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COMMUNICATION

Control over preference for binding sites of polyoxometalates to silver ethynide clusters by surface charge modification[†]

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Sho Tamari,^a Kosuke Ono,^b Masato Hashimoto^c and Tomoji Ozeki*^d

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A polyoxometalate—silver ethynide composite cluster, $[\text{Ag}_{42}(\text{CO}_3)(\text{C}\equiv\text{C}(\text{CH}_3)_3)_{27}(\alpha\text{-A-SiW}_9\text{Nb}_3\text{O}_{40})_2]^-$ (1**), demonstrates that we can select the binding site of a polyoxometalate to the silver alkynide cluster by tuning the surface charge of the precursor polyoxometalate. Multidimensional and multinuclear NMR spectra revealed that **1** maintains its precise atomic connectivity in the solution.**

Polyoxometalates^{1–3} have long been attracting increasing interest due to various applications based on versatile structures. Polyoxometalate—silver alkynide composite clusters^{4–11} can potentially exhibit much wider structural variety. We are especially interested in those where polyoxometalates are partially covered by silver alkynide moieties^{5, 7, 11} because they will give us information about the difference in the affinity to the silver alkynide cluster moieties between various sites on the surface of the precursor polyoxometalates. We recently reported that triply Nb-substituted Dawson polyoxotungstate, $[\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62}]^{9-}$, selectively bind to silver alkynide cluster at its Nb-substituted hemisphere.¹¹ Here we report the reaction of Nb-substituted Keggin polyoxotungstate, $[\alpha\text{-A-SiW}_9\text{Nb}_3\text{O}_{40}]^{7-}$, with silver alkynide, from which a novel polyoxometalate—silver alkynide composite cluster, $[\text{Ag}_{42}(\text{CO}_3)(\text{C}\equiv\text{C}^t\text{Bu})_{27}(\text{SiW}_9\text{Nb}_3\text{O}_{40})_2]^-$ (**1**), was obtained [^tBu = C(CH₃)₃]. In **1**, the Keggin polyoxometalate is bonded to the silver alkynide cluster moiety at the opposite site compared with its analogue, $[\text{Ag}_{42}(\text{CO}_3)(\text{C}\equiv\text{C}^t\text{Bu})_{27}(\text{CH}_3\text{CN})_2(\text{CoW}_{12}\text{O}_{40})_2]^+$ (**2**).⁵ Specifically, the corner shared triad of metal-oxo octahedra bind to the silver ethynide groups in **1** while the edge shared triad of metal-oxo octahedra bind to the silver ethynide groups in **2**.

The reaction of $[(\text{C}_4\text{H}_9)_4\text{N}]_7[\alpha\text{-A-SiW}_9\text{Nb}_3\text{O}_{40}]$ with $\text{AgC}\equiv\text{C}^t\text{Bu}$ and $\text{CF}_3\text{SO}_3\text{Ag}$ in CH_3CN yielded colourless crystals of $[(\text{C}_4\text{H}_9)_4\text{N}][\text{Ag}_{42}(\text{CO}_3)(\text{C}\equiv\text{C}^t\text{Bu})_{27}(\text{SiW}_9\text{Nb}_3\text{O}_{40})_2] \cdot 5\text{CH}_3\text{CN}$ (**1a**) that shows characteristic IR absorption at 210 cm^{-1} assignable to the stretching of $\text{C}\equiv\text{C}$.[†] Single crystal X-ray diffraction revealed that compound **1a** contains a polyoxometalate—silver alkynide composite cluster, $[\text{Ag}_{42}(\text{CO}_3)(\text{C}\equiv\text{C}^t\text{Bu})_{27}(\text{SiW}_9\text{Nb}_3\text{O}_{40})_2]^-$ (**1**, Fig. 1), where two $[\alpha\text{-A-SiW}_9\text{Nb}_3\text{O}_{40}]^{7-}$ polyoxometalates are capping the both openings of a toroidal Ag_{42} cluster. The exterior of the Ag_{42} toroid is decorated by 27 $\text{C}\equiv\text{C}^t\text{Bu}$ ligands and its central cavity is occupied by a CO_3^{2-} core.⁵

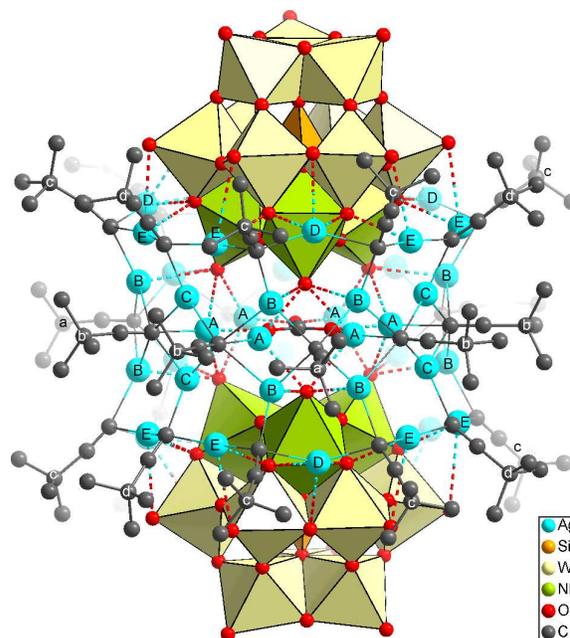


Fig. 1. A mixed polyhedral (for the polyoxometalates) and ball-and-stick (for the Ag ethynide cluster) representation of **1**. Hydrogen atoms are omitted for clarity. Ag atoms and $\text{C}\equiv\text{C}^t\text{Bu}$ ligands are labelled according to their type (A–E for Ag and a–d for $\text{C}\equiv\text{C}^t\text{Bu}$; see text).

The structure of **1** approximates to the D_{3h} symmetry, based on which its Ag atoms are classified into five types (type

^a Department of Chemistry and Materials Science, Tokyo Institute of Technology, 2-12-1 O-okayama, Meguro-ku, Tokyo 152-8551, Japan.

^b Department of Chemistry, Faculty of Science, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku-ku, Tokyo 162-8601, Japan.

^c Department of Material Science and Chemistry, Faculty of Systems Engineering, Wakayama University, 930 Sakaedani, Wakayama 640-8510, Japan.

^d Department of Chemistry, College of Humanities and Sciences, Nihon University, 3-25-40 Sakurajosui, Setagaya-ku, Tokyo 156-8550, Japan.

[†] Electronic Supplementary Information (ESI) available: Experimental details, additional crystallographic illustrations, powder X-ray diffraction pattern, IR spectrum and the NMR spectra. CCDC 1413590. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x

A to E). The 42 Ag atoms are arranged in five layers that are perpendicular to the 3-fold axis. The central layer consists of hexagonally arranged six Ag atoms (type A). A type A Ag atom is bonded to an O atom of the central CO_3^{2-} core with the $\text{Ag}\cdots\text{O}$ distance ranging from 2.18 to 2.21 Å and is also bonded to two terminal O(Nb) atoms of two $[\alpha\text{-A-SiW}_9\text{Nb}_3\text{O}_{40}]^{7-}$. Above and below the central layer are Ag_9 rings, each of which consists of six type B and three type C Ag atoms. A type B Ag atom is bonded to a terminal O(Nb) of $[\alpha\text{-A-SiW}_9\text{Nb}_3\text{O}_{40}]^{7-}$, while the type C Ag atoms have no short contacts with polyoxometalate oxygen atoms.¹¹ The top and bottom layers consist of Ag_9 rings (three type D and six type E Ag atoms each) that are staggered to their adjacent Ag_9 rings. A type D Ag atom is bonded to two $\mu_2\text{-O(NbW)}$ and a $\mu_2\text{-O(edge-sharing W}_2)$, while a type E Ag atom is bonded to a $\mu_2\text{-O(NbW)}$ and a terminal O(W) atom.

The 27 $\text{C}\equiv\text{C}^t\text{Bu}$ ligands are arranged in three layers and can be classified into four types (type a to d, Fig. 2). The central layer contains nine $\text{C}\equiv\text{C}^t\text{Bu}$ ligands (three type a and six type b). A type a ligand bridges four type B Ag atoms, while a type b ligand bridges one type A, two type B and two type C Ag atoms. Top and bottom layers contain nine $\text{C}\equiv\text{C}^t\text{Bu}$ ligands each (six type c and three type d). A type c ligand bridges one type B, one type D and one type E Ag atoms, while a type d ligand bridges one type C and two type E Ag atoms.

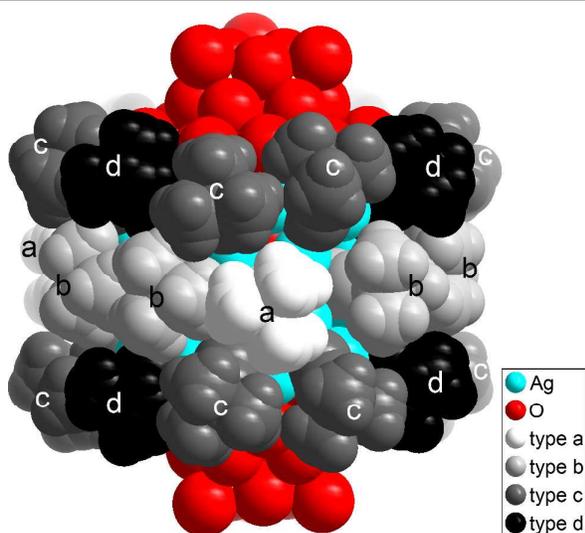


Fig. 2. Space filling representation of **1**. Atoms in the $\text{C}\equiv\text{C}^t\text{Bu}$ ligands of types a, b, c and d are shown as white, light grey, dark grey and black spheres, respectively.

The ^1H NMR spectra unambiguously demonstrate that the structure of **1** is maintained in the solution. **1** gives four ^1H NMR signals at 1.78, 1.66, 1.51 and 1.46 ppm with an approximate integrated intensity ratio of 2:1:2:4. Although this ratio allowed us to assign the signals at 1.66 and 1.46 ppm to the protons in the $\text{C}\equiv\text{C}^t\text{Bu}$ ligands of types a (3 groups in **1**) and c (12 groups in **1**), signals at 1.78 and 1.51 ppm remained unassigned. A 2-D NOESY spectrum (Fig. 3) clearly resolved the problem. The signal at 1.66 ppm (type a $\text{C}\equiv\text{C}^t\text{Bu}$) showed through-space correlation with the signals at 1.78 and 1.46

ppm but showed no correlation with the one at 1.51 ppm. Thus the peaks at 1.51 and 1.78 ppm were unambiguously assigned to the H atoms in types d and b $\text{C}\equiv\text{C}^t\text{Bu}$ ligands, respectively. This correlation pattern is fully consistent with the X-ray structure of **1** (see Fig. 2) and tells that the structure of **1** in the solution is kept unchanged from that in the solid state including the coordination of the $\text{C}\equiv\text{C}^t\text{Bu}$ ligands. ^{13}C NMR that showed consistent integrated intensity ratio (Fig. S11) and C-H heteronuclear correlation (Fig. S13),¹¹ ^{29}Si NMR with single peak (Fig. S14),¹ and ^{183}W NMR with two peaks of the integrated intensity ratio of 1:2 (Fig. S15)¹¹ all support the retention of the solid-state structure in the solution. By using analytical ultracentrifugation, we demonstrated that a polyoxometalate—silver alkyne composite cluster, $[\text{Ag}_{25}(\text{C}\equiv\text{C}^t\text{Bu})_{16}(\text{CH}_3\text{CN})_4(\text{P}_2\text{W}_{15}\text{Nb}_3\text{O}_{62})]$, retains its structural integrity in the solution.¹¹ The current work further demonstrates that the retention is not only with respect to the overall molecular size but also with respect to the precise atomic connectivity. Also demonstrated by the NMR measurement was the stability of **1** in the solution: no deterioration of the sample was detected from the NMR signals measured after more than one month since the preparation of the solution.

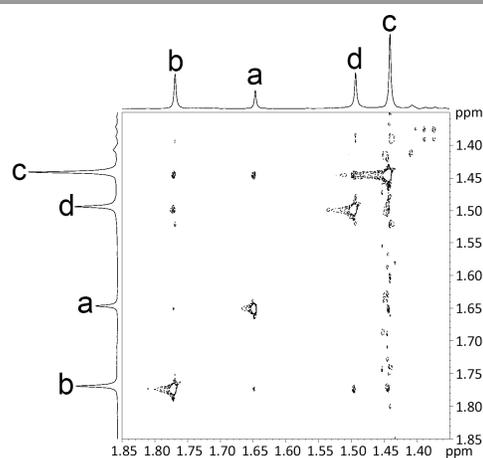


Fig. 3. ^1H NOESY spectrum of **1** in DMF-d_7 .

The largest structural difference between **1** and its analogue, $[\text{Ag}_{42}(\text{CO}_3)(\text{C}\equiv\text{C}^t\text{Bu})_{27}(\text{CH}_3\text{CN})_2(\text{CoW}_{12}\text{O}_{40})_2]^+$ (**2**),⁵ is the binding site of the Keggin polyoxometalates to the toroidal Ag_{42} clusters. The Ag_{42} cluster in **1** binds to the corner-shared triads of NbO_6 octahedra of $[\alpha\text{-A-SiW}_9\text{Nb}_3\text{O}_{40}]^{7-}$, whereas the Ag_{42} cluster in **2** binds to the edge-shared triads of WO_6 octahedra of $[\text{CoW}_{12}\text{O}_{40}]^{6-}$. Judging from the structure of **2** where the addenda atoms of the Keggin polyoxometalate are all tungsten, the affinity with the silver ethynide cluster seems stronger for the edge-shared triad than for the corner-shared triad. Increasing the surface negative charge of the corner-shared triad by the selective substitution of less positively charged Nb(V) for W(VI) successfully inverted the affinity and lead to the formation of **1** where the polyoxometalates show opposite preference for the binding site compared to the unsubstituted analogue of **2**.

The current result demonstrates that we can select the binding site of the Keggin polyoxometalate (namely, edge-shared triad or corner shared triad of metal-oxo octahedra) by tuning the surface electron density. Also demonstrated here is that the structure of polyoxometalate—silver alkynide composite cluster seems fairly robust even in the solutions.

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Notes and references

‡ Synthesis of **1a**: $\text{AgC}\equiv\text{C}^t\text{Bu}^{12}$ (55 mg, 0.29 mmol) and $\text{CF}_3\text{SO}_3\text{Ag}$ (39 mg, 0.14 mmol) were dissolved into 15 mL of CH_3CN , to which 10 mL CH_3CN dissolving 89 mg $[(\text{C}_4\text{H}_9)_4\text{N}]_7[\text{SiW}_9\text{Nb}_3\text{O}_{40}]^{13}$ was added. The reaction mixture was kept at 5 °C overnight, from which colourless crystals of

$(\text{C}_4\text{H}_9)_4\text{N}[\text{Ag}_{42}(\text{CO}_3)(\text{C}\equiv\text{C}^t\text{Bu})_{27}(\text{SiW}_9\text{Nb}_3\text{O}_{40})_2] \cdot 5\text{CH}_3\text{CN}$ were precipitated in ca. 56 % yield. Elemental analysis after drying under vacuum: calcd for $(\text{C}_4\text{H}_9)_4\text{N}[\text{Ag}_{42}(\text{CO}_3)(\text{C}\equiv\text{C}^t\text{Bu})_{27}(\text{SiW}_9\text{Nb}_3\text{O}_{40})_2]$ ($\text{C}_{179}\text{H}_{279}\text{Ag}_{42}\text{NNb}_6\text{O}_{83}\text{Si}_2\text{W}_{18}$): C, 17.58; H, 2.30; Ag, 37.06; N, 0.11; Nb, 4.56; O, 10.86; Si, 0.46; W, 27.07 %; found: C, 17.5; H, 2.21; Ag, 36.5; N, 0.17; Nb, 4.52; O, 10.1; Si, 0.50; W, 26.9 %. IR (KBr, ν/cm^{-1}): 2010m, 1629m, 1472m, 1454m, 1428m, 1389w, 1362m, 1238m, 1201w, 992w, 970sh, 956m, 909vs, 786vw, 748m, 725s, 539m, 492m. The formation of the composite cluster can be confirmed by the splitting of the band assignable to the M-O-M bending modes (786, 748 and 725 cm^{-1}). ^1H NMR (500 MHz, DMF- d_7) δ/ppm 1.78, 1.66, 1.51, 1.46. ^{13}C NMR (125 MHz, DMF- d_7) δ/ppm 3.87, 32.72, 32.32, 31.81. ^{29}Si NMR (79.4 MHz, DMPU/DMF- d_7) δ/ppm -81.3 [DMPU = *N,N'*-dimethylpropyleneurea]. ^{183}W NMR (16.6 MHz, DMPU/DMF- d_7) δ/ppm -56.6 (12W) and -102.6 (6W).

§ Crystal data for **1a**,

$[(\text{C}_4\text{H}_9)_4\text{N}][\text{Ag}_{42}(\text{CO}_3)(\text{C}\equiv\text{C}^t\text{Bu})_{27}(\text{SiW}_9\text{Nb}_3\text{O}_{40})_2] \cdot 5\text{CH}_3\text{CN}$: $\text{C}_{189}\text{H}_{294}\text{Ag}_{42}\text{N}_6\text{Nb}_6\text{O}_{83}\text{Si}_2\text{W}_{18}$, $M = 12431.8$, triclinic, space group $P\bar{1}$, $a = 21.172(1) \text{ \AA}$, $b = 24.383(1) \text{ \AA}$, $c = 31.630(1) \text{ \AA}$, $\alpha = 90.138(1)^\circ$, $\beta = 95.802(2)^\circ$, $\gamma = 93.545(1)^\circ$, $V = 16213.2(11) \text{ \AA}^3$, $Z = 2$, $T = 123 \text{ K}$, $\mu(\text{synchrotron}, \lambda = 0.6890 \text{ \AA}) = 8.306 \text{ mm}^{-1}$.

168053 reflections measured, of which 59080 independent ($R_{\text{int}} = 0.0996$). The final $R_1(F) = 0.0823$ (40942 reflections with $I > 2\sigma(I)$) and $wR(F^2) = 0.2425$ (all data). Intensity data for **1** were collected on a Rigaku Mercury CCD diffractometer using at the NW2A beamline of the Advanced Ring in the Photon Factory (PF-AR), Institute of Materials Structure Science, High Energy Accelerator Research Organization (KEK).

¶ Each of these Ag atom is disordered over two sites: the majority at the C site and the minority (whose site occupancy factor sums up to 1.02 per **1**) at a position 2.17 Å from $\mu_2\text{-O}(\text{Nb}_2)$; see ESI. However, the influence of the disorder was not detectable in any of ^1H , ^{13}C , ^{29}Si or ^{183}W NMR spectra.

|| Although it seems interesting that the H atoms in the peripheral layer show upfield shift from those in the central layer, this tendency does not apply to the ^{13}C chemical shift. HETCOR spectrum (Fig. S13) lead to the following assignment: 32.9 (type d), 32.7 (type b), 32.3 (type c) and 31.8 (type a).

⊥ The ^{29}Si NMR chemical shift of **1** in mixed DMPU/DMF- d_7 (-81.3 ppm) is comparable to those of Li^+ , Na^+ and K^+ salts of $[\alpha\text{-A-SiW}_9\text{Nb}_3\text{O}_{40}]^{7-}$ (-82.8 to -82.9 ppm in D_2O and -82.5 ppm in DMSO;⁴ see Table S5).

⊗ While both two types of W atoms in **1** show downfield (high frequency) shift compared to the corresponding signals for $[\alpha\text{-A-SiW}_9\text{Nb}_3\text{O}_{40}]^{7-}$ (W atoms adjacent to Nb: -56.6 ppm for **1** and -93.9 to -122.2 ppm for $[\alpha\text{-A-SiW}_9\text{Nb}_3\text{O}_{40}]^{7-}$; W atoms opposite to Nb: -102.6 ppm for **1** and -113.1 to -128.2 ppm for $[\alpha\text{-A-SiW}_9\text{Nb}_3\text{O}_{40}]^{7-}$),^{14, 15} a larger shift is observed for the W atoms adjacent to the Nb atoms. It is consistent with the fact that $[\alpha\text{-A-SiW}_9\text{Nb}_3\text{O}_{40}]^{7-}$ bind to the Ag_{42} toroid at the Nb substituted triad and therefore the W atoms adjacent to the Nb atoms experience larger environmental change upon the formation of the composite cluster of **1**.

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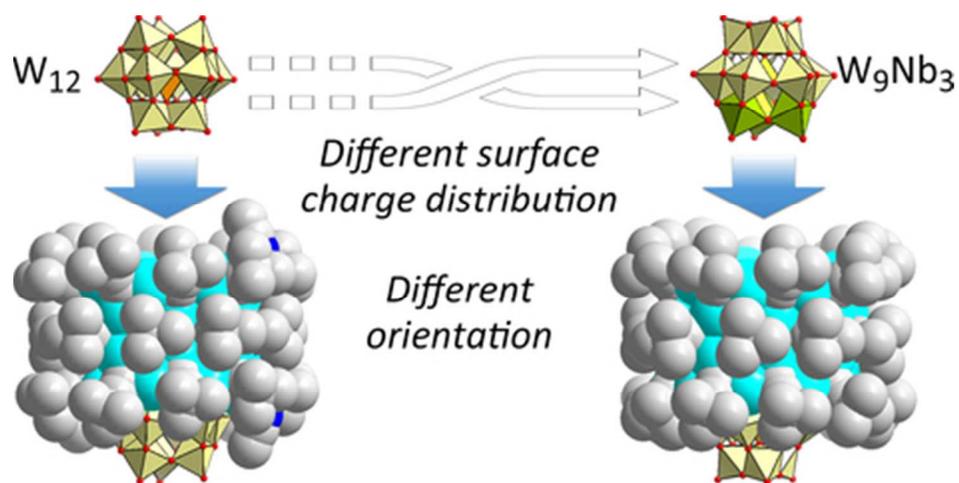
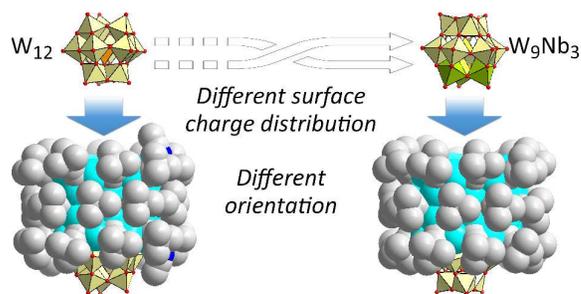


Illustration for the graphical abstract of "Control over preference for binding sites of polyoxometalates to silver ethynide clusters by surface charge modification" by Tamari, Ono, Hashimoto and Ozeki
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Graphics and text for the graphical abstract for “Control over preference for binding sites of polyoxometalates to silver ethynide clusters by surface charge modification” by Sho Tamari, Kosuke Ono, Masato Hashimoto and Tomoji Ozeki



Site-specific substitution of Nb for W in an α -Keggin polyoxometalate lead to the formation of $[Ag_{42}(CO_3)\{C\equiv CC(CH_3)_3\}_{27}(\alpha\text{-A-Si}W_9Nb_3O_{40})_2]^-$, where corner-shared triads of NbO_6 octahedra bind to the Ag_{42} cluster moiety.