

Supporting Information

Silver ion integrated organically functionalized Anderson-type polyoxometalate exhibiting photochromism and sensitive ultraviolet detection

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Fig. S17 XPS spectra of **1** before and after Xe lamp irradiation.

Table S1 Crystal Data and Structure for complexes prec-**1b** and **1**.

References

Chemicals and materials

Silver tetrafluoroborate (98%) and n-butyl isocyanate (98%) were purchased from Aladdin. Dimethyl sulfoxide was obtained from Sinopharm, and acetonitrile was obtained from Alfa Aesar. All chemicals and solvents obtained from the supplier were used directly without further purification. $(\text{TBA})_3[\alpha\text{-Mo}_8\text{O}_{26}]^1$ and $(\text{TBA})_3\{\text{MnMo}_6\text{O}_{18}[(\text{OCH}_2)_3\text{CNH}_2]_2\}^2$ was prepared following procedures described in the literature.

Characterization methods

FT-IR spectra were recorded in the 400-4000 cm^{-1} region on an Alpha Centaur FT-IR spectrophotometer (KBr pellets). The structures of the samples were identified by XRD (Rigaku Ultima IV) with Cu $K\alpha$ radiation (50 kV). X-ray photoelectron spectroscopy (XPS) were obtained via the VG ESCALAB MK II X-ray photoelectron spectrometer (the C1s of carbon was calibrated as around 284.8 eV). The optical power of different photosource was measured with the CEL-NP2000-2(10)A fully automatic optical power meter (CEAULIGHT, China). Cyclic voltammetry measurements were performed via a CHI 660E electrochemistry workstation (ChenHua, China), which was also used to record the electrochemical impedance spectra. The isotope distribution of prec-**1b** was tested using the AB SCIEX X500R QTOF high-resolution mass spectrometry system from the United States. The absorbance of **1** was measured with a UV-8000S ultraviolet-visible spectrophotometer. Raman testing was performed using a Raman spectrometer (Labramis, Horiba Jobbin Yvon, Paris, France). The wavelength was 532 nm. The laser power was 5 mW for all experiments. Spectra were collected

with a 50-object lens for 4 s.

X-ray crystallography

The diffraction data were collected on a Rigaku XtaLAB Synergy diffractometer with Cu K α radiation ($\lambda = 1.54184 \text{ \AA}$). The intensity data were scaled and corrected for absorption, and final cell constants were calculated from the xyz centroids of strong reflections from the actual data collections after integration. The space group was determined based on systematic absences and intensity statistics. The structure was solved using the charge-flipping algorithm, as implemented in the program SUPERFLIP2 and refined by full-matrix least-squares techniques against F² using the programs SHELXS-97 and SHELXL-97 within OLEX2.4.³ All nonhydrogen atoms were refined anisotropically, and the hydrogen atoms were included at idealized positions. The SQUEEZE option of PLATON was used at the final refinement to account for the contribution of disordered solvent molecules to the calculated structure factors.⁴ The positions of the metal atoms and their first coordination spheres were located from direct-methods. Other non-hydrogen atoms were found in alternating difference Fourier syntheses and least-squares refinement cycles. During the final cycles, except for some solvent molecules, all other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions refined using idealized geometries and assigned fixed isotropic displacement parameters. The joint Cambridge Crystallographic Data Center (CCDC) number of 2500935 for prec-**1b** and 2424718 for **1**.

Supporting Figures

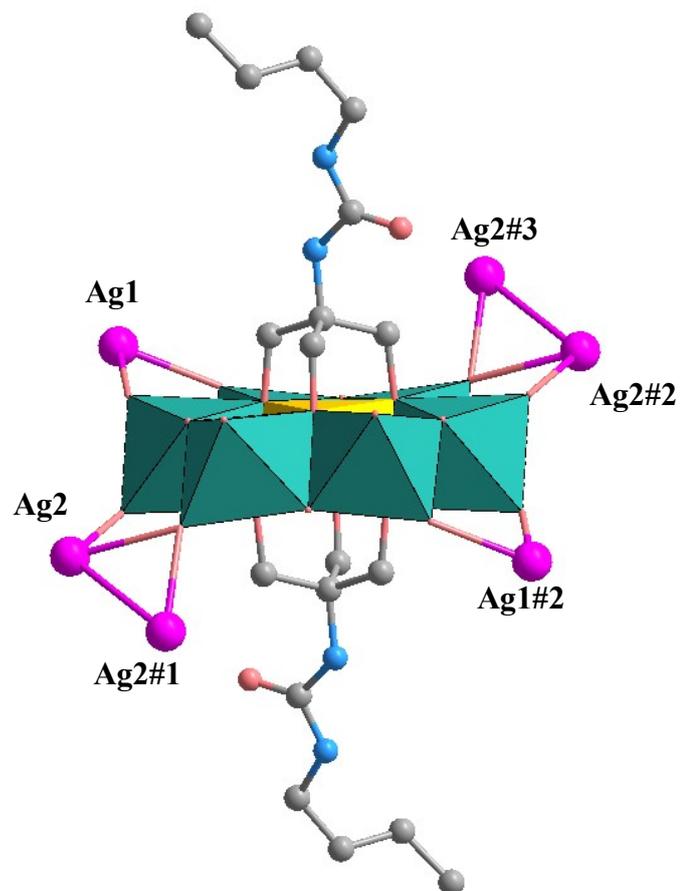


Fig. S1 Coordination environment of Ag⁺ and prec-**1b** polyoxoanion. Symmetric code:

#1 2-x, 1-x+y, 1.5-z; #2 2-x, 1-y, 1-z; #3 x, x-y, 0.5+z.

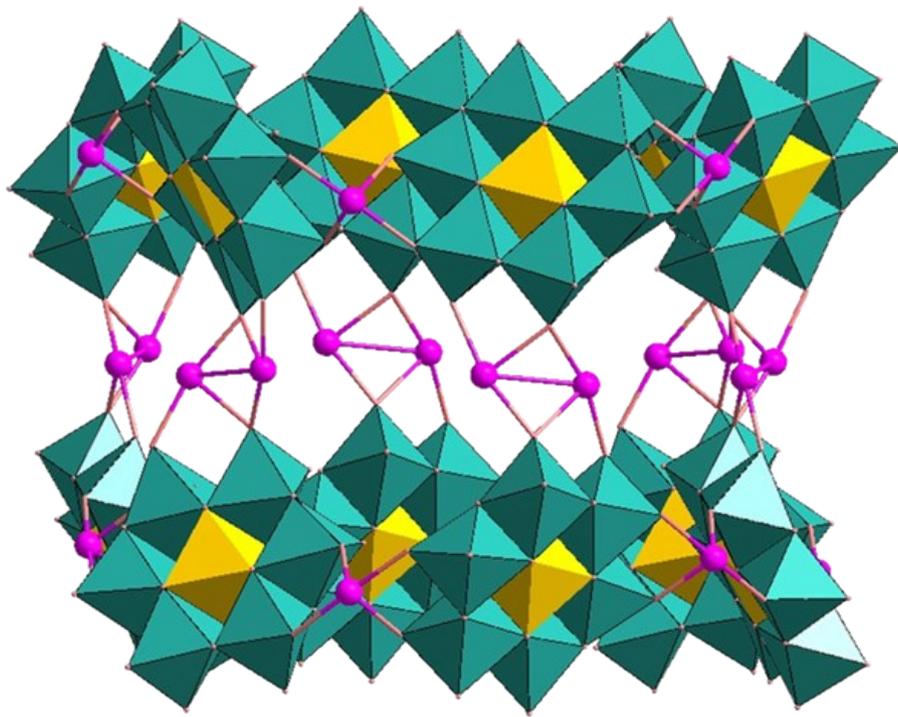


Fig. S2 The interlayer connection mode.

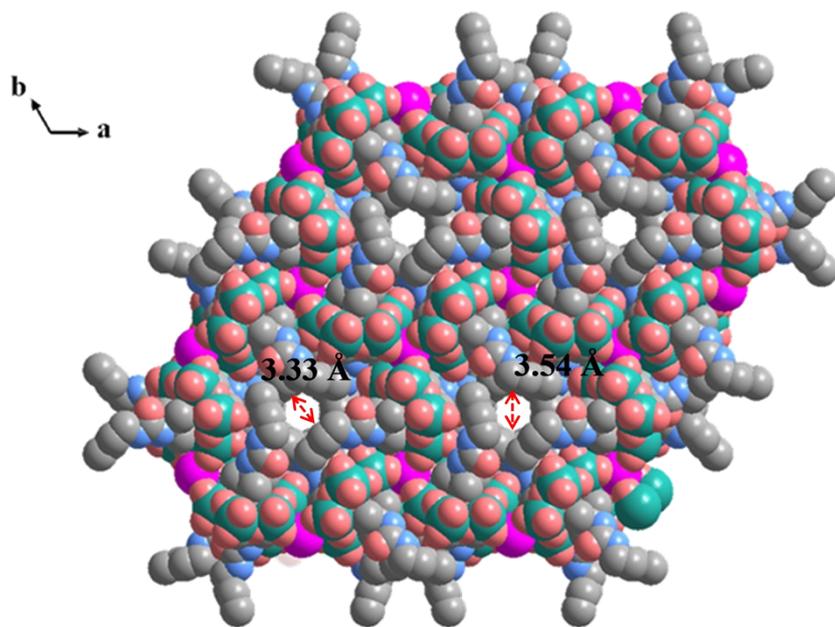


Fig. S3 Filling diagram of **1** along the *c*-axis.

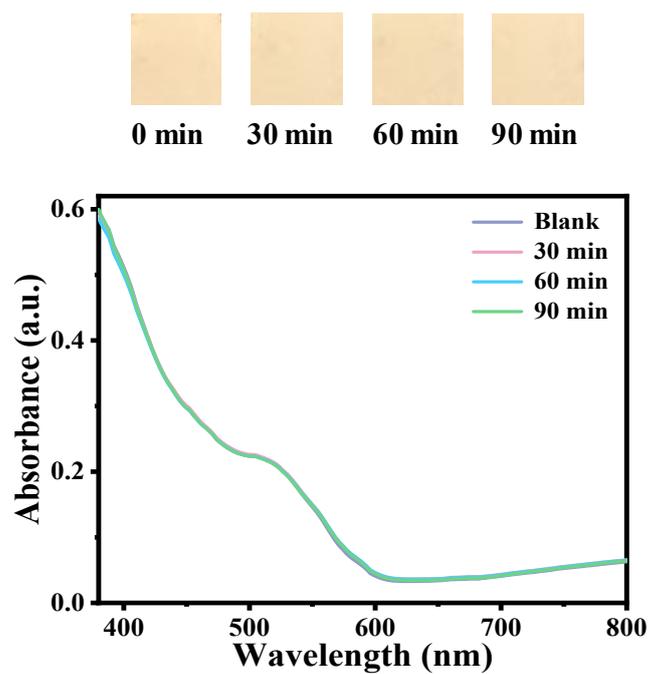


Fig. S4 Colour (top) and UV-Vis spectra (bottom) of prec-**1b** upon Xe lamp irradiation at 20 cm height for different times.

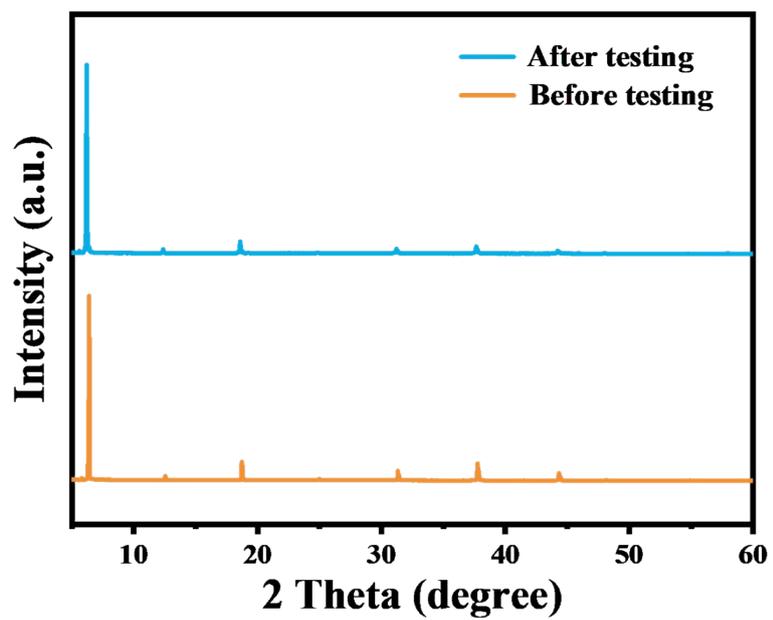


Fig. S5 PXRD of prec-**1b** upon 300 W Xe lamp irradiation at 20 cm height for different times.

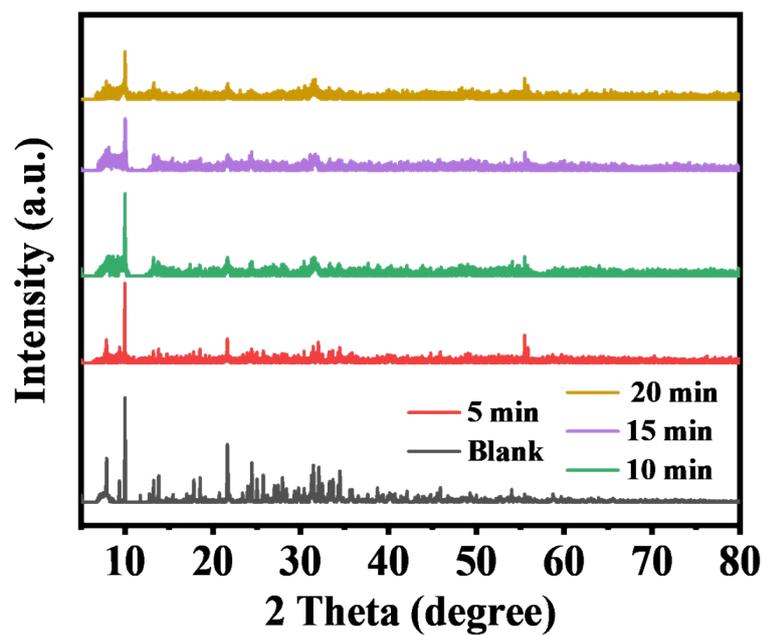


Fig. S6 PXRD changes of **1** upon 300 W Xe lamp irradiation at 20 cm height for different times.

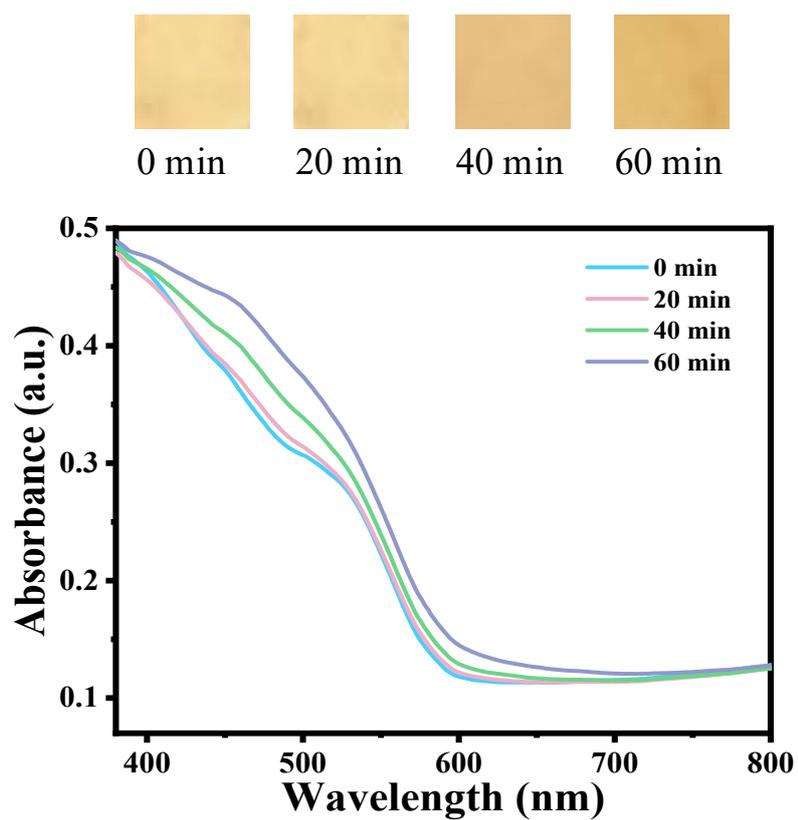


Fig. S7 Colour (top) and UV-Vis spectra (bottom) changes of **1** upon 12 W 254 nm UV lamp irradiation at 20 cm height for different times.

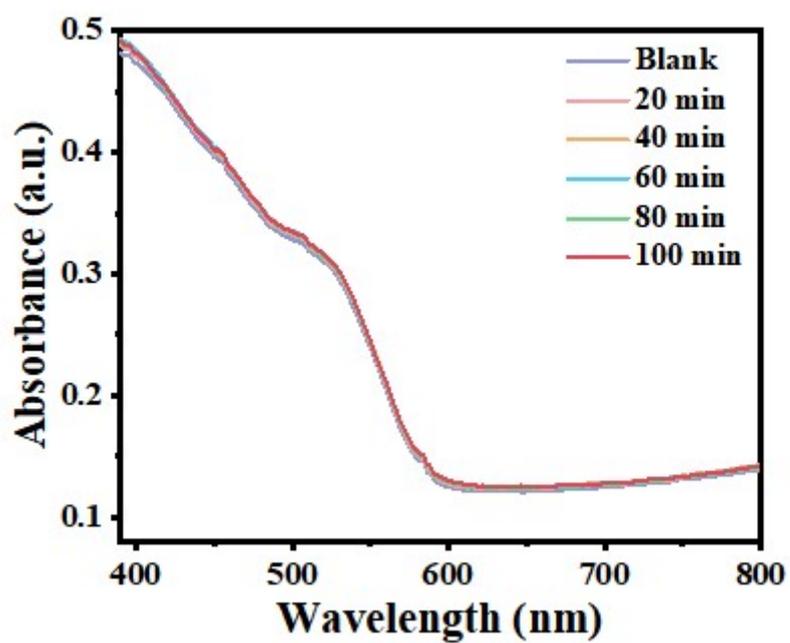


Fig. S8 UV-Vis spectra changes of **1** upon 5 W UV lamp irradiation at 5 cm height for different times.

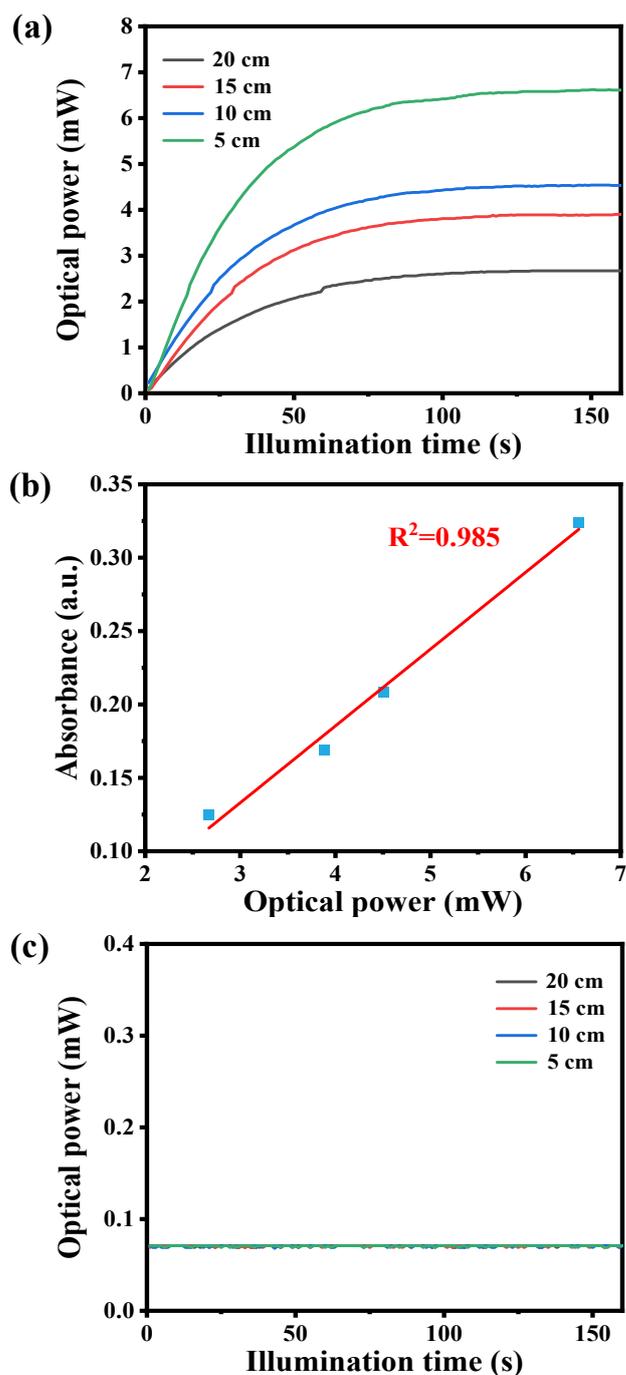


Fig. S9 (a) Variations of 300 W Xe lamp intensity measured by a commercial light intensity meter at different distances. (b) The linear relationship between the absorbance of **1** and the light intensity of Xe lamp at different distances. (c) Variations of 12 W 254 nm UV lamp intensity measured by a commercial light intensity meter at different distances.

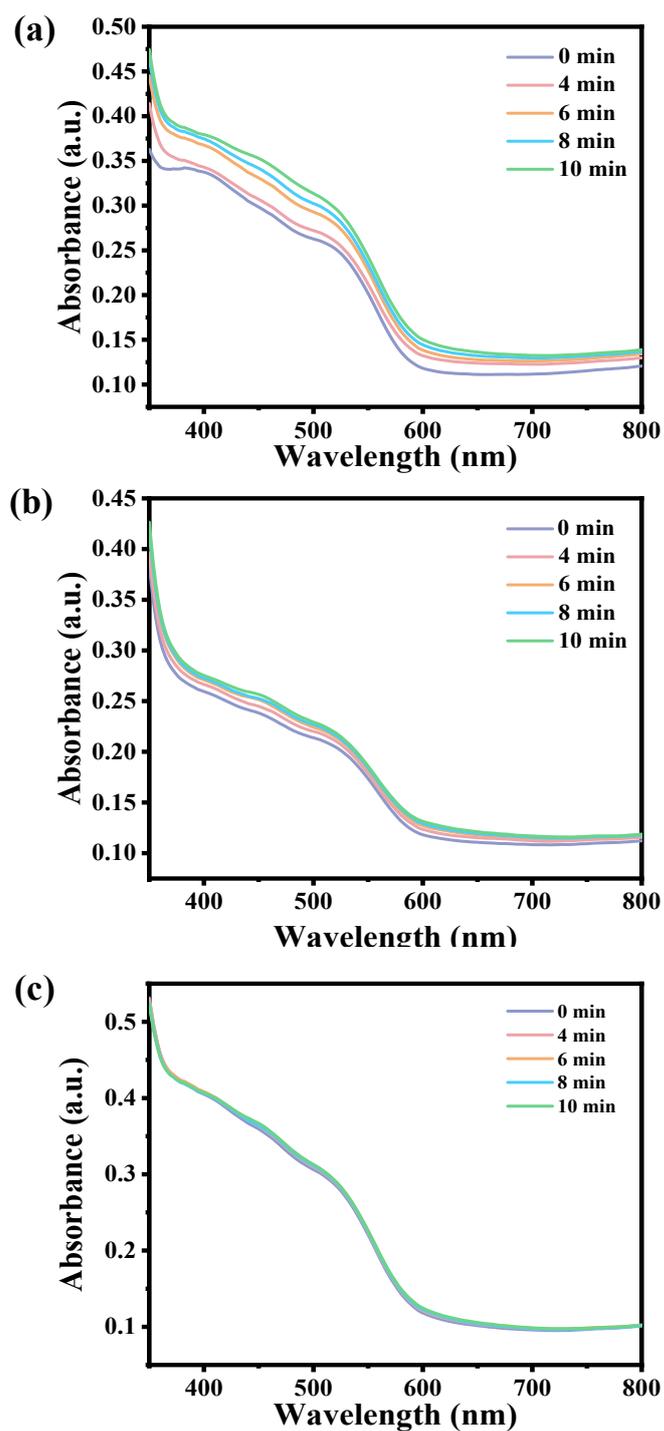


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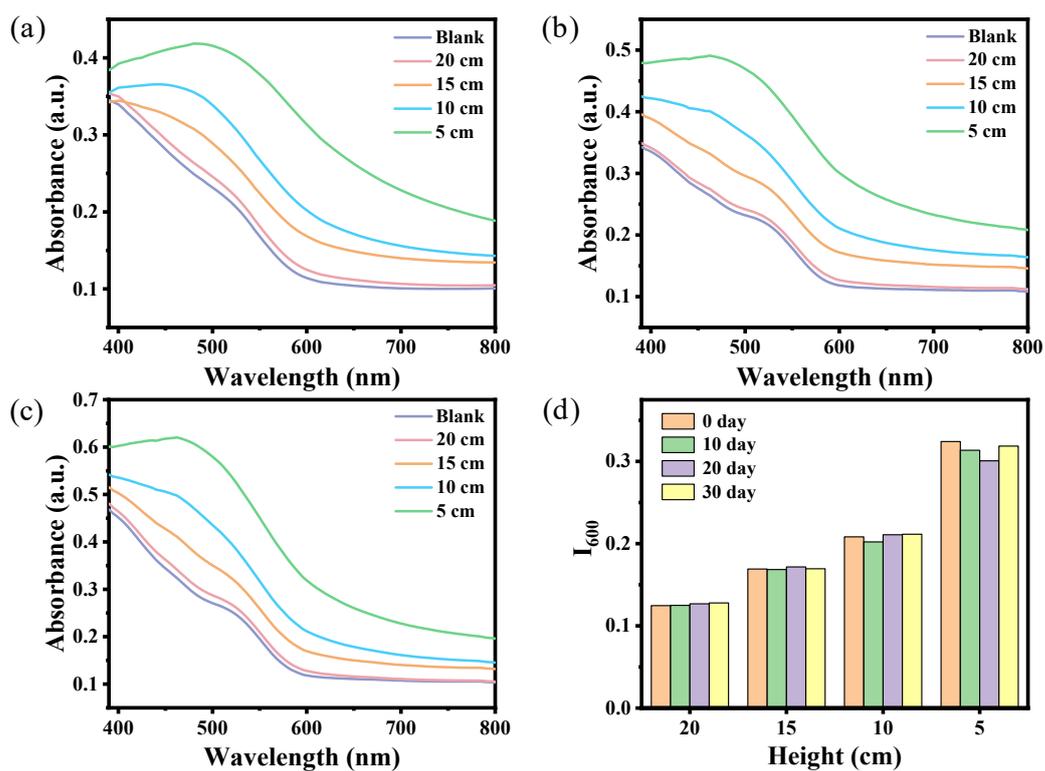


Fig. S11 UV-Vis spectra of **1** after storage for (a) 10, (b) 20, and (c) 30 days, respectively, followed by 1 min irradiation at different heights under a 300 W Xe lamp, and (d) the corresponding absorbance comparison.

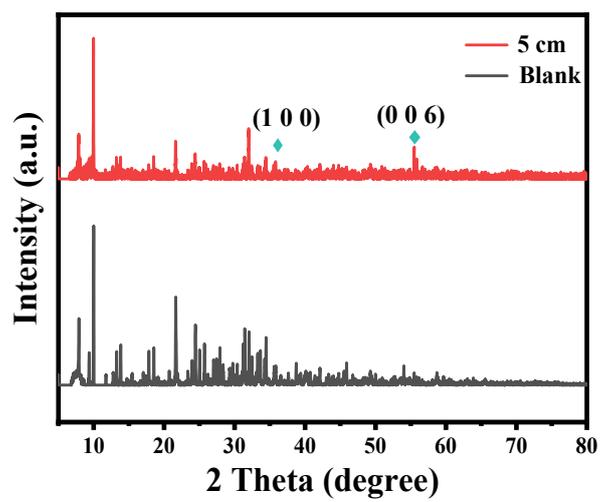


Fig. S12 PXRd comparison of **1** before and after irradiation.

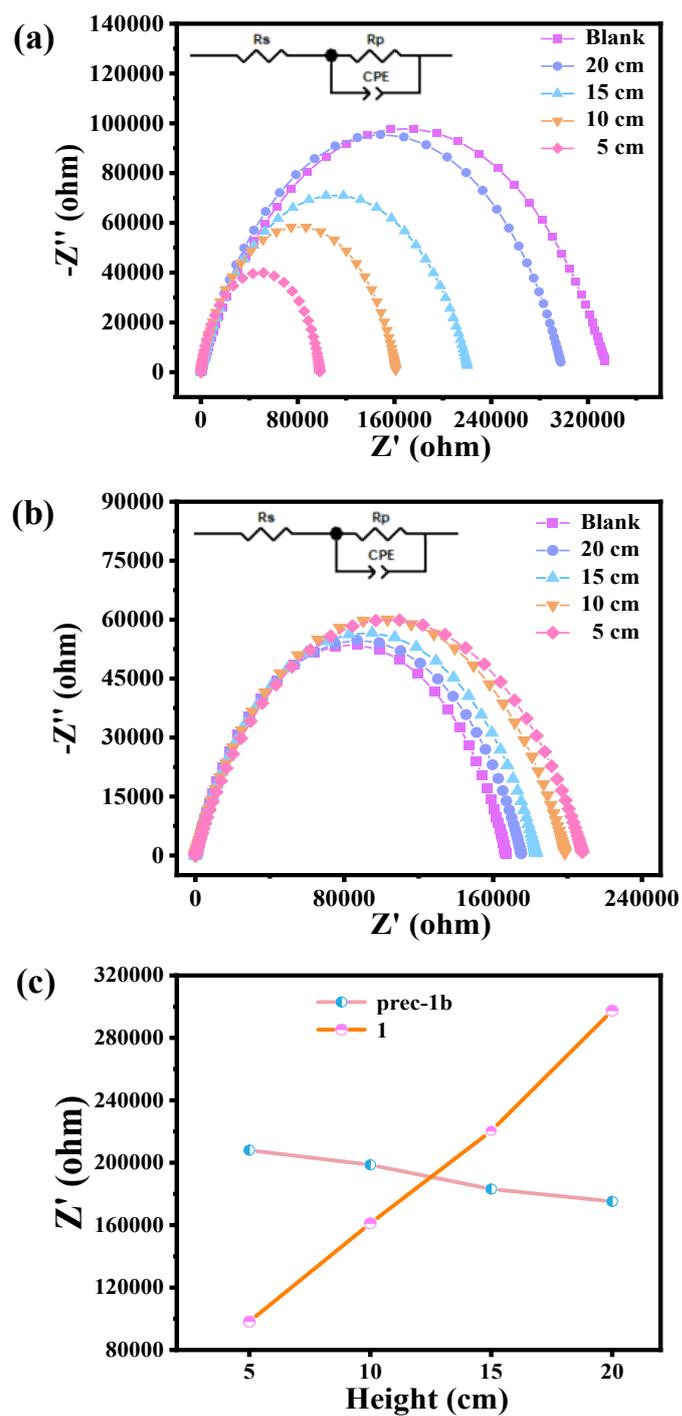


Fig. S13 Impedance changes of **1** (a) and **prec-1b** (b) upon Xe lamp irradiation at different distances for 1 min, and their comparison (c).

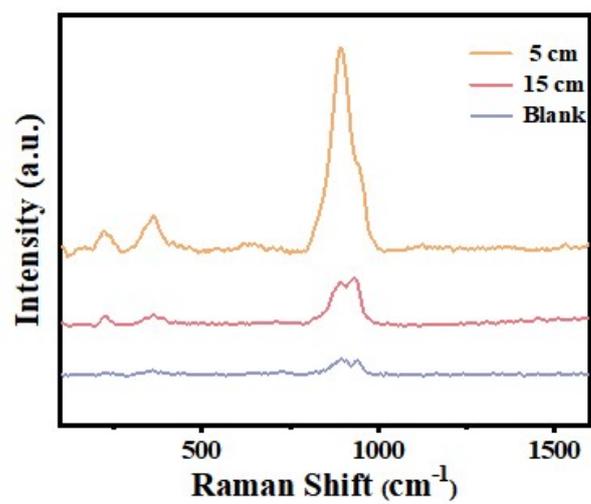


Fig. S14 Raman spectra of **1** before and after Xe lamp irradiation.

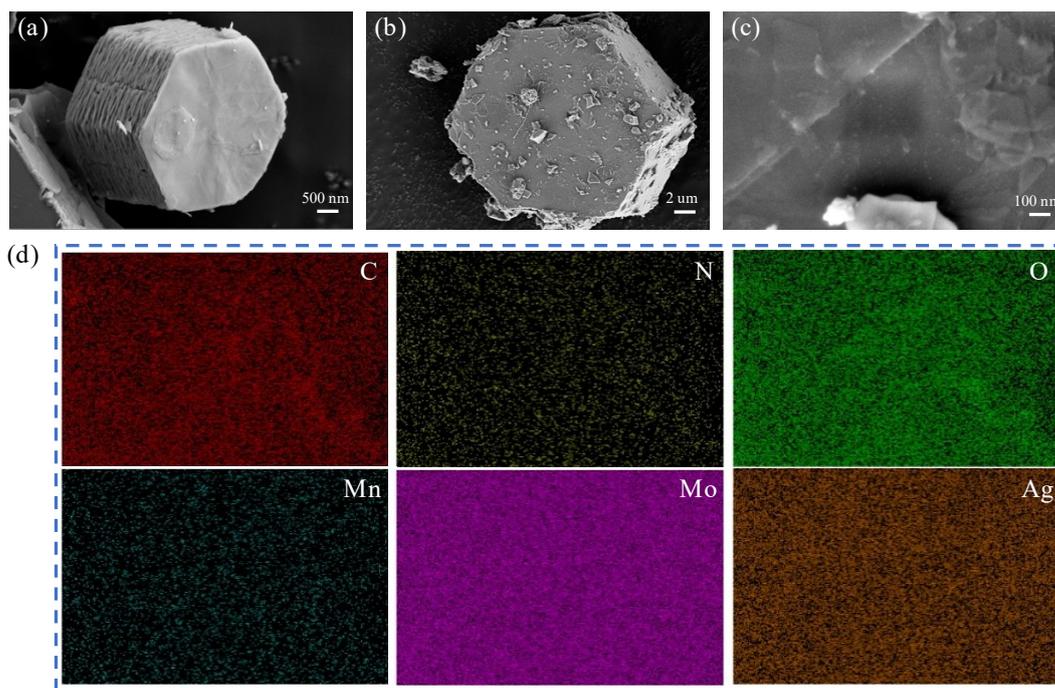


Fig. S15 SEM images of **1** (a) before reduction and (b) after irradiation under a 300 W Xe lamp at a height of 5 cm for 1 min, along with (c) a magnified view of the reduced sample and (d) the corresponding elemental mapping.

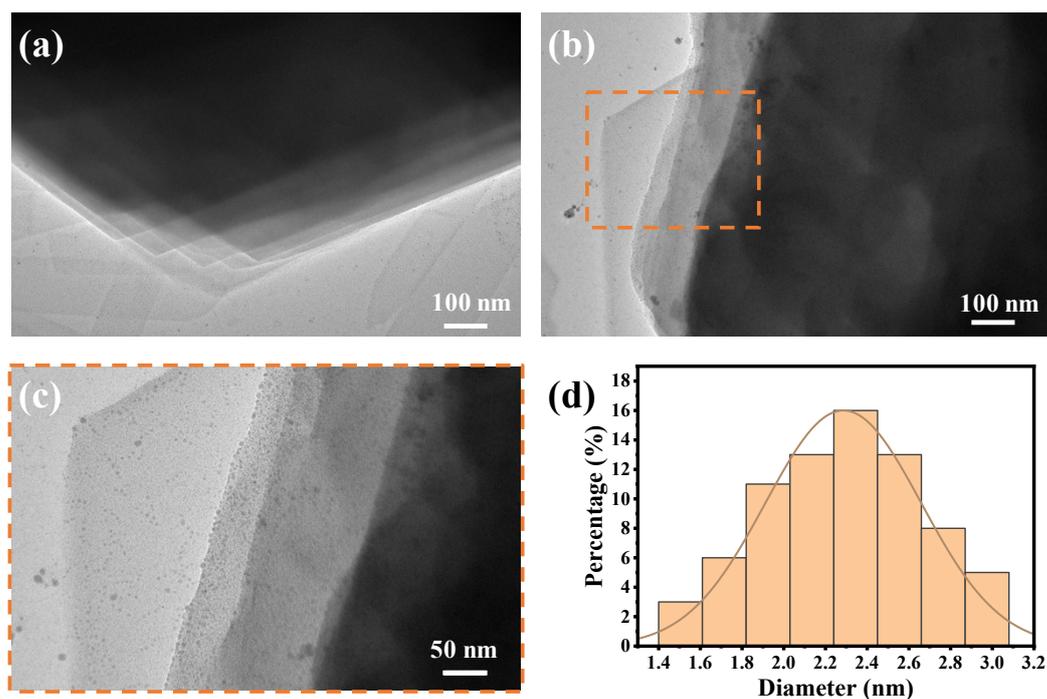


Fig. S16 TEM images of **1** (a) before reduction and (b) after irradiation under a 300 W Xe lamp at a height of 5 cm for 1 min, along with (c) a magnified view of the reduced sample and (d) particle size distribution histogram of the reduced silver nanoparticles.

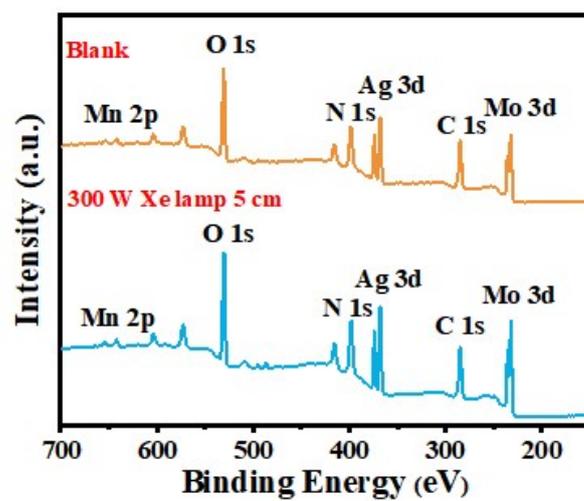


Fig. S17 XPS spectra of **1** before and after Xe lamp irradiation.

Table S1 Crystal Data and Structure for complexes prec-**1b** and **1**.

Parameter	prec- 1b	1
Temperature [K]	100	300
Crystal system	Monoclinic	Trigonal
Space group	$P2_1/c$	$P\bar{3}c1$
a [Å]	27.8840(3)	20.3614 (2)
b [Å]	27.9982(2)	20.3614(2)
c [Å]	28.3825(3)	24.6912 (3)
α [°]	90	90
β [°]	117.108(10)	90
γ [°]	90	120
V [Å ³]	19724.2(4)	8865.2(2)
Z	4	6
ρ_{calc} [g·cm ⁻³]	1.527	2.043
μ [mm ⁻¹]	8.150	19.380
$F(000)$	9367.0	5110.0
λ [Å]	1.54184	1.54184
$R_{\text{(int)}}$	0.0393	0.0407
Limiting indices	$-32 \leq h \leq 33, -33 \leq k \leq 30, -33 \leq l \leq 33$	$-12 \leq h \leq 24, -24 \leq k \leq 22, -29 \leq l \leq 28$
Reflections collected	85121	36565

Independent reflections	34715	5133
Data/restraints/parameters	34715/361/2125	5133/76/345
Goodness-of-fit	1.095	1.042
$R_1^a, wR_2^b (I > 2\sigma(I))$	0.1292, 0.2845	0.0653, 0.1772
R_1^a, wR_2^b (all data)	0.1390, 0.2882	0.0692, 0.1820

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$. ^b $wR_2 = \{\sum [w (F_o^2 - F_c^2)^2] / \sum [w (F_o^2)^2]\}^{1/2}$.

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