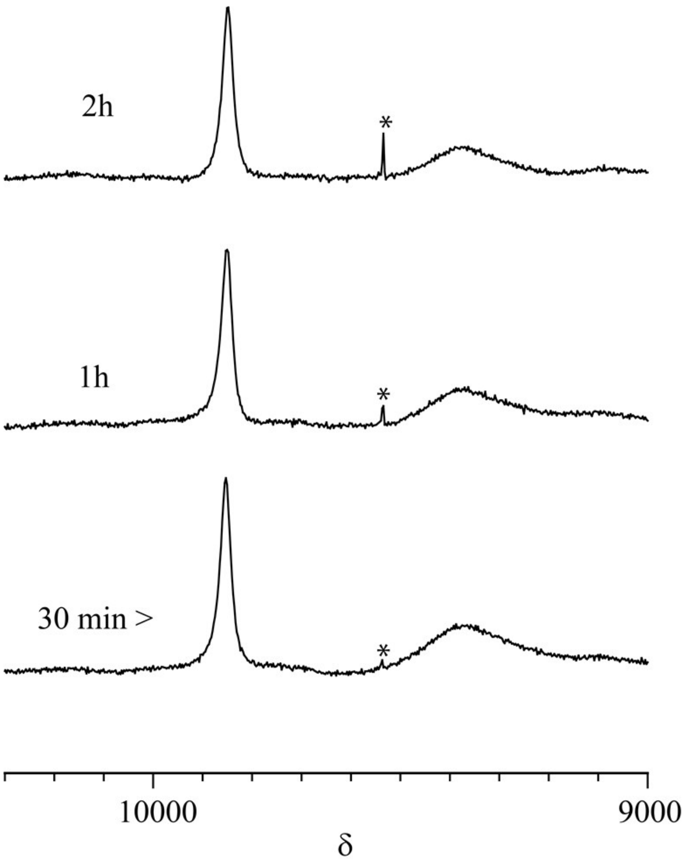

Figure S5. Time-dependent ^{59}Co NMR studies for cluster **3** in water.

* is a signal from $[Co(tacn)(H_2O)_3]^{3+}$ and the integration ratio indicate the dissociation of cluster **3** group is less than 5% at 2h.