Supplementary Material (ESI) for Chemical Communications

Supporting Information

Design Synthesis and Photocatalytic Activity of a Novel Lilac-like Silver-Vanadate Hybrid Solid Based on Dicyclic Rings of $[V_4O_{12}]^{4-}$ with $\{Ag_7\}^{7+}$ Cluster

Yan Hu, Fang Luo* and Fangfang Dong

Key Lab of Polyoxometalate Science of Ministry of Education, Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China

* Corresponding author.
E-mail: luof746@nenu.edu.cn

Materials and Measurements

All reagents were obtained from commercial sources and used without further purification. The C, H and N elemental analysis were conducted on a Perkin-Elmer 240 C elemental analyzer. The FT-IR spectra were recorded from KBr pellets in the range 4000-400 cm^{-1} on a Mattson Alpha-Contauri spectrometer. TGA was performed on a PYRIS DIAMOND in flowing N_2 with a heating rate of 10 °C min^{-1}. X-ray powder diffraction (XRD) measurements of the as-prepared samples were performed on a Rigaku D/max-ⅡB X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å). UV-vis spectroscopy was performed on a U-3010 spectrophotometer (Hitachi, Japan). Energy Dispersive Spectrum (EDS) was used to determine the chemical composition of compound **1** on a S4800 Field-Emission Scanning Electron Microscope (Hitachi, Japan).

Crystallographic Analysis

The intensity data were recorded on a Bruker APEX-II CCD system with Mo-Kα radiation (λ = 0.71069 Å). The crystal structure was solved by means of Direct Methods and refined employing full-matrix least squares on F^2 using the *SHELXTL-97*[1] crystallographic software package. The ADDSYM program in PLATON[2] was used to check the space group of **1** and no other lower symmetry or unresolved disorder was found, indicating that the refinement of **1** was reasonable. All the non-hydrogen atoms were refined anisotropically, and the hydrogen atoms on the carbon and nitrogen atoms were located in a Fourier map and refined as riding on their C or N atoms. The detailed crystallographic data and structure refinement parameters for **1** are summarized in **Table S1**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Reference:

1 G. M. Sheldrick, Shelxs-97, *Program for X-Ray Crystal Structure Solution*, University of Göttingen, Göttingen, Germany, 1997; G. M. Sheldrick, Shelxs-97, *Program for X-Ray Crystal Structure Refinement*, University of Göttingen, Göttingen, Germany, 1997.

2 A. L. Spek, PLATON, *A Multipurpose Crystallographic Tool*, Utrecht University, Utrecht, The Netherlands, 1998.

Table S1. Details of data collection and structure refinement for compound **1**.

Formula	$C_{50}\,H_{74}\,Ag_8\,N_{20}\,O_{26}\,V_8$
Mr	2641.78
CCDC	759774
Cryst. Size, mm^3	0.29 × 0.23 × 0.21
Crystal system	Triclinic
space group	$P\bar{1}$
a, Å	12.107(5)
b, Å	12.154(5)
c, Å	15.078(5)
α, deg	83.821(5)
β, deg	68.816(5)
γ, deg	68.176(5)
V, $Å^3$	1919.6(13)
Z	1
D_{calcd}, g cm^{-3}	2.285
F(000), e	1282.0
hkl range	$-14 \le h \le 14$
	$-13 \le k \le 14$
	$-8 \le l \le 17$
θ range, deg	2.12 - 25.00
Reflections collected/unique	9721 / 6685 [*R*(int) = 0.0189]
Absorption coefficient, mm^{-1}	2.997
Data/parameters	6685 / 508
GoF (F^2)	1.096
R_1/wR_2 [$I > 2\sigma(I)$]	0.0523 / 0.1279
R_1/wR_2 (all data)	0.0598 / 0.1320
Largest diff. peak/hole, e $Å^{-3}$	1.244/-1.203

GoF = $[\Sigma w(F_o^2-F_c^2)^2/(n_{obc} - n_{param})]^{1/2}$; $R_1 = ||F_o|-|F_c||/\Sigma|F_o|$, $wR_2 = [\Sigma w(F_o^2-F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$

Table S2. Selected bond lengths (Å) and angles (°) for compound **1**.

Bond lengths (Å)			
Ag(1)-O(6)	2.437(6)	Ag(1)-O(9)	2.459(6)
Ag(1)-Ag(2)#1	3.0580(14)	Ag(2)-O(10)#1	2.195(5)
Ag(2)-O(9)	2.204(5)	Ag(2)-O(7)#1	2.536(7)
Ag(3)-N(1)	2.133(7)	Ag(3)-N(3)	2.138(7)
Ag(3)-O(12)	2.549(6)	Ag(4)-N(6)	2.123(7)
C(23)-N(8)	1.350(11)	Ag(5)-N(7)	2.091(7)
Ag(5)-N(9)	2.094(7)	C(22)-C(23)	1.341(13)
C(22)-N(7)	1.398(13)	C(21)-N(7)	1.309(11)
C(21)-N(8)	1.338(10)	C(11)-C(12)	1.343(14)
C(11)-N(3)	1.378(12)	C(15)-C(14)	1.604(17)
C(24)-N(8)	1.464(10)	C(24)-C(25)	1.522(11)
C(13)-C(14)	1.418(16)	C(13)-N(4)	1.487(13)
C(4)-N(2)	1.491(16)	C(8)-C(9)	1.498(14)
C(8)-N(5)	1.450(13)	C(17)-N(9)	1.377(10)
C(16)-N(9)	1.319(11)	C(16)-N(10)	1.336(11)
C(7)-C(6)	1.353(16)	C(1)-N(1)	1.312(12)
C(1)-N(2)	1.338(14)	N(1)-C(2)	1.365(12)
C(3)-N(2)	1.296(15)	C(3)-C(2)	1.347(14)
N(5)-C(5)	1.335(11)	N(5)-C(7)	1.362(14)
C(19)-N(10)	1.474(11)	C(19)-C(20)	1.516(13)
C(18)-N(10)	1.361(10)	C(18)-C(17)	1.341(12)
C(10)-N(3)	1.312(11)	C(10)-N(4)	1.334(12)
C(12)-N(4)	1.351(13)	C(6)-N(6)	1.355(12)
C(5)-N(6)	1.311(12)	O(1)-V(2)	1.620(5)
O(2)-V(1)	1.791(6)	O(2)-V(2)	1.793(5)
O(3)-V(1)	1.789(6)	O(3)-V(4)	1.810(5)
O(4)-V(3)	1.797(6)	O(4)-V(4)	1.812(7)
O(5)-V(3)	1.791(5)	O(5)-V(2)	1.815(6)
O(6)-V(2)	1.664(6)	O(7)-V(4)	1.642(6)
O(8)-V(3)	1.619(6)	O(9)-V(3)	1.669(5)
O(10)-V(1)	1.669(5)	O(11)-V(4)	1.618(6)

O(12)-V(1)	1.639(5)		
Angles (°)			
O(6)-Ag(1)-O(9)	97.70(19)	O(6)#1-Ag(1)-O(9)	82.30(19)
O(6)#1-Ag(1)-O(6)	180.0(2)	O(9)-Ag(1)-O(9)#1	180.0(3)
O(6)#1-Ag(1)-Ag(2)#1	124.05(15)	O(6)-Ag(1)-Ag(2)#1	55.95(15)
O(9)-Ag(1)-Ag(2)#1	134.49(13)	O(9)#1-Ag(1)-Ag(2)#1	45.51(13)
O(10)#1-Ag(2)-O(9)	174.0(2)	O(10)#1-Ag(2)-O(7)#1	91.6(2)
O(9)-Ag(2)-O(7)#1	94.3(2)	N(1)-Ag(3)-N(3)	153.0(3)
N(1)-Ag(3)-O(12)	99.9(2)	N(3)-Ag(3)-O(12)	102.4(2)
N(6)-Ag(4)-N(6)#2	180.0(1)	N(7)-Ag(5)-N(9)	174.3(3)
C(23)-C(22)-N(7)	109.2(8)	N(7)-C(21)-N(8)	113.6(8)
C(12)-C(11)-N(3)	108.3(8)	C(22)-C(23)-N(8)	107.9(8)
N(8)-C(24)-C(25)	111.8(7)	C(14)-C(13)-N(4)	107.8(10)
N(5)-C(8)-C(9)	112.9(9)	N(1)-C(1)-N(2)	111.3(10)
C(1)-N(1)-Ag(3)	125.4(7)	C(2)-N(1)-Ag(3)	129.9(6)
C(10)-N(3)-Ag(3)	129.6(7)	C(11)-N(3)-Ag(3)	123.9(6)
C(21)-N(7)-Ag(5)	128.8(6)	C(22)-N(7)-Ag(5)	127.5(6)
C(16)-N(9)-Ag(5)	131.0(6)	C(17)-N(9)-Ag(5)	124.6(6)
C(5)-N(6)-Ag(4)	126.4(6)	C(6)-N(6)-Ag(4)	125.7(7)
V(1)-O(2)-V(2)	134.4(3)	V(1)-O(3)-V(4)	132.2(3)
V(3)-O(4)-V(4)	133.9(4)	V(3)-O(5)-V(2)	137.6(3)
V(2)-O(6)-Ag(1)	125.4(3)	V(4)-O(7)-Ag(2)#1	129.2(3)
V(3)-O(9)-Ag(2)	166.3(4)	V(3)-O(9)-Ag(1)	111.1(3)
Ag(2)-O(9)-Ag(1)	81.77(19)	V(1)-O(10)-Ag(2)#1	118.7(3)
V(1)-O(12)-Ag(3)	136.1(3)	O(12)-V(1)-O(10)	109.7(3)
O(12)-V(1)-O(3)	108.7(3)	O(10)-V(1)-O(3)	109.4(3)
O(12)-V(1)-O(2)	109.1(3)	O(10)-V(1)-O(2)	110.7(3)
O(3)-V(1)-O(2)	109.3(3)	O(1)-V(2)-O(6)	109.7(3)
O(1)-V(2)-O(2)	109.3(3)	O(6)-V(2)-O(2)	109.1(3)
O(1)-V(2)-O(5)	108.8(3)	O(6)-V(2)-O(5)	109.5(3)
O(2)-V(2)-O(5)	110.4(3)	O(8)-V(3)-O(9)	109.0(3)
O(8)-V(3)-O(5)	108.6(3)	O(9)-V(3)-O(5)	108.5(3)
O(8)-V(3)-O(4)	109.7(3)	O(9)-V(3)-O(4)	111.0(3)

O(11)-V(4)-O(7)	110.3(4)	O(11)-V(4)-O(3)	108.9(3)
O(7)-V(4)-O(3)	108.5(3)	O(11)-V(4)-O(4)	108.7(4)
O(7)-V(4)-O(4)	110.1(3)	O(3)-V(4)-O(4)	110.3(3)

Symmetry transformations used to generate equivalent atoms: #1 -x+2,-y,-z； #2 -x+1,-y+1,-z+1； #3 x+1,y-1,z ； #4 x-1,y+1,z； #5 -x+3,-y-1,-z； #6 -x+1,-y,-z； #7 -x+2,-y,-z+1

IR spectrum of compound 1

The IR spectrum has strong bands at 906.3939 and 887.1089 cm^{-1} assigning to the terminal V-O stretching. The bands at 757.8996 and 653.7607 cm^{-1} are due to the symmetrical and asymmetrical V-O-V stretching. The bands at 1402.018, 1442.516, 1515.799 and 1639.223 cm^{-1} are the characteristic vibrations of bbi ligand.

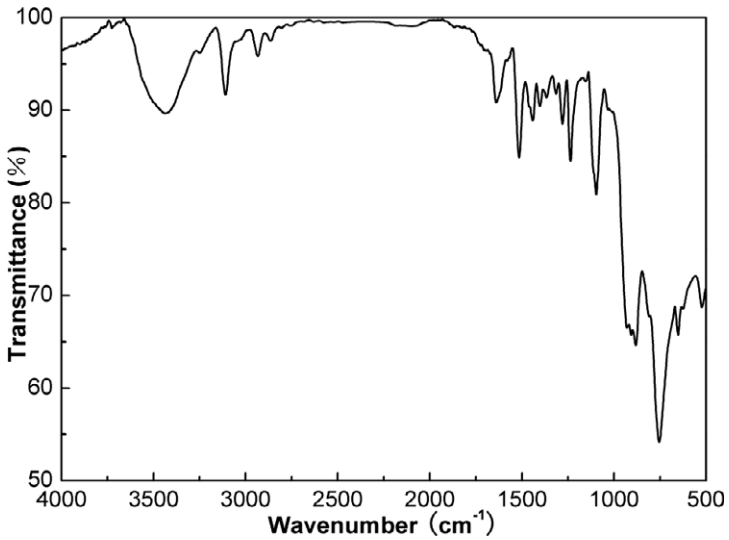

Fig. S1 IR spectrum of compound **1**

TG curve of compound 1

TGA was performed in the range of 50-1000 °C on a Perkin-Elmer TG-7 analyzer in flowing N_2 with a heating rate of 10 °C·min^{-1}. The TG curve of compound **1** shows four weight-loss steps in the temperature range of 50-1000 °C. The first weight-loss of 1.45% (calcd 1.36%) in the temperature range of 50-190 °C, is corresponding to the loss of two free water molecules per formula unit. A second weight-loss of 11.85% (calcd 11.29%) is attributed to the loss of the free $[Ag(bbi)]^{+\infty}$ chain, with the temperature range of 190-284 °C. The last two weight-loss total of 28.80% (calcd 28.69%) in the temperature range of 284-536 °C, is likely corresponding to the reduction of Ag^+ to Ag(s) and the loss of Ag-bbi

, then the construction based on $[V_4O_{12}]^{4-}$ disintegrated. It took on ascend trend of the curve in the temperature range of 650-1000 °C, because the decomposition products were oxidized again at high temperature.

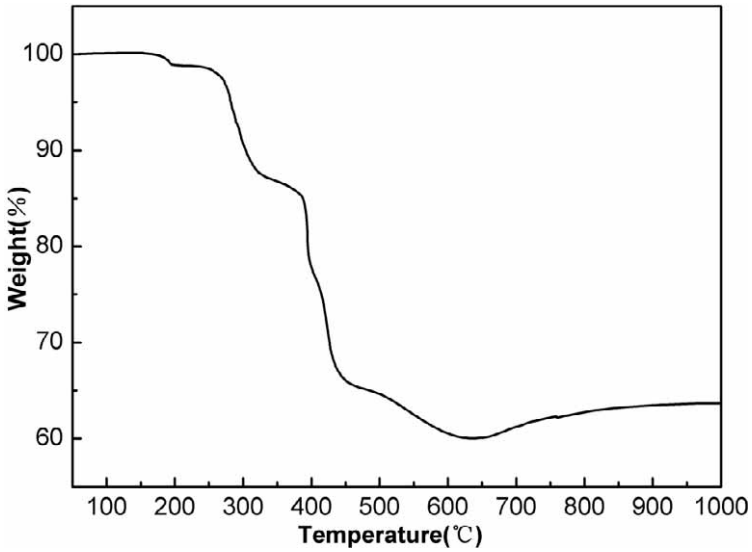

Fig. S2 TG curves of compound **1**.

Photocatalytic activity:

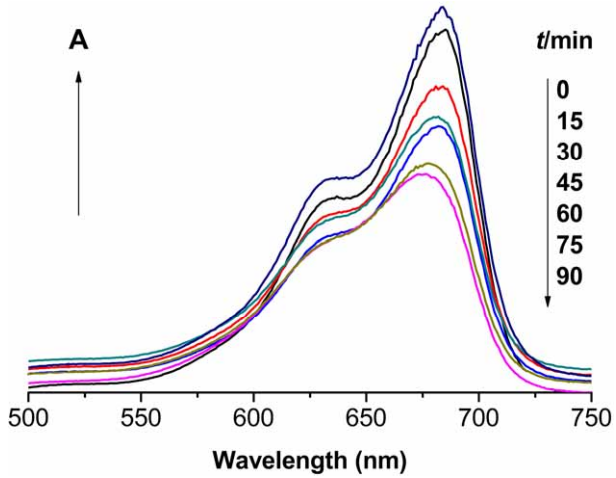

Fig. S3 Absorption spectra of the MB solution during the decomposition reaction under UV light irradiation with the use of $\{[Ag(bipy)]_3[HSiW_{12}O_{40}]\}[bipy]$ (abbreviated as Ag_3+SiW_{12}).

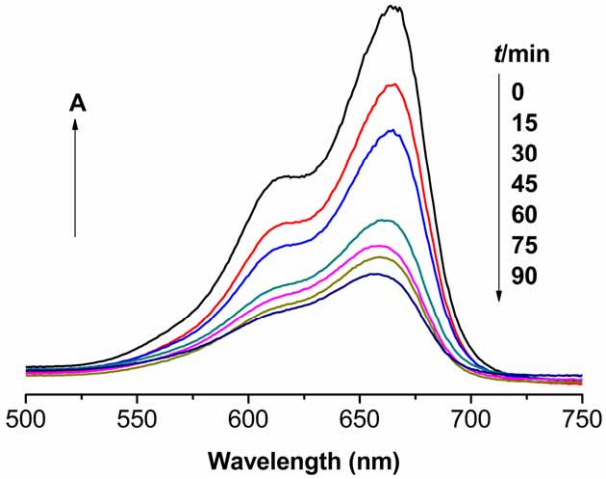

Fig. S4 Absorption spectra of the MB solution during the decomposition reaction under UV light irradiation with the use of $[V_4O_{10}(phen)_2]$ (abbreviated as V_4).

PXRD of compound 1

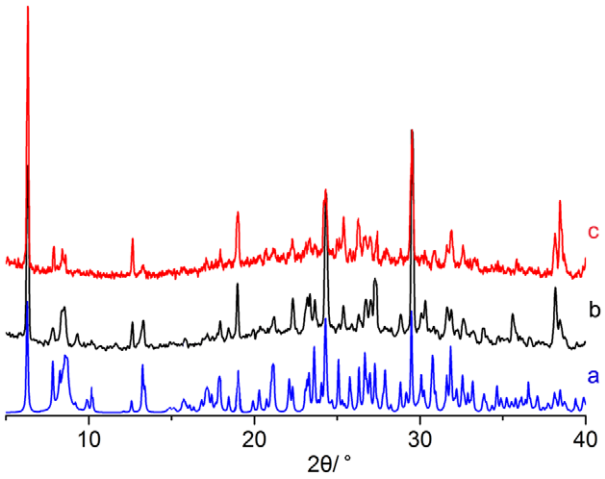

Fig. S5 PXRD patterns of compound **1**: blue a, simulated; black b, as-synthesized; red c, after photocatalytic reaction.

The recycle experiment of compound 1:

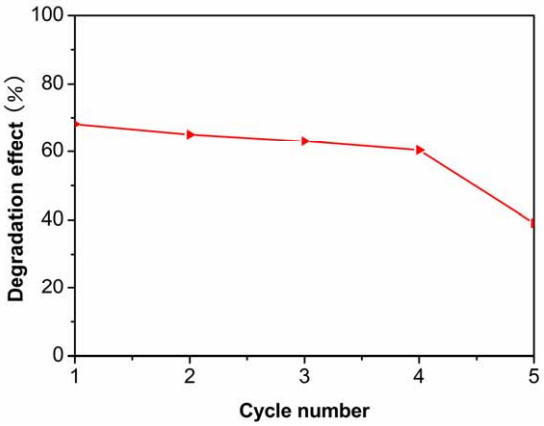

Fig. S6 Cycling runs of **1** in the degradation of MB solution (90 ml of 10 mg L^{-1}).

EDS of compound 1:

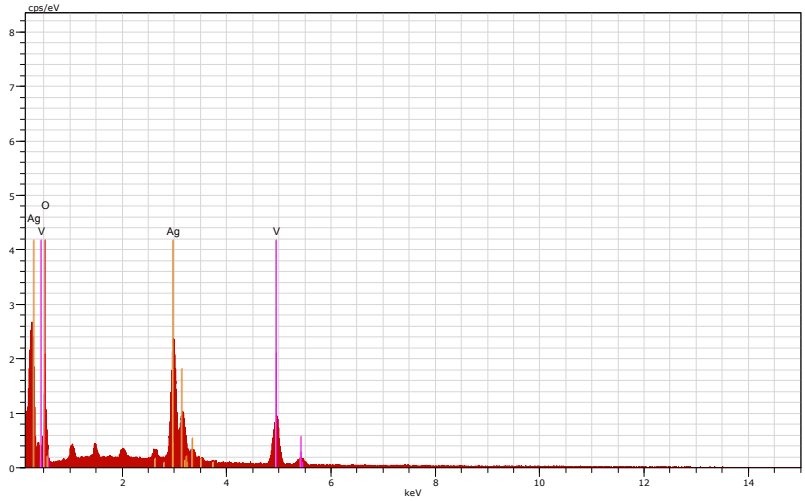

Fig. S7 Energy Dispersive Spectrum (EDS) of compound **1**.

Table S3. The data of EDS analysis (HV:15.0kV, Puls th.:2.06kcps)

El	AN	Series	unn. [wt.%]	C norm. [wt.%]	C Atom. [at.%]	C Error [%]
O	8	K-series	21.62	26.24	63.83	26.4
V	23	K-series	19.54	23.71	18.12	0.6
Ag	47	L-series	41.23	50.05	18.06	1.3
	Total:		82.39	100.00	100.00	