Supplementary Information

A silver-substituted phosphomolybdate prevents the growth of bacteria without affecting the balance of reactive oxygen species†

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1. Supplementary Figures and Tables

Table S1 Crystallographic data and structural refinements for SPM

Empirical formula	$C_4H_{24}Ag_2Mo_5N_4O_{25}P_2$
Formula weight	1285.65
Crystal system	Monoclinic
Space group	*C2/c*
a / Å	12.374(3)
b / Å	12.165(3)
c / Å	17.437(5)
α / deg	90.00
β / deg	91.265(4)
γ / deg	90.00
V / Å^3	17.437(5)
Z	4
D_c / g cm^{-3}	3.254
μ / mm^{-1}	4.008
T / K	296(2)
Limiting indices	$-14 \le h \le 14$
	$-14 \le k \le 14$
	$-14 \le l \le 20$
Measured reflections	6518
Independent reflections	2305
R_{int}	0.0199
Data / restrains / parameters	2305 / 3 / 200
GOF on F^2	1.075

Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0189,
	wR_2 = 0.0461
R indices (all data)	R_1 = 0.0203
	wR_2 = 0.0468
Completeness	99.40 %

Table S2 Selected bond length (Å) for SPM

Mo(1)-O(1)	1.705(2)	Mo(2)-O(2)	1.699(2)	Mo(2)-O(6)	1.894(9)
Mo(1)-O(4)	1.911(2)	Mo(2)-O(5)	1.717(3)	Mo(2)-O(10)	2.325(2)
Mo(1)-O(9)	2.300(2)	Mo(2)-O(7)	1.890(2)	Mo(2)-O(12)	2.395(2)
Mo(3)-O(3)	1.698(3)	Mo(3)-O(8)	1.705(3)	Mo(3)-O(4)	1.916(2)
Mo(3)-O(7)	1.940(2)	Mo(3)-O(10)	2.214(2)	Mo(3)-O(9)	2.332(2)
Ag(1)-O(11)	2.275(2)	Ag(1)-O(12)	2.317(2)	Ag(1)-O(1)	2.537(3)
P(1)-O(9)	1.549(2)	P(1)-O(10)	1.553(2)	P(1)-O(11)	1.511(2)
P(1)-O(12)	1.529(2)				

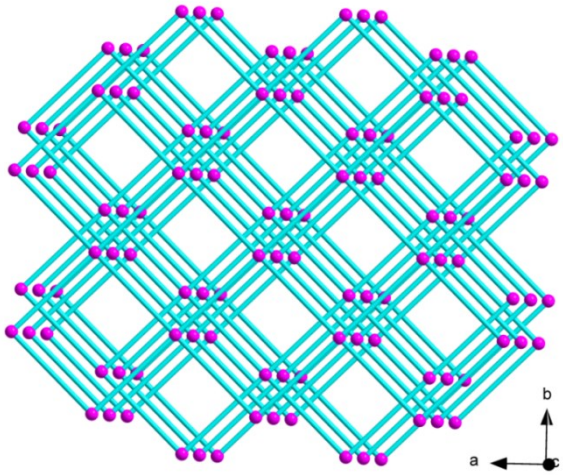

Fig. S1 The topology of SPM, purple ball for Strandberg-type cluster and turquiose stick for Ag^{+} (View of C axis).

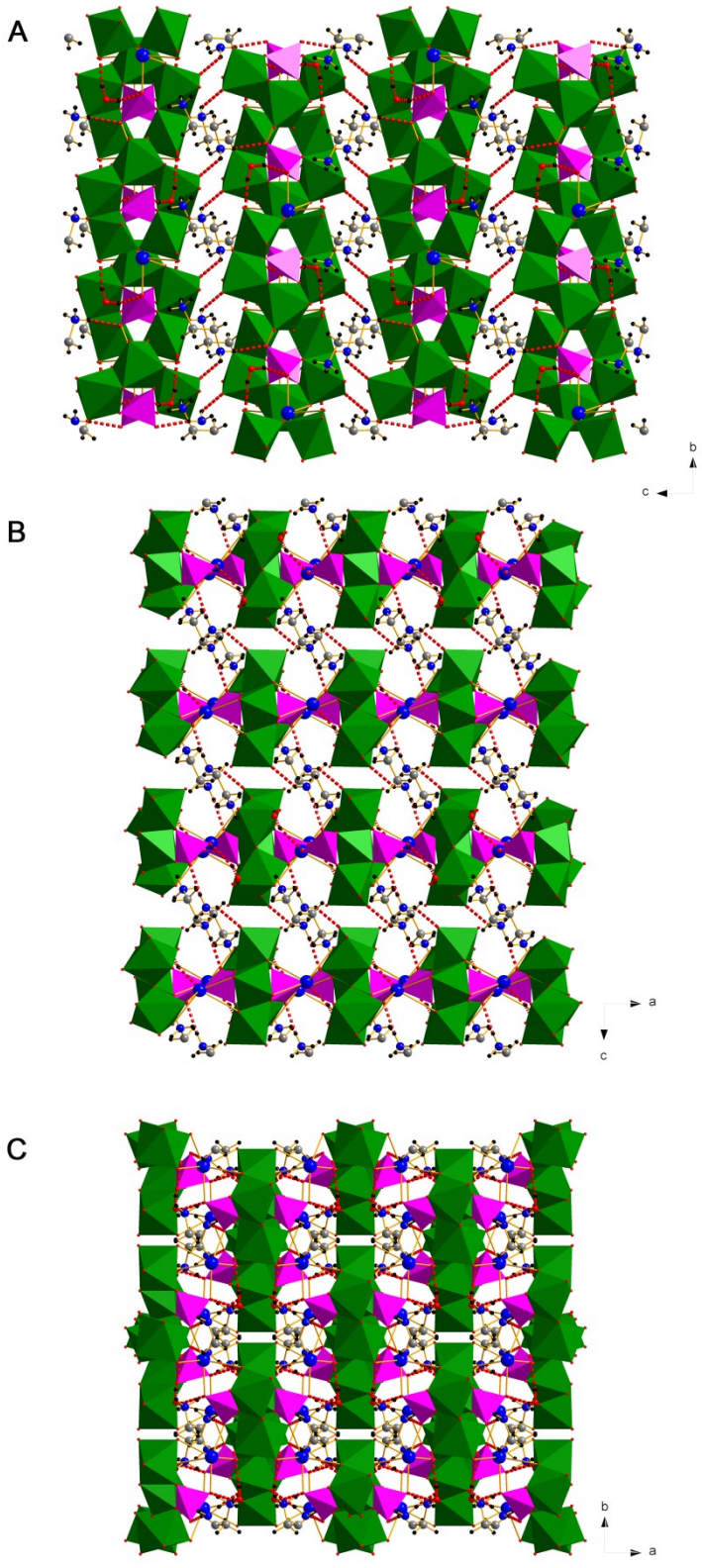

Fig. S2 Three-dimensional stacking diagram of SPM from a-axis (A), b-axis (B), and c-axis (C).

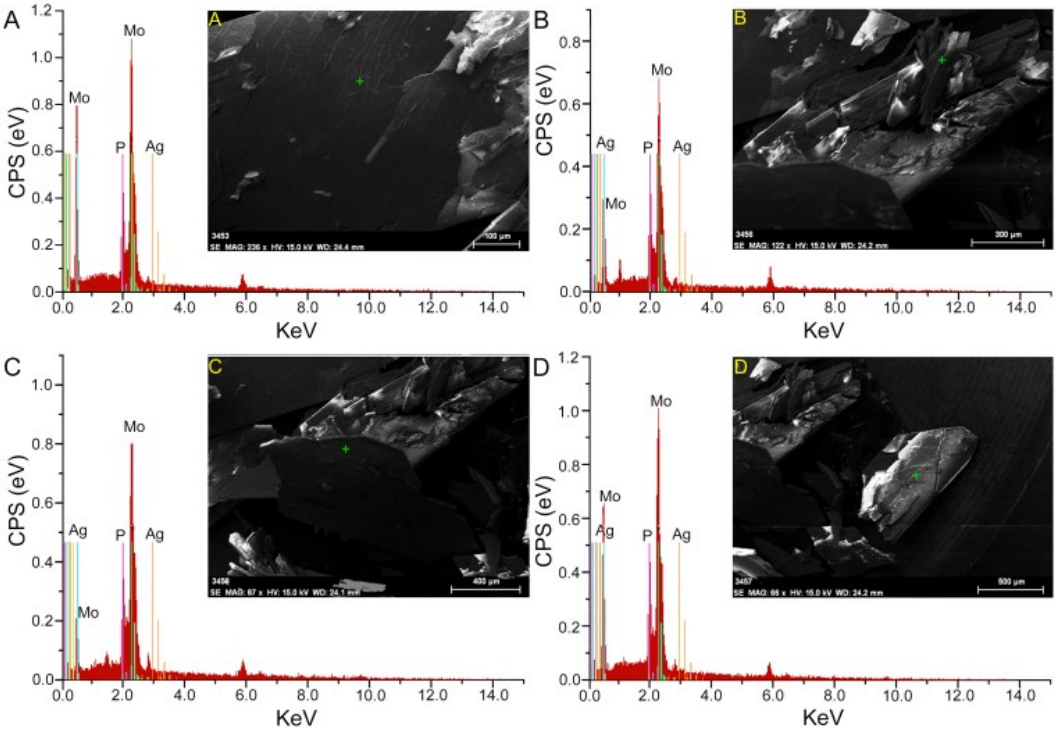

Fig. S3 EDX spectra of SPM (inset: corresponding images of SPM crystal surface).

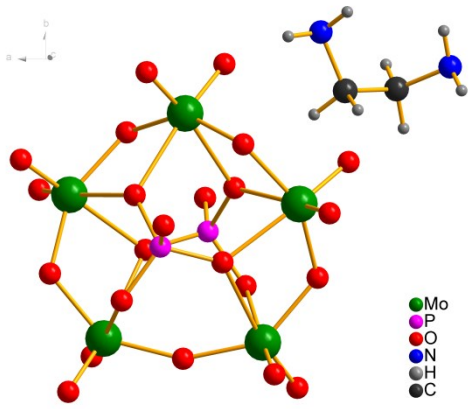

Fig. S4 Combined polyhedral/ball-and-stick representation of the $H_6(en)P_2Mo_5O_{23}$.

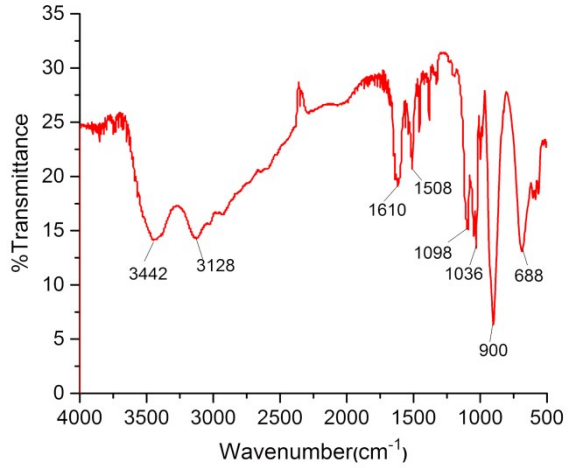

Fig. S5 IR spectrum for SPM.

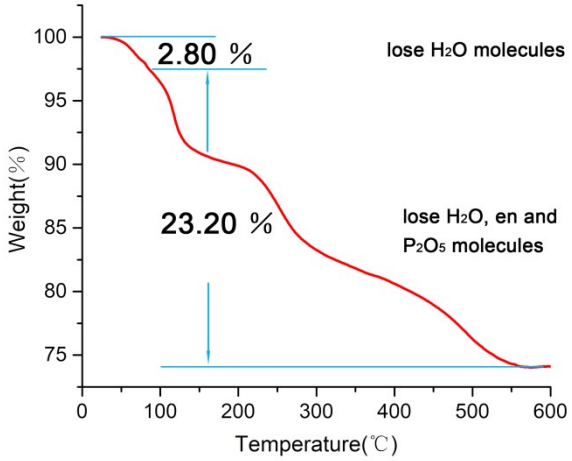

Fig. S6 TGA curve of SPM.

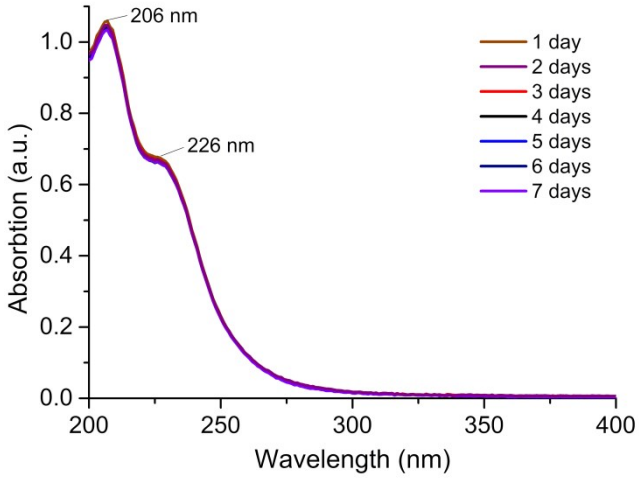

Fig. S7 UV-Vis spectra of SPM in deionized water for 1–7 days.

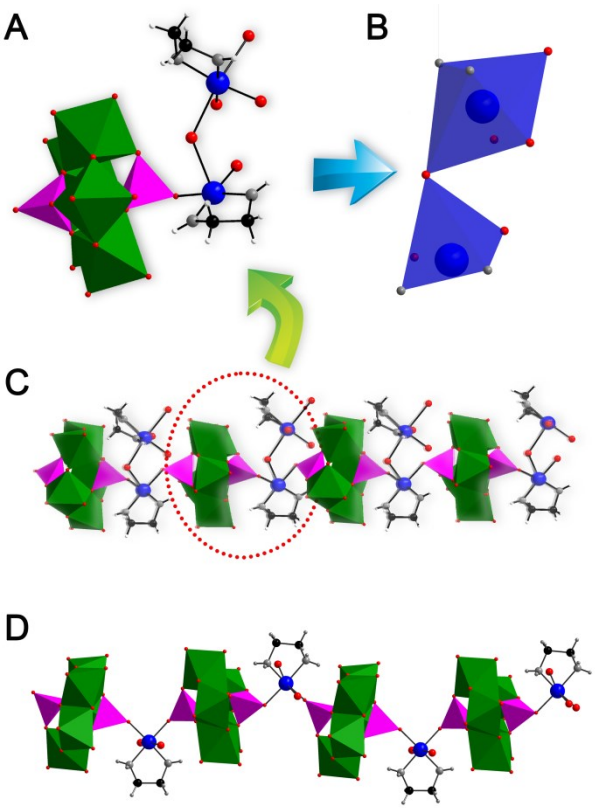

Fig. S8 (A) Combined polyhedral/ball-and-stick representation of one Cu_2PM subunit in the crystal. (B) Polyhedral view of the coordination mode of di-nuclear Cu cluster in Cu_2PM. (C) Combined polyhedral/ball-and-stick view of the 1-D linear structure of Cu_2PM. (D) Combined polyhedral/ball-and-stick view of the 1-D linear structure of Cu_1PM. (lattice water molecules and protonated en molecules are omitted)[1]

2. Experimental Section

2.1 Materials and methods

Reagents used in this study were all of analytical grade, purchased from commercial suppliers and used as received unless otherwise stated. 2′,7′-dichlorofluorescin diacetate (DCFH-DA) was purchased from Sigma-Aldrich. $AgNO_3$, $NaMoO_4{\cdot}2H_2O$, $Na_2HPO_4{\cdot}12H_2O$ and ethanediamine were purchased from J & K. All the solutions were prepared with Milli-Q water and filtered through a 0.22 μm filter (Millipore). E. coli DH5 and puc57 plasmid were purchased from Sangon Biotech, Shanghai in China.

The single crystal data of SPM and (en)$[H_6P_2Mo_5O_{23}]$ were collected on a Bruker CCD, Apex-II diffractometer with graphite monochromated Mo Kα (λ = 0.71073 Å) radiation at room temperature. Routine Lorentz and polarization corrections were applied and an absorption correction was performed using the SADABS program. The structure was solved by direct methods and refined using full-matrix least squares on F^2. All calculations were performed using the SHELXL-97 program package. Turbidity and DCF fluorescence were conducted on a Thermo Scientific

Varioskan Flash microplate reader. Elemental analysis was performed on a PQEXCe II ICP-MS. IR/UV spectra were recorded on a NICOLET iS10 and UV-3600 spectrometer respectively.

2.2 Synthesis of SPM

Two solutions were prepared separately. Solution A: $Na_2MoO_4{\cdot}2H_2O$ (2.416 g, 10.00 mmol) and $Na_2HPO_4{\cdot}12H_2O$ (2.399 g, 6.70 mmol) were dissolved in water (30 mL) under stirring. Solution B: $AgNO_3$ (1.70 g, 10.00 mmol) and en (0.10 mL, 1.49 mmol) were added to water (30 mL) under stirring. The resulting mixture of B is added to solution A. The mixture was stirred for 10 min at room temperature and then the pH value was adjusted to 6.0 by adding 4 $mol{\cdot}L^{-1}$ HNO_3 dropwise. The solution was kept at 85 °C for 1h and filtered when it was still hot. The filtrate was allowed to evaporate in an open beaker at room temperature. Silver gray strip crystals were collected after one week. Yield: 0.71 g. ca. 27% (based on $Na_2MoO_4{\cdot}2H_2O$). Anal. Calcd. (found %) for $(H_2en)_2[Ag_2(P_2Mo_5O_{23})]{\cdot}2H_2O$ (SPM): C 3.74 (3.61), H 1.88 (1.98), N 4.36 (4.21).

2.3 Synthesis of $H_6P_2Mo_5O_{23}$

Solution A: $Na_2MoO_4{\cdot}2H_2O$ (2.416 g, 10.00 mmol) and $Na_2HPO_4{\cdot}12H_2O$ (2.399 g, 6.70 mmol) were dissolved in water (30 mL) under stirring. Then, en (0.10 mL, 1.49 mmol) and 30 mL water were added into the solution A, and the mixture was stirred for 10 min at room temperature and then the pH value was adjusted to 5.5 by adding 4 $mol{\cdot}L^{-1}$ HCl dropwise. The solution was kept at 85 ºC for 1h and filtered when it was still hot. The filtrate was allowed to evaporate in an open beaker at room temperature. Pale strip crystals were collected after one week.

As shown in Fig. S1, the molecular structural unit of (en)$[H_6P_2Mo_5O_{23}]$ consists an isolated $H_6P_2Mo_5O_{23}$ cluster and a diprotonated en as counter cation. Interestingly, the diprotonated en is very important in inducing the formation of $H_6P_2Mo_5O_{23}$ cluster. When we use NH_4^+, 1,3-propanediamine, 1,4,7,10-tetraazacyclododecane (Cyclen) and 1,4,7,10-tetraaza cyclododecane (Cyclam) instead of en, no strandberg-type structure was obtained. Hence, diprotonated en may be a template agent for inducing the formation of $[P_2Mo_5O_{23}]^{6-}$ clusters.

2.4 EDX-SEM

The SEM images of SPM as well as the corresponding EDX spectra were detected according to the reported method.[2]

2.5 Stability of SPM

The stability of SPM was studied by using UV-Vis spectroscopy according to the reported method.[3]

2.6 Catalytic ROS production of SPM

DCFH-DA stock solution (1 mM) was prepared with a buffer (20 mM Tris-HCl/150 mM NaCl, pH 7.4) according to the reported procedures.[4] Horseradish peroxidase (HRP) stock solution (4 μM) was prepared with the same buffer. Ascorbate (10 μM) without or with SPM (10 mg) were added to each sample and incubated at 37 °C. The sample (200 μL) was transferred to the wells of a flat-bottomed 96-well black plate. HRP (0.04 μM) and DCFH-DA (100 μM) were added to each solution and incubated in the dark at 37 °C for 1 h. Fluorescence spectra (λ_{ex} = 485 nm) at λ_{em} = 525 nm were measured by a Varioskan Flash microplate reader (Thermo Scientific) every 10 min for 40 h.

2.7 Inhibition of E. coli DH5 growth

Inhibition of *E. coli* DH5 growth was studied according to the reported procedures.[5] E. coli DH5 cells transformed with the puc57 plasmid were cultivated in the LB medium (10 g/L tryptone, 5 g/L yeast extract, 10 g/L NaCl) supplemented with 50 g/ml of ampicillin. The cells were cultivated

at 37˚C with constantly shaking at 250 rpm following a 1:100 inoculation from an overnight culture. Turbidity of the solution was measured using the absorbance at 600 nm by a Varioskan Flash microplate reader (Thermo Scientific) every 30 min. After inoculation for 1.5 h, we divided the LB medium into two parts to insure the same concentration from the beginning. Then, SPM (50 mg in 25 ml solution) was added, and the turbidity was measured every 15-30 min until the growth rate slowed down.

[1] X. Ma, C. Zhang, J. A. Hua, P. T. Ma, J. P. Wang and J. Y. Niu, *CrystEngComm*, 2019, **21**, 394–398.
[2] J. Hua, X. Ma, P. Ma, J. P. Wang and J. Y. Niu, *J. Clust Sci.*, 2013, **24**, 689–700.
[3] N. Gao, H. J. Sun, K. Dong, J. S. Ren, T. C. Duan, C. Xu and X. G. Qu, *Nature Commun.*, 2014, **5**, 3422–3431.
[4] X. H. Wang, X. Y. Wang, C. L. Zhang, Y. Jiao and Z. J. Guo, *Chem. Sci.,* 2012, **3**, 1304–1312.
[5] B. Zartl, K. Silberbauer, R. Loeppert, H. Viernstein, W. Praznik and M. Mueller, *Food & func.*, 2018, **9**, 1638–1646.