Supporting Information

Supplementary Movies

Movie 1: Time course of the formation of Ag₂-ox from Cs₂-red in AgNO₃aq (0 to 22 s).

Beakers on the left and right of the images are $AgNO_3aq$ and Cs_2 -red in water (reference), respectively. Cs_2 -red (dark blue solid) is added to the beaker on the left at 0 s, and the color of the solid turns immediately from dark blue to brown, showing that the POM is oxidized and Ag_2 -ox is formed.

Movie 2: Time course of the PL image of Cs_2 -red in AgNO₃aq (-2 to 15 s). Fig. 3c shows the snapshots from this movie.

Experimental Details: Powder X-ray di action (PXRD) patterns were measured with a XRD-DSCII (Rigaku Corporation) by using Cu K α radiation ($\lambda = 1.54056$ Å, 50 kV-300 mA) at $2\theta = 3-15^{\circ}$ and 3 s/step (0.02 deg/step). Prior to the PXRD measurements, the compounds were passed through a 150-mesh sieve and deposited onto the Al sample plate to unify the particle size and to avoid preferred orientation. Diffuse-reflectance UV-vis spectra were measured in the range of 10000–20000 cm⁻¹ (1000–500 nm) with a V-770 iRM UV-vis spectrometer (JASCO). The samples were prepared by grinding and diluting the compounds (ca. 1 mg) with ca. 100 mg of NaCl. FT-IR spectra were measured by transmission method using a JASCO FT/IR 4100 instrument (JASCO). The pelletized samples were prepared by grinding and diluting the compounds (ca. 1 mg) with ca. 100 mg of KBr followed by compressing at 100 kgf cm⁻². SEM-EDS images and mappings were obtained with a Hitachi TM4000Plus Miniscope (Hitachi High-Technologies) with an accelerating voltage of 15 kV. X-band CW-EPR spectra were recorded on a Bruker EMX Plus system (Bruker) with a microwave frequency of 9.51 GHz and modulation amplitude of 2 mT. The samples were cooled by liquid nitrogen to a temperature of 80 K. Thermogravimetry (TG) data were measured with a Thermo Plus 2 thermogravimetric analyzer (Rigaku Corporation) with α -Al₂O₃ as a reference under a dry N₂ flow. Atomic absorption spectrometry (AAS) analysis (Hitachi, ZA3000) was used for the quantitative analysis of Cu and Na.

Single-Crystal X-ray Di raction (SXRD) Analysis: X-ray di raction data of **Ag**₂**-ox** was collected at 93 K with a CCD 2-D detector by using Rigaku Saturn di ractometer with graphite monochromated Mo K α radiation. Structures were solved by direct methods (SHELX97), expanded using Fourier techniques, and refined by full-matrix least squares against F^2 with the SHELXL-2014 package. Molybdenum, chromium, and phosphorous atoms were refined anisotropically. Carbon and oxygen atoms of $[Cr_3O(OOCH)_6(mepy)_3]^+$ were refined anisotropically. Oxygen atoms of $[PMo_{12}O_{40}]^{3-}$ were refined isotropically. Hydrogen atoms were not included in the model. While elemental analysis suggested the existence of 2 silver atoms per formula, which probably existed in the one-dimensional channel along the *c*-axis, the positions could not be resolved due to clustering and/or severe disordering. The high R_1 and wR_2 values are probably due to the unlocated silver species. Water of crystallization (3 molecules per formula as suggested by thermogravimetry and elemental analysis) were not assigned. Crystal data for Ag₂-ox: monoclinic C2/*c* (No. 15), *a* = 32.44(3) Å, *b* = 25.21(2) Å, *c* = 13.548(12) Å, *β* = 113.170(15), *V* = 10187(15), *Z* = 4, R_1 = 0.1877, wR_2 = 0.5098, GOF = 1.665. See Table S1 for further details. CCDC-1876337 contains the crystallographic data for Ag₂-ox.

Chemical Formula	C48 Cr6 Mo12 N6 O66 P	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 32.44(3) b = 25.21(2) c = 13.548(12) $\beta = 113.170(15)$	
Volume	10187(15)	
Ζ	4	
$D_{\rm calc} ({ m g \ cm^{-3}})$	2.093	
F(000)	6996	
<i>h, k, l</i> range	-38/37, -29/30, -15/16	
μ (Mo K α) (mm ⁻¹)	2.146	
$R_1(I > 2\sigma(I))$	0.1877	
wR_2 (all data)	0.5098	
GOF on F^2	1.665	

 Table S1. Crystallographic data of Ag₂-ox

Material	Method	Time to reach sorption equilibrium in water	Reference
Cs ₂ -red	reduction-induced ion-exchange $(Cs^+ \rightarrow Ag^+ \& Ag)$	1 min at r.t.	This work
HKUST-1 (Cu-benzene-tricarboxylate)	adsorption of Ag nanoparticles	10 min at 298-313K	1
$[{Ni(C_{10}H_{26}N_6)}_3(bpdc)_3] \cdot 2C_5 H_5N \cdot 6H_2O^a$	reduction-induced formation of Ag nanoparticles of 3 nm-size from Ag ⁺	10 min at r.t. in methanol	2
polyimide film	ion-exchange $(K^+ \rightarrow Ag^+)$	20 min at 298 K	3
mesoporous graphitic carbon nitride	chelating and/or coordination to amine functionalities (adsorbed as Ag ⁺ & Ag)	30 min at 273 K	4
TS-1 (titanium silicate)	ion-exchange (Na ⁺ →Ag ⁺)	1 h at r.t.	5
Ca-LTA zeolite	ion-exchange (Ca ²⁺ \rightarrow Ag ⁺)	2 h at 313 K	6
α-Al ₂ O ₃	adsorption of Ag nanoparticles	1 h at r.t. in ethanol	7
MOF-5 (Zn-benzene- dicarboxylate)	in-situ synthesis of Ag nanoparticles with the starting materials of MOF-5	3 h reflux in DMF/ethanol	8
porous cellulose acetate	electrostatic interaction and ion-exchange $(H^+ \rightarrow Ag^+)$	4 h at r.t.	9
porous graphitic carbon nitride nano-sheets	electrostatic interaction and ion-exchange $(H^+ \rightarrow Ag^+)$	6 h at r.t.	10
Ca-hydroxyapatite, (Ca ₅ (PO ₄) ₃ (OH))	ion-exchange (Ca ²⁺ \rightarrow Ag ⁺)	6 h at r.t.	11
Na-FAU, Na-LTA, K-LTA zeolite	ion-exchange (Na ⁺ , K ⁺ \rightarrow Ag ⁺)	12 h at r.t.	12
Na-ZSM-5 zeolite	ion-exchange (Na ⁺ \rightarrow Ag ⁺)	12 h at 343 K	13
Amberlyst-15 (ion-exchange resin)	ion-exchange ($H^+ \rightarrow Ag^+$)	10-14 h at r.t.	14
MOF-74Ni (Ni ₂ (dhtp)(H ₂ O) ₂) ^b	in-situ formation and adsorption of Ag nanoparticles	24 h at r.t. in ethanol	15
Na-montmorillonite	ion-exchange (Na ⁺ \rightarrow Ag ⁺)	24 h at r.t.	16
uranyl diphosphate	ion-exchange (Cs ⁺ \rightarrow Ag ⁺)	1 week at r.t.	17

Table S2. Uptake of silver species (by ion-exchange, etc.) into reported materials

 a bpdc=4,4'-biphenyldicarboxylate, b H₄dhpt = 2,5-dihydroxyterephthalic acid

References of Table S2

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Fig. S1 IR (left) and Diffuse reflectance UV-vis (right) spectra of (a) Cs_2 -red, (b) Ag_2 -ox, and (c) Cs-ox. The v_{as} (Mo=O) band in the IR spectrum shifts from 952 to 957 cm⁻¹ by treating Cs_2 -red with AgNO₃aq to form Ag₂-ox, which agrees with the oxidation of [PMo^VMo₁₁^{VI}O₄₀]⁴⁻ to [PMo^{VI}₁₂O₄₀]^{3-.S1} Note that the v_{as} (Mo=O) band of Cs-ox is also observed at 957 cm⁻¹. The strong broad intervalence charge transfer (IVCT) band among Mo(V) and Mo(VI) centered around 14000 cm⁻¹ in the diffuse-reflectance UV-vis spectrum disappeared by treating Cs₂-red with AgNO₃aq.^{S2} Therefore, the IR and UV-vis data indicate that the POM in Cs₂-red and Ag₂-ox are in one-electron reduced and fully oxidized states, respectively. Possible formation of two-electron reduced species [PMo^V₂Mo^{VI}₁₀O₄₀]⁵⁻ in Cs₂-red can be excluded, since further redshift of the v_{as} (Mo=O) band to 940 cm⁻¹ has been reported in the IR spectrum of *in situ* generated [PMo^V₂Mo^{VI}₁₀O₄₀]⁵⁻.^{S3}

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Fig. S2 Thermogravimetry. (a) Ag-ox and (b) Ag₂-ox.



Fig. S3 PXRD patterns of (a) Ag_2-ox (calc), (b) Cs_2-red , (c) Ag_2-ox , (d) Cs-ox, and (e) Ag-ox (24 h, ionexchange rate of ca.50%). The numbers in (a) indicate the Miller indices of the diffraction peaks. The difference especially in the relative intensities of the diffraction peaks between (a) calculated and (c) experimental data of Ag_2-ox (e.g., 110 is barely visible in the calculated data) is probably due to the fact that silver species could be not located by SXRD. The inset shows the PXRD pattern of Ag-ox (48 h) together with that calculated for silver metal (fcc, d = 4.0862),^{S4} showing that silver metal is formed probably on the surface of Ag-ox particles at an ion-exchange rate of $\geq 100\%$, which is also supported by the color change by prolonged stirring (see photo images).

[S4] R. W. G. Wyckoff, Crystal Structures Vol. 1, Second edition, Interscience Publishers, 1964.



Fig. S4 SEM-EDS images. (a) SEM image and the corresponding (b) cesium mapping of Cs_2 -red. (c) SEM image and the corresponding (d) silver and (e) cesium mappings of Ag_2 -ox. Note that cesium is barely observed and silver is uniformly distributed in the Ag_2 -ox particles, confirming the successful exchange of Cs⁺ with Ag^+/Ag^0 .



Fig. S5 Crystal structures of Ag_2 -ox in the *ab*-plane. (a) Polyhedral and (b) space filling representations. Green and orange polyhedra show the [MoO₆] and [CrO₅N] units, respectively. Black lines in (a) show the C-C, C-N, and C-O bonds in [Cr₃O(OOCH)₆(mepy)₃]⁺. Light blue transparent circles in (a) show the one-dimensional channels along the *c*-axis. Red, black, and blue spheres in (b) show the oxygen, carbon, and nitrogen atoms, respectively. Note that the positions of the silver species, which probably resides in the channels, could not be resolved due to the clustering and/or severe disordering.



Fig. S6 Time course of the amounts of (a) Ag or Cu incorporated into Cs_2 -red by reduction-induced ionexchange (formula suggested at 20 min is $Cu_{0.66}[Cr_3O(OOCH)_6(mepy)_3]_2[PMo_{12}O_{40}] \cdot 5H_2O$, which corresponds to 100%), (b) Cu incorporated into Cs-ox by simple ion-exchange (assumed formula at ion-exchange rate of 100% is $Cu_{0.5}[Cr_3O(OOCH)_6(mepy)_3]_2[PMo_{12}O_{40}] \cdot 5H_2O$).



Fig. S7 PXRD patterns of (a) powdered and (b) single crystals of Cs_2 -red. Inset shows the photo image of the single crystals for the PXRD measurement. Note that the diffractions of *h*00 and 0*k*0 were barely observed in (b) so that it can be assumed that the *c*-axis lies in the flat plane of the single crystal and that probably the long side corresponds to the *c*-axis.



Fig. S8 Time-dependent PL line profiles of the single crystal shown in Fig. 3c.