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Investigation of Intermediates Involved in the Photochemical Formation of Mo-Blue Nanoring by Capillary Electrophoresis–Mass Spectrometry

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Capillary electrophoresis (CE) coupled with electrospray ionization mass spectrometry (ESI-MS) was employed to detect the intermediates involved in the photochemical formation of the Mo-blue nanoring $[Mo^{V}_{28}Mo^{VI}_{114}O_{429}H_{10}(H_2O)_{49}(CH_3CO_2)_5(C_2H_5CO_2)]^{30-}$ ≡ $Mo_{142}(Ac)_5(Pr)$ in the photolysis of the $[Mo_7O_{24}]^{6-}/CH_3CO_2H$ system at pH 3.4. The CE electropherogram indicated successful separation of the photolyte species into three migration times. The relative peak areas of the three kinds of signals were dependent on the duration of the photolysis. The signals in two of the regions could be identified to species (with additional defects due to the removal of binuclear $\{Mo_2\} \equiv [Mo^{VI}_2O_5(H_2O)_2]^{2+}$ linkers) derived from the intermediates $\{Mo_{37}\}$ to $\{Mo_{42}\}$ and Mo-blue nanoring $Mo_{142}(Ac)_5(Pr)$.

Introduction

High-nuclearity polyoxometalates (>100 transition metal atoms) can be synthesized by UV photolysis of lower-nuclearity polyoxometalates in the presence of electron donors.[1–4] The stepwise pathways of the photoreductive self-assembly from $[Mo^{VI}_7O_{24}]^{6-}$ into Mo-blue nanoring, $[Mo^{V}_{28}Mo^{VI}_{114}O_{429}H_{10}(H_2O)_{49}(CH_3CO_2)_5(C_2H_5CO_2)]^{30-}$ $[Mo_{142}(Ac)_5(Pr)]$, has been proposed, in which a variety of intermediates such as $\{Mo_{20}\}/\{Mo_{21}\}$, $\{Mo_{40}\}/\{Mo_{41}\}$, $\{Mo_{82}\}$, and $\{Mo_{122}\}$ are involved.[3] The proposed intermediates always comprise binuclear linkers, $\{Mo_2\} \equiv [Mo^{VI}_2O_5(H_2O)_2]^{2+}$, $\{Mo_2(Ac)\} \equiv [Mo^{VI}_2O_5(Ac)]^{+}$, or $\{Mo_2(Pr)\} \equiv [Mo^{VI}_2O_5(Pr)]^{+}$, which are readily removed partially under specific conditions (high pH level, for example).[5,6] Although it is crucial to identify these intermediates to better understand the UV-induced self-assembly of polyoxometalates and the molecular design of highly functionalized Mo-blue nanorings, attempts to detect the above intermediate species involved in the photolysis have not been successful. We tried to detect the intermediates for Mo-blue nanorings by using electrospray ionization mass spectrometry (ESI-MS).[7]

The mild ionization technique employed for ESI-MS and cryospray ionization mass spectrometry (CSI-MS)[8] seems to be suitable for the investigation of high-nuclearity polyoxometalate species in solutions. Lower-nuclearity polyoxometalates have been characterized by ESI- and CSI-MS.[9–21] Because the response factor for ionization differs among each species and because ionization may be prevented by coexisting different species,[7,22] it is necessary to separate the species in the reaction solution in advance. We employed capillary electrophoresis (CE)[23,24] for ESI-MS analysis of the solution of polyoxometalates instead of chromatographic separation[25–27] to avoid their irreversibly strong adsorption on packing materials. This CE procedure is quite compatible with ESI-MS, and CE–MS has been successfully applied to many biological/pharmaceutical systems.[28]

Here, we describe detection and reaction pathways of the intermediates involved in the photochemical formation of $Mo_{142}(Ac)_5(Pr)$ by using ESI- and CSI-MS and CE–MS. It is noteworthy that the ESI-MS signals obtained for the Mo-blue nanoring are assigned to the species with additional defects due to partial removal of the binuclear linkers.

Results and Discussion

ESI- and CSI-MS of $Mo_{142}(Ac)_5(Pr)$

Figure 1a shows the ESI mass spectrum of a water/acetonitrile (7:3) solution containing $2–10 \times 10^{-6}$ M $Mo_{142}(Ac)_5(Pr)$. The signals for species with a charge of 2– and 1–, observed when $m/z < 1100$, were assigned to the chain-like anions comprising corner-shared MoO_4 tetrahedra,[11] which are produced through ESI of the molybdate fragments (Table S1, Supporting Information). Broad signals observed in the range m/z = 1700–2400 were unambiguously assigned to species with a charge of 12–, 11–, and 10–, corresponding to a mass of 20810 ± 10, in the same order

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as the mass (*fw*: 21748.3) of the anion of $Mo_{142}(Ac)_5(Pr)$. Because the natural abundances of the isotopes of Mo ($^{92,94–98,100}Mo$ atoms) gave broad signals in the mass spectrum obtained by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) relative to those in the mass spectra of high nuclearity compounds such as $[Mo_{78}Fe_{30}O_{274}(H_2O)_{94}(CH_3CO_2)_{12}]\cdot{\approx}150H_2O$,[29] $[Mo_{102}O_{252}(H_2O)_{78}(CH_3CO_2)_{12}]\cdot{\approx}150H_2O$,[29] and $Na_{32-n}H_nMo_{176}O_{528}(H_2O)_{63}(CH_3OH)_{17}]\cdot{\approx}600H_2O\cdot{\approx}30CH_3OH$,[30] the broad signals of the ESI mass spectrum arise from the $Mo_{142}(Ac)_5(Pr)$-derived multiply charged ions. A small displacement of the molecular mass from the value expected for the anion of $Mo_{142}(Ac)_5(Pr)$ could be associated with removal of three binuclear linkers, two $\{Mo_2(Ac)\}$ and one $\{Mo_2(Pr)\}$, from $Mo_{142}(Ac)_5(Pr)$ through the ionization procedure. The broad signals in Figure 1a were thus tentatively assigned to $[(NH_4)_3H_{28+x}Mo^{V}_{28}Mo^{VI}_{108}O_{414}(H_2O)_{49}(Ac)_3]^{(12-x)-}$ [*fw*: 20813.8 + *x*, *x* = 0–2; $Mo_{136}(Ac)_3$].

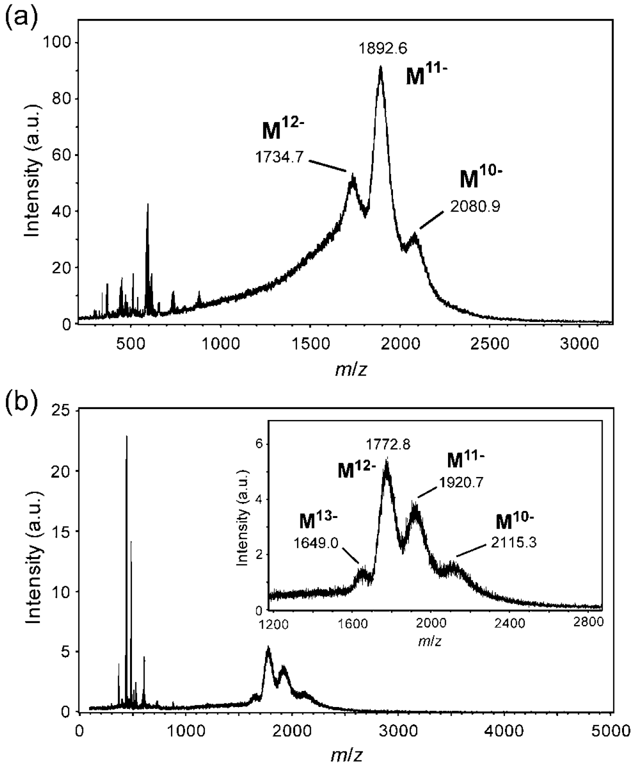

Figure 1. (a) ESI mass spectrum of a water/acetonitrile (7:3) solution of $Mo_{142}(Ac)_5(Pr)$; assignments of the peaks observed for *m/z* < 1100 are listed in Table S1 (Supporting Information). (b) CSI mass spectrum of a water/acetonitrile (1:4) solution of $Mo_{142}(Ac)_5(Pr)$; inset: magnified spectrum in the range *m/z* = 1200–2800; assignments of the peaks observed for *m/z* < 1000 are listed in Table S2 (Supporting Information).

The broad signals for species with a charge of 12–, 11–, and 10– in the range *m/z* = 1700–2400 were observed only under the mild ionization condition with capillary exit-skimmer potential difference = 30 V, whereas many fragmented ions produced through collision-induced dissociation (CID) were observed under harsher ionization conditions. In solution, $Mo_{142}(Ac)_5(Pr)$ was oxidized with color fading by air under ambient atmosphere for one week with an accompanying disappearance of the broad signals in the ESI mass spectrum.

The CSI mass spectrum was also measured, as shown in Figure 1b. In addition to the signals for species with a charge of 2– and 1– with *m/z* < 1100 (Table S2, Supporting Information), the CSI mass spectrum of a water/acetonitrile (1:4) solution containing ca. 1×10^{-6} M $Mo_{142}(Ac)_5(Pr)$ under the desolvation temperature of 10 °C showed a set of broad signals for species with a charge of 13– to 10– in the range *m/z* = 1600–2300, which corresponds to a mass of 21300 ± 200. The 21300 ± 200 species was tentatively assigned to $[H_{28+x}Mo^{V}_{28}Mo^{VI}_{112}O_{424}(H_2O)_{49}(Ac)_4(Pr)]^{(13-x)-}$ [*fw*: 21435.6 + *x*, *x* = 0–3; $Mo_{140}(Ac)_4(Pr)$] or $[H_{29+x}Mo^{V}_{28}Mo^{VI}_{110}O_{419}(H_2O)_{49}(Ac)_3(Pr)]^{(13-x)-}$ [*fw*: 21105.7 + *x*, *x* = 0–3; $Mo_{138}(Ac)_3(Pr)$], which were derived from removal of small amounts of binuclear linkers from $Mo_{142}(Ac)_5(Pr)$.

The above ESI- and CSI-MS measurements gave the signals of $Mo_{142}(Ac)_5(Pr)$ derivatives with additional defects due to further removal of one to three binuclear linker unit(s). This seems to be characteristic of the signals for Mo-blue nanoring species. The number of the removed linkers is affected by the desolvation temperature, time of acquisition of the spectroscopic data, and the amounts of acetonitrile in solution.

ESI-MS and CE–MS of Photolytes

Figure 2 shows the ESI mass spectrum of 100-fold diluted photolyte after a 24-h period of photolysis; strong and intense signals due to the chain-like anions with *m/z* < 1200 (Table S3, Supporting Information) and very weak broadened signals due to the $Mo_{142}(Ac)_5(Pr)$-derived multiply charged ions 11– to 9– (of mass 21450 ± 50) were observed. The latter could be tentatively assigned to $[H_{30+x}Mo^{V}_{28}Mo^{VI}_{112}O_{424}(H_2O)_{49}(Ac)_4(Pr)]^{(11-x)-}$ (*fw*: 21437.6 + *x*, *x* = 0–2). Because there was no observation of the broadened signals of the $Mo_{142}(Ac)_5(Pr)$-derived multiply charged ions when the photolyte was diluted less than 10-fold, it seems essential to dilute the photolyte for observation of these species, probably to avoid the masking of their ionization by other species coexisting in the photolyte. Thus, CE–MS analysis was attempted to separate a variety of species in the photolyte.

Figure 3 exemplifies the CE–MS electropherogram and spectra of the photolyte for the 24-h photolysis period, showing a successful separation of the photolyte species into three migration time regions (in min): 5.9–17.6 (**I**), 17.6–18.1 (**II**), and 18.1–18.7 (**III**) without any dilution of the photolyte. At first, the CE–MS signals in region **I** were sharp lines for species with a charge of 2– and 1– with *m/z* < 1500 (Figure 3b; Table S4, Supporting Information), which resemble the dominant signals (Figure 2) of the

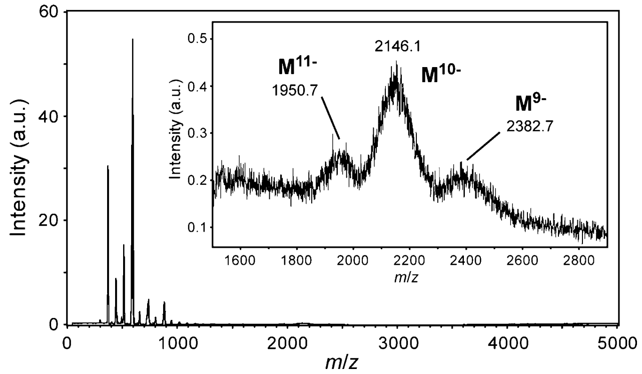

Figure 2. ESI mass spectrum of the photolyte after a 24-h period of photolysis (diluted to 1:100 concentration); inset: magnified spectrum for the range m/z = 1600–2800. Assignments of the peaks observed for $m/z < 1200$ are listed in Table S3 (Supporting Information).

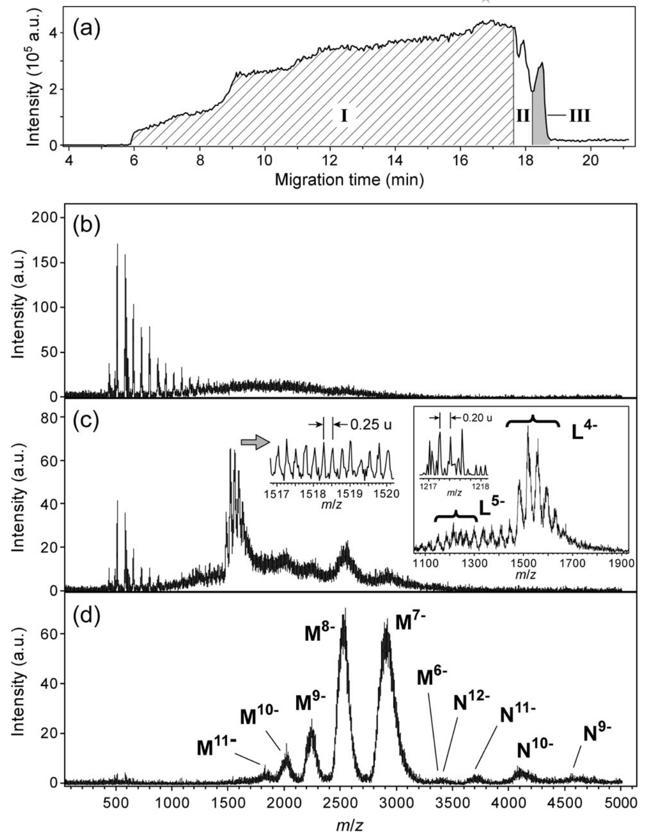

Figure 3. CE–MS electropherogram and spectra of the photolyte after a 24-h period of photolysis: (a) CE–MS electropherogram (total ion current); shaded areas represent regions **I**, **II**, and **III**, in which different signals were observed (see text); (b) CE–MS signals in region **I**; assignments of the peaks are listed in Table S4 (Supporting Information); (c) CE–MS signals in region **II**; inset: CE mass spectrum in the range m/z = 1100–1900; assignments of charge states are indicated in the figure; (d) CE–MS signals in region **III**; assignments of charge states are indicated in the figure; signals with the same character were assigned to multiply charged ions derived from the common parent ions.

chain-like anions observed for the above 100-fold diluted photolyte.

Secondly, the signals in region **II** were observed in the range m/z = 1400–1700 and showed six major signals at m/z = 1444.4, 1481.3, 1515.5, 1554.7, 1593.7, and 1628.9 as species with a charge of 4– (with isotopic separation of 0.25 m/z unit), each of which was accompanied by a species with a charge of 5– (Figure 3c). Thereby, the signals at **II** were assigned to the species with molecular weight of 5780 ± 20, 5925 ± 20, 6070 ± 20, 6220 ± 20, 6360 ± 20, and 6515 ± 20, which were likely to be intermediates of $Mo_{142}(Ac)_5(Pr)$.

Finally, the signals in region **III** were broad and consisted of two sets of signals: species with charged states of 11– to 6– at m/z = 1830.4, 2021.4, 2523.6, 2904.5, and 3388.9 in the range of m/z 1800–3500 and species with charged states of 12– to 9– with weak intensity at m/z = 3388.9, 3687.9, 4104.9, and 4567.2 with $m/z > 3000$ (Figure 3d). The signals at m/z = 1800–3500 were thus assigned to the $Mo_{142}(Ac)_5(Pr)$-derived multiply charged ions (of mass 20230 ± 100), which were tentatively identified as $[(NH_4)_5H_{31+x}Mo^{V}_{28}Mo^{VI}_{104}O_{404}(H_2O)_{45}(Ac)_3]^{(11-x)-}$ [fw = 20237.1 + x, x = 0–5; $Mo_{132}(Ac)_3$] is associated with the removal of two $\{Mo_2\}$, two $\{Mo_2(Ac)\}$, and one $\{Mo_2(Pr)\}$ linkers from $Mo_{142}(Ac)_5(Pr)$. Thus, it is interesting that $Mo_{142}(Ac)_5(Pr)$ derivatives with additional defects due to the removal of further binuclear linkers were observed also in the CE–MS measurements. Also, the weak signals of the highly charged states at $m/z > 3000$ were tentatively assigned to the dimer derivatives (of mass 41000 ± 500) such as $\{Mo_{132}(Ac)_3\}_2$ and/or $\{Mo_{134}(Ac)_3\}_2$, interestingly suggesting that the oligomerization of the Mo-blue nanorings proceeds in the photolyte.

The time profiles of the signals observed in regions **I**–**III** during the photolysis were investigated to obtain a kinetic feature of the formation of the above three kinds of signals. Figure 4 shows the relative peak areas for representative signals in regions **I** ($m/z \approx 512$), **II** ($m/z \approx 1555$), and **III** ($m/z \approx 2520$). The time profile of the signals in region **I** derived from the chain-like anions showed a decrease with photolysis, reached a plateau after 168 h, and remained even after 336 h, probably because the chain-like anions with a high response factor are easily observable. The signals in region **II** derived from the plausible intermediates increased from the beginning of the photolysis up to 50 h (Figure 4b), and then decreased into an undetectable level. The signals in region **III** of $Mo_{142}(Ac)_5(Pr)$ derivatives increased after an induction period of 2 h. The results of the time profiles for the above three kinds of signals clearly indicates that the signals in region **II** with molecular weights of 5750–6550 are due to the intermediates for $Mo_{142}(Ac)_5(Pr)$. Figure 5 shows electronic absorption spectra of 1-h and 24-h photolytes and $Mo_{142}(Ac)_5(Pr)$. Two absorption maxima around 723 and 1050 nm for the 1-h photolyte are shifted to 749 and 1115 nm through 750 and 1190 nm for the 24-h photolyte. The change in such electronic absorption maxima suggests that the intermediates as the precursor of $Mo_{142}(Ac)_5(Pr)$ derivatives show absorption maxima around 750 and 1190 nm.

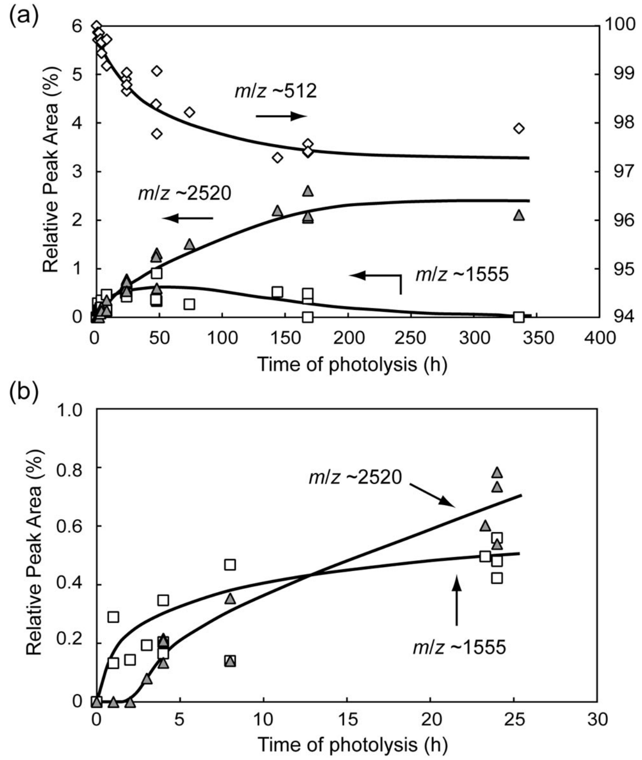

Figure 4. (a) Time profiles of relative peak areas for signals at *m*/*z* ≈ 512 (open diamonds), ≈1555 (open squares), and ≈2520 (grey-filled triangles) observed by CE–MS for the photolytes after a 0- to 336-h period of photolysis. (b) Magnified time profiles of relative peak areas for signals at *m*/*z* ≈ 1555 and ≈2520 for the photolytes after a 0- to 30-h period of photolysis.

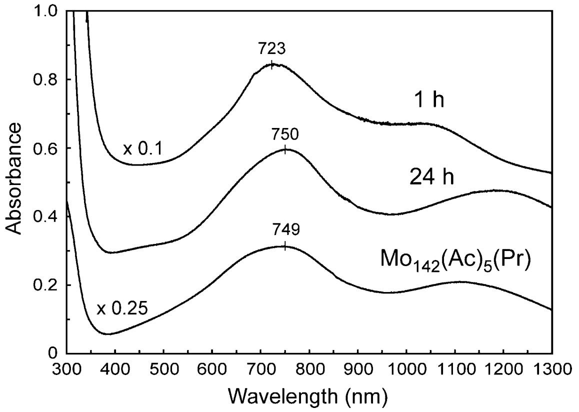

Figure 5. Electronic absorption spectra of the photolytes after a 1- and 24-h period of photolysis and aqueous solution of $Mo_{142}(Ac)_5(Pr)$ (1×10^{-5} M). A quartz cell with an optical length of 0.1 mm was used for the photolyte after a 24-h period of photolysis, and a cell of 10 mm for other solutions. The baseline for each spectrum is different for clarity. The peak positions around 750 nm are indicated in the figure.

In the self-assembly pathways to $Mo_{142}(Ac)_5(Pr)$, intermediates with a moderate nuclearity were proposed: $\{Mo_{20}\}/\{Mo_{21}\}$, $\{Mo_{40}\}/\{Mo_{41}\}$, $\{Mo_{82}\}$, and $\{Mo_{122}\}$.[3] On the basis of this proposal, the signal in region **II** with mass 6220 ± 20 can be tentatively assigned to $[(NH_4)_5H_7Mo^{V}_6Mo^{VI}_{34}O_{125}(H_2O)_{16}]^{4-}$ (*fw*: 6223.0; $\{Mo_{40}\}$). Similarly, other signals with mass values of 5780 ± 20, 5925 ± 20, 6070 ± 20, 6360 ± 20, and 6515 ± 20 can be tentatively attributed to $[(NH_4)_7H_7Mo^{V}_6Mo^{VI}_{31}O_{117}(H_2O)_{13}]^{4-}$ (*fw*: 5789.2; $\{Mo_{37}\}$), $[(NH_4)_6H_8Mo^{V}_6Mo^{VI}_{32}O_{120}(H_2O)_{14}]^{4-}$ (*fw*: 5934.2; $\{Mo_{38}\}$), $[(NH_4)_6H_6Mo^{V}_6Mo^{VI}_{33}O_{122}(H_2O)_{15}]^{4-}$ (*fw*: 6078.1; $\{Mo_{39}\}$), $[(NH_4)_5H_5Mo^{V}_6Mo^{VI}_{35}O_{127}(H_2O)_{17}]^{4-}$ (*fw*: 6367.0; $\{Mo_{41}\}$), and $[(NH_4)_5H_3Mo^{V}_6Mo^{VI}_{36}O_{129}(H_2O)_{18}]^{4-}$ (*fw*: 6510.9; $\{Mo_{42}\}$), respectively. A transient spectrum suggesting other intermediates (Figure 6b) was obtained for the 8-h photolyte, indicating the signals with mass 17800 ± 200 (denoted by P^{10-}–P^{6-} in Figure 6). This species may be assigned to $[(NH_4)_2H_{23+x}Mo^{V}_{22}Mo^{VI}_{94}O_{353}(H_2O)_{44}(Ac)_3]^{(10-x)-}$ [*fw*: 17805.9+*x*, *x* = 0–4; $Mo_{116}(Ac)_3$]. These results support the stepwise condensation formation of $Mo_{142}(Ac)_5(Pr)$.[3]

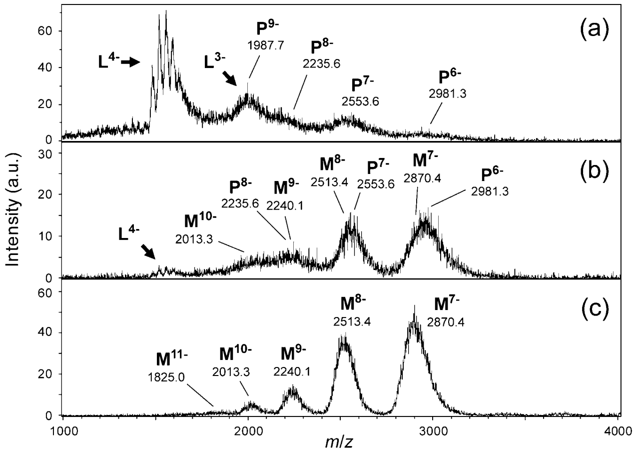

Figure 6. Transient CE–MS of the photolyte after an 8-h period of photolysis: (a) CE–MS signals in region **II**; (b) transient CE–MS; (c) CE–MS signals in region **III**; assignments of charge states are indicated in the figure; signals with the same character were assigned to multiply charged ions derived from the common parent ions.

Conclusions

High nuclearity Mo-blue nanoring of $Mo_{142}(Ac)_5(Pr)$ and its formation process were investigated by ESI- and CSI-MS and CE–MS spectrometry. Discrete $Mo_{142}(Ac)_5(Pr)$ derivatives with additional defects due to the removal of one to five binuclear linker unit(s) were observed as broad signals of multiply charged ions with a mass of 21000 ± 500. The CE–MS procedure enabled online separation and detection of coexisting species of $\{Mo_{37}\}$ to $\{Mo_{42}\}$ with mass values of 5750–6550 as intermediates for $Mo_{142}(Ac)_5(Pr)$. Other plausible intermediates such as $\{Mo_{116}(Ac)_3\}$ were also detected by transient CE–MS. The ESI-MS signals of photolytes indicative of an increase in the number of the building blocks during the photolysis support the stepwise assembly processes to $Mo_{142}(Ac)_5(Pr)$. A separation–detection procedure such as CE–MS has promising potential for the analysis of the self-assembly reaction of polyoxometalate species in solutions.

Experimental Section

Materials: $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, ammonium acetate, and acetic acid (Kanto) were used as received. Ultrapure water (ca. 18 MΩcm) delivered from a Toraypure LV-08 (Toray) system was used for the preparation of aqueous solutions. Methanol and acetonitrile (HPLC grade, Kanto) were used as organic solvents.

Preparation of $Mo_{142}(Ac)_5(Pr)$ and Photolytes: $[Mo_{142}O_{429}H_{10}(H_2O)_{49}(CH_3CO_2)_5(C_2H_5CO_2)]^{30-}$ [$Mo_{142}(Ac)_5(Pr)$] was prepared according to the photolysis of the $[Mo_7O_{24}]^{6-}/CH_3CO_2H$ system at pH 3.4 at room temperature.[3] Electronic absorption spectra of the photolyte at each stage of the photolysis were measured with a V-570 spectrometer (JASCO) by using a quartz cell with an optical length of 0.1 mm or 10 mm without dilution.

Electrospray and Cryospray Ionization Mass Spectrometry: Electrospray ionization and cryospray ionization mass spectrometry (ESI- and CSI-MS) measurements were carried out with a microTOF electrospray time-of-flight mass spectrometer (Bruker Daltonics). A CSI unit was attached to the ESI-MS measurement system for the CSI-MS measurements. Negative mode was employed for all measurements (capillary voltage: 3500 V, capillary exit-skimmer potential difference: 30 V). ESI-MS spectra were obtained by direct infusion of the water/acetonitrile (7:3–10:0) solutions of $Mo_{142}(Ac)_5(Pr)$ ($2–10\times10^{-6}$ M in final) or the photolytes after a 24-h period of photolysis (with 0–100 fold dilution by water) by using a syringe pump with a rate of 180 $\mu L\,h^{-1}$. The desolvation temperature was set to 160 or 180 °C. CSI-MS spectra of $Mo_{142}(Ac)_5(Pr)$ were obtained by direct infusion of water/acetonitrile (1:4) solutions of $Mo_{142}(Ac)_5(Pr)$ (ca. 1×10^{-6} M in final) by using a syringe pump with a rate of 750 $\mu L\,h^{-1}$. The desolvation temperature was set to 10 °C.

Capillary Electrophoresis Mass Spectrometry: Capillary electrophoresis electrospray ionization mass spectrometry (CE–MS) measurements were performed with a P/ACE MDQ system (Beckman Coulter) coupled to the microTOF spectrometer by using a sheath-flow interface. The photolyte sample for each CE–MS measurement was injected into a fused silica capillary (1 m length, 50 µm internal diameter), and separated at 20 °C under a constant voltage of –30 kV and a pressure of 0.3 psi. Acetic acid (0.3 M) was used as a running buffer. The sheath liquid consisting of 10 mM CH_3COONH_4/methanol (1:1) was applied with a rate of 0.6 $mL\,h^{-1}$. CE–MS spectra were acquired with the same parameters as those for ESI-MS. The peak areas of the signals were estimated from the CE–MS electropherogram and spectra by using DataAnalysis software (Bruker Daltonics).

Supporting Information (see footnote on the first page of this article): Assignments of signals in the low *m/z* region of the spectra acquired by ESI- and CSI-MS and by CE–MS for the solution of $Mo_{142}(Ac)_5(Pr)$ and photolytes.

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[1] T. Yamase, *Chem. Rev.* **1998**, *98*, 307–325.
[2] a) T. Yamase, *J. Chem. Soc., Dalton Trans.* **1991**, 3055–3063; b) T. Yamase, E. Ishikawa, *Langmuir* **2000**, *16*, 9023–9030; c) T. Yamase, E. Ishikawa, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 983–991.
[3] T. Yamase, Y. Yano, E. Ishikawa, *Langmuir* **2005**, *21*, 7823–7832.
[4] a) T. Yamase, P. V. Prokop, *Angew. Chem. Int. Ed.* **2002**, *41*, 466–469; b) T. Yamase, P. Prokop, Y. Arai, *J. Mol. Struct.* **2003**, *656*, 107–117; c) T. Yamase, E. Ishikawa, Y. Abe, Y. Yano, *J. Alloys Compd.* **2006**, *408–412*, 693–700.
[5] a) A. Müller, C. Serain, *Acc. Chem. Res.* **2000**, *33*, 2–10; b) A. Müller, C. Beugholt, M. Koop, S. K. Das, M. Schmidtmann, H. Bögge, *Z. Anorg. Allg. Chem.* **1999**, *625*, 1960–1962; c) A. Müller, R. Maiti, M. Schmidtmann, H. Bögge, S. K. Das, W. Zhang, *Chem. Commun.* **2001**, 2126–2127.
[6] S. Shishido, T. Ozeki, *J. Am. Chem. Soc.* **2008**, *130*, 10588–10595.
[7] a) R. B. Cole (Ed.), *Electrospray Ionization Mass Spectrometry: Fundamentals, Instrumentation, and Applications*, Wiley, New York, **1997**; b) J. B. Fenn, M. Mann, C. K. Meng, S. F. Wong, C. M. Whitehouse, *Science* **1989**, *246*, 64–71; c) R. D. Smith, J. A. Loo, C. G. Edmonds, C. J. Barinaga, H. R. Udseth, *Anal. Chem.* **1990**, *62*, 882–899; d) N. B. Cech, C. G. Enke, *Mass Spectrom. Rev.* **2001**, *20*, 362–387.
[8] K. Yamaguchi, *J. Mass Spectrom.* **2003**, *38*, 473–490.
[9] a) R. Colton, J. C. Traeger, *Inorg. Chim. Acta* **1992**, *201*, 153–155; b) J. Le Quan Tuoi, E. Muller, *Rapid Commun. Mass Spectrom.* **1994**, *8*, 692–694; c) T.-C. Lau, J. Wang, R. Guevremont, K. W. M. Siu, *J. Chem. Soc., Chem. Commun.* **1995**, 877–878.
[10] M. J. Deery, O. W. Howarth, K. R. Jennings, *J. Chem. Soc., Dalton Trans.* **1997**, 4783–4788.
[11] D. K. Walanda, R. C. Burns, G. A. Lawrance, E. I. von Nagy-Felsobuki, *J. Chem. Soc., Dalton Trans.* **1999**, 311–321.
[12] a) C. S. Truebenbach, M. Houalla, D. M. Hercules, *J. Mass Spectrom.* **2000**, *35*, 1121–1127; b) C. E. Easterly, D. M. Hercules, M. Houalla, *Appl. Spectrosc.* **2001**, *55*, 1671–1675.
[13] a) B. Salignac, S. Riedel, A. Dolbecq, F. Sécheresse, E. Cadot, *J. Am. Chem. Soc.* **2000**, *122*, 10381–10389; b) C. R. Mayer, C. Roch-Marchal, H. Lavanant, R. Thouvenot, N. Sellier, J.-C. Blais, F. Sécheresse, *Chem. Eur. J.* **2004**, *10*, 5517–5523.
[14] M. Bonchio, O. Bortolini, V. Conte, A. Sartorel, *Eur. J. Inorg. Chem.* **2003**, 699–704.
[15] M. T. Ma, T. Waters, K. Beyer, R. Palamarczuk, P. J. S. Richardt, R. A. J. O'Hair, A. G. Wedd, *Inorg. Chem.* **2009**, *48*, 598–606.
[16] a) C. Dablemont, A. Proust, R. Thouvenot, C. Afonso, F. Fournier, J.-C. Tabet, *Inorg. Chem.* **2004**, *43*, 3514–3520; b) C. Dablemont, A. Proust, R. Thouvenot, C. Afonso, F. Fournier, J.-C. Tabet, *Dalton Trans.* **2005**, 1831–1841.
[17] S. Nellutla, J. van Tol, N. S. Dalal, L.-H. Bi, U. Kortz, B. Keita, L. Nadjo, G. A. Khitrov, A. G. Marshall, *Inorg. Chem.* **2005**, *44*, 9795–9806.
[18] T. Kurata, A. Uehara, Y. Hayashi, K. Isobe, *Inorg. Chem.* **2005**, *44*, 2524–2530.
[19] a) Y. Nakagawa, K. Kamata, M. Kotani, K. Yamaguchi, N. Mizuno, *Angew. Chem. Int. Ed.* **2005**, *44*, 5136–5141; b) S. Yamaguchi, Y. Kikukawa, K. Tsuchida, Y. Nakagawa, K. Uehara, K. Yamaguchi, N. Mizuno, *Inorg. Chem.* **2007**, *46*, 8502–8504.
[20] a) C. Boglio, G. Lenoble, C. Duhayon, B. Hasenknopf, R. Thouvenot, C. Zhang, R. C. Howell, B. P. Burton-Pye, L. C. Francesconi, E. Lacôte, S. Thorimbert, M. Malacria, C. Afonso, J.-C. Tabet, *Inorg. Chem.* **2006**, *45*, 1389–1398; b) C. Boglio, K. Micoine, P. Rémy, B. Hasenknopf, S. Thorimbert, E. Lacôte, M. Malacria, C. Afonso, J.-C. Tabet, *Chem. Eur. J.* **2007**, *13*, 5426–5432.
[21] a) C. Ritchie, E. M. Burkholder, D.-L. Long, D. Adam, P. Kögerler, L. Cronin, *Chem. Commun.* **2007**, 468–470; b) C. P. Pradeep, D.-L. Long, P. Kögerler, L. Cronin, *Chem. Commun.* **2007**, 4254–4256.
[22] a) E. Leize, A. Jaffrezic, A. Van Dorsselaer, *J. Mass Spectrom.* **1996**, *31*, 537–544; b) D.-S. Young, H.-Y. Hung, L. K. Liu, *J. Mass Spectrom.* **1997**, *32*, 432–437; c) S. M. Blair, E. C.

Kempen, J. S. Brodbelt, *J. Am. Chem. Soc. Mass Spectrom.* **1998**, *9*, 1049–1059; d) G. V. Oshovsky, W. Verboom, R. H. Fokkens, D. N. Reinhoudt, *Chem. Eur. J.* **2004**, *10*, 2739–2748; e) R. Zadmard, A. Kraft, T. Schrader, U. Linne, *Chem. Eur. J.* **2004**, *10*, 4233–4239; f) R. Tagore, H. Chen, R. H. Crabtree, G. W. Brudvig, *J. Am. Chem. Soc.* **2006**, *128*, 9457–9465.

[23] a) P. D. Grossman, J. C. Colburn (Eds.), *Capillary Electrophoresis: Theory & Practice*, Academic Press, San Diego, **1992**; b) A. R. Timerbaev, *Electrophoresis* **2002**, *23*, 3884–3906.

[24] a) K. Hettiarachchi, Y. Ha, T. Tran, A. P. Cheung, *J. Pharm. Biomed. Anal.* **1995**, *13*, 515–523; b) S. Himeno, I. Kitazumi, *Inorg. Chim. Acta* **2003**, *355*, 81–86.

[25] a) A. D. Kirk, W. Riske, D. K. Lyon, B. Rapko, R. G. Finke, *Inorg. Chem.* **1989**, *28*, 792–797; b) Q.-D. Zeng, M.-H. Zhu, Y.-D. Xu, *Acta Chim. Sinica* **1987**, *45*, 96–98.

[26] a) B. S. Bassil, U. Kortz, A. S. Tigan, J. M. Clemente-Juan, B. Keita, P. de Oliveira, L. Nadjo, *Inorg. Chem.* **2005**, *44*, 9360–9368; b) K. Ruuttunen, T. Vuorinen, *Carbohydrate Polym.* **2004**, *58*, 443–448; c) S. P. Harmalker, M. A. Leparulo, M. T. Pope, *J. Am. Chem. Soc.* **1983**, *105*, 4286–4292.

[27] B. Chen, H. Jiang, Y. Zhu, A. Cammers, J. P. Selegue, *J. Am. Chem. Soc.* **2005**, *127*, 4166–4167.

[28] a) C. G. Edmonds, J. A. Loo, C. J. Barinaga, H. R. Udseth, R. D. Smith, *J. Chromatogr.* **1989**, *474*, 21–37; b) J. Cai, J. Henion, *J. Chromatogr. A* **1995**, *703*, 667–692; c) M. Moini, *Anal. Bioanal. Chem.* **2002**, *373*, 466–480.

[29] A. Müller, E. Diemann, S. Q. N. Shah, C. Kuhlmann, M. C. Letzel, *Chem. Commun.* **2002**, 440–441.

[30] A. Tsuda, E. Hirahara, Y.-S. Kim, H. Tanaka, T. Kawai, T. Aida, *Angew. Chem. Int. Ed.* **2004**, *43*, 6327–6331.

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