Electronic Supplementary Information

Grafting transition metal–organophosphonate fragments onto heteropolyoxomolybdate: activity in photocatalysis

Xiaopeng Sun, Zhijie Liang, Pengtao Ma, Ran Ban, Mingshuang Jiang, Dongdi Zhang,* Jingping Wang and Jingyang Niu*

Henan Key Laboratory of Polyoxometalate Chemistry,
Institute of Molecular and Crystal Engineering,
College of Chemistry and Chemical Engineering,
Henan University, Kaifeng 475004, Henan, China,
E-mail: ddzhang@henu.edu.cn, jyniu@henu.edu.cn; Fax: (+86)371-23886876.

CONTENTS

Section1. IR spectra of **1** and H_3L

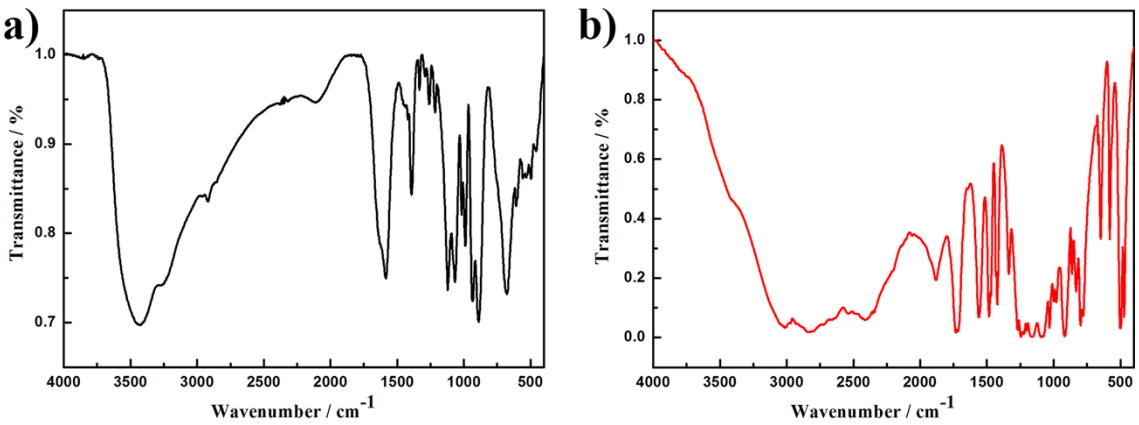

Fig. S1 IR spectra of **1** (a) and H_3L (b)

Section2. The comparison of experimental XRPD pattern and simulated of **1**

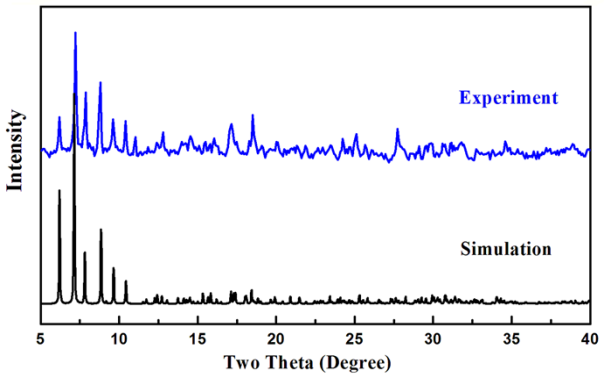

Fig. S2 The comparison of experimental XRPD patterns (blue) and simulated (black) of **1**

Section3. The synthetic pathway of **1**

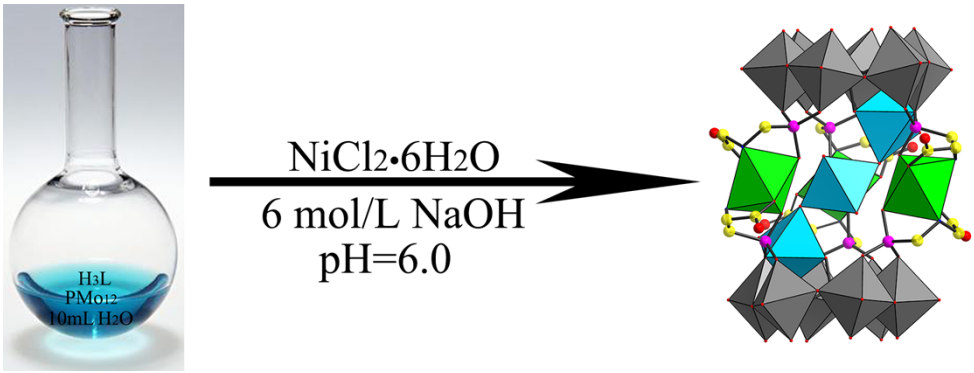

Fig. S3 The synthetic pathway of compound **1** with stirring approximately 2h at 80 °C

Section4. Thermogravimetric analyses of **1**

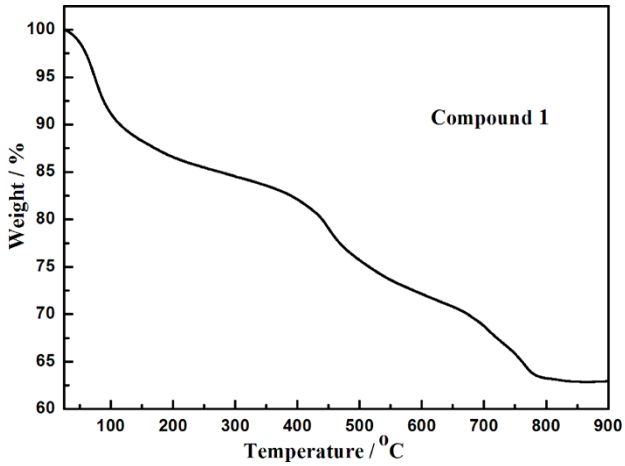

Fig. S4 Thermogravimetric analysis curve of **1**

Section5. Bond valence sum calculations of Mo, Ni, P and O atoms on POM fragments in **1**

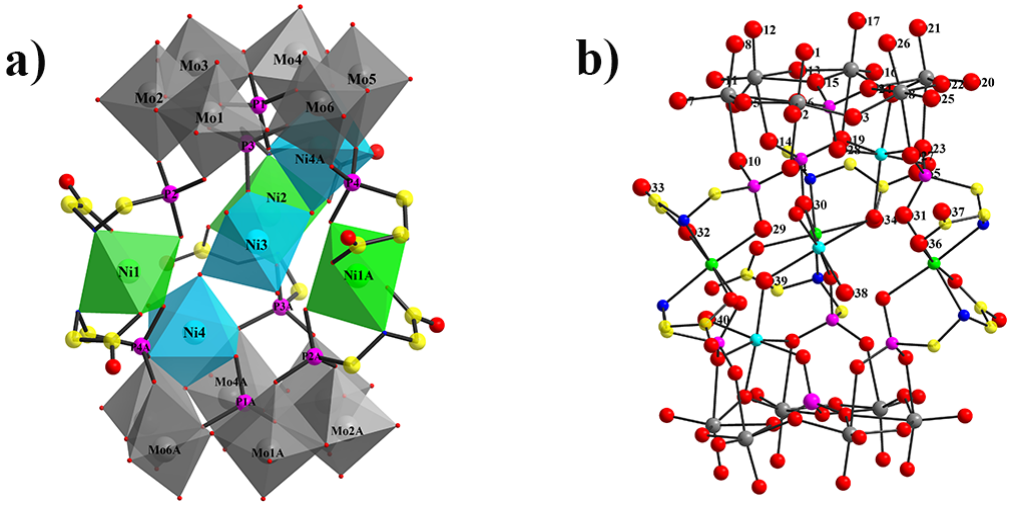

Fig. S5 The representation of Mo, Ni, P atoms (a), and O atoms (b) labeling in polyanion **1a**

Symmetry code; A: 2−x, y, 0.5−z.

Table S1 Bond valence sum parameters for Mo atoms on POM fragments in **1**

Bond	Bond length	Bond Valence	Valence Sum
Mo(1)−O(1)	1.710	1.703	
Mo(1)−O(2)	1.714	1.685	
Mo(1)−O(5)	1.913	0.984	Σ(Mo1) = 6.015
Mo(1)−O(3)	1.926	0.950	
Mo(1)−O(4)	2.267	0.378	
Mo(1)−O(6)	2.334	0.315	
Mo(2)−O(7)	1.713	1.689	
Mo(2)−O(8)	1.714	1.685	
Mo(2)−O(9)	1.914	0.981	Σ(Mo2) = 6.024
Mo(2)−O(5)	1.938	0.920	
Mo(2)−O(10)	2.222	0.427	

Mo(2)−O(6)	2.326	0.322	
Mo(3)−O(12)	1.705	1.726	Σ(Mo3) = 6.051
Mo(3)−O(11)	1.716	1.676	
Mo(3)−O(9)	1.907	1.000	
Mo(3)−O(13)	1.944	0.905	
Mo(3)−O(14)	2.223	0.426	
Mo(3)−O(15)	2.330	0.319	
Mo(4)−O(16)	1.700	1.750	Σ(Mo4) = 6.037
Mo(4)−O(17)	1.710	1.703	
Mo(4)−O(13)	1.879	1.079	
Mo(4)−O(18)	1.952	0.885	
Mo(4)−O(15)	2.318	0.329	
Mo(4)−O(19)	2.364	0.291	
Mo(5)−O(21)	1.694	1.778	Σ(Mo5) = 6.108
Mo(5)−O(20)	1.704	1.731	
Mo(5)−O(22)	1.887	1.056	
Mo(5)−O(18)	1.959	0.869	
Mo(5)−O(24)	2.270	0.375	
Mo(5)−O(23)	2.353	0.300	
Mo(6)−O(25)	1.707	1.717	Σ(Mo6) = 6.041
Mo(6)−O(26)	1.714	1.685	
Mo(6)−O(3)	1.902	1.013	
Mo(6)−O(22)	1.948	0.895	
Mo(6)−O(27)	2.225	0.423	
Mo(6)−O(24)	2.344	0.307	

Bond valence sum parameters for Mo(1A), Mo(2A), Mo(3A), Mo(4A), Mo(5A) and Mo(6A) are the same as Mo(1), Mo(2), Mo(3), Mo(4), Mo(5) and Mo(6), so they are omitted.

Table S2 Bond valence sum parameters for Ni atoms on POM fragments in **1**

Bond	Bond length	Bond Valence	Valence Sum
Ni(1)−O(32)	2.048	0.345	Σ(Ni1) = 2.029
Ni(1)−O(36A)	2.054	0.339	
Ni(1)−O(31A)	2.088	0.309	
Ni(1)−O(29)	2.092	0.306	
Ni(1)−N(1)	2.106	0.382	
Ni(1)−N(3A)	2.141	0.348	
Ni(2)−O(34)	2.030	0.362	Σ(Ni2) = 2.128
Ni(2)−O(34A)	2.030	0.362	
Ni(2)−O(30)	2.081	0.315	
Ni(2)−O(30A)	2.080	0.316	
Ni(2)−N(2A)	2.102	0.386	
Ni(2)−N(2)	2.102	0.386	
Ni(3)−O(38A)	2.024	0.368	

Ni(3)−O(38)	2.024	0.368	Σ(Ni3) = 1.952
Ni(3)−O(30A)	2.054	0.339	
Ni(3)−O(30)	2.054	0.339	
Ni(3)−O(39A)	2.140	0.269	
Ni(3)−O(39)	2.140	0.269	
Ni(4)−O(23A)	2.034	0.358	Σ(Ni4) = 1.958
Ni(4)−O(19A)	2.036	0.356	
Ni(4)−O(18A)	2.057	0.336	
Ni(4)−O(40)	2.084	0.313	
Ni(4)−O(28A)	2.101	0.299	
Ni(4)−O(39)	2.105	0.296	

Bond valence sum parameters for Ni(1A) and Ni(4A) are the same as Ni(1) and Ni(4), so they are omitted.

Table S3 Bond valence sum parameters for P atoms on POM fragments in **1**

Bond	Bond length	Bond Valence	Valence Sum
P(1)−O(28)	1.520	1.300	Σ(P1) = 4.918
P(1)−O(6)	1.542	1.225	
P(1)−O(15)	1.550	1.199	
P(1)−O(24)	1.551	1.195	
P(2)−O(4)	1.526	1.279	Σ(P2) = 2.658
P(2)−O(10)	1.527	1.275	
P(2)−O(29)	1.535	1.248	
P(2)−C(1)	1.800	1.145	
P(3)−O(14)	1.517	1.310	Σ(P3) = 2.736
P(3)−O(30)	1.524	1.286	
P(3)−O(19)	1.535	1.248	
P(3)−C(4)	1.812	1.108	
P(4)−O(27)	1.512	1.328	Σ(P4) = 2.720
P(4)−O(31)	1.526	1.279	
P(4)−O(23)	1.535	1.248	
P(4)−C(7)	1.803	1.135	

Bond valence sum parameters for P(1A), P(2A), P(3A) and P(4A) are the same as P(1), P(2), P(3) and P(4), so they are omitted.

Table S4 Bond valence sum parameters for O atoms on POM fragments in **1**

Atom	Valence Sum	Atom	Valence Sum
O1	1.703	O21	1.778
O2	1.685	O22	1.951
O3	1.964	O23	1.906
O4	1.657	O24	1.877
O5	1.904	O25	1.717
O6	1.862	O26	1.685
O7	1.689	O27	1.752

O8	1.685	O28	1.598
O9	1.981	O29	1.554
O10	1.702	O30	1.940
O11	1.676	O31	1.588
O12	1.726	O32	1.861
O13	1.983	O33	1.575
O14	1.736	O34	1.712
O15	1.847	O35	1.429
O16	1.750	O36	1.715
O17	1.703	O37	1.541
O18	2.091	O38	0.368
O19	1.895	O39	0.564
O20	1.731	O40	0.313

Σ(O38) = 0.368 ->OH2 Σ(O39) = 0.564 ->OH2 Σ(O40) = 0.313 ->OH2;

Bond valence sum parameters for O(1A), O(2A), O(3A)……O(40A) are the same as O(1), O(2), O(3)……O(40), so they are omitted.

Section6. Crystallographic data for **1**

Table S5 Crystallographic data for **1**

Empirical formula	$C_{18}H_{86}CsMo_{12}N_6Na_9Ni_6O_{101}P_8$
Formula weight	4094.04
T [K]	296.15
Space group	*C2/c*
Crystal system	Monoclinic
a [Å]	14.8247(8)
b [Å]	45.237(2)
c [Å]	18.8324 (9)
β [°]	103.371(10)
V [Å^3]	12287.1(11)
Z	4
Crystal size [mm^3]	0.50 x 0.18 x 0.17
ρ_{calc} [g cm^{-3}]	2.213
μ [mm^{-1}]	2.617
F(000)	7960.0
Limiting indices	$-17 \le h \le 17$
	$-45 \le k \le 53$
	$-22 \le l \le 22$
2Θ for data collection [°]	2.964 − 49.998
Reflections collected / unique	31456 / 10802
R_{int}	0.0274
Goodness-of-fit on F^2	1.048
Final *R* indices [I>2σ(I)][a]	R_1 = 0.0439 wR_2 = 0.1332
Final *R* indices (all data)[b]	R_1 = 0.0554 wR_2 = 0.1445

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

Section7. Selected bond angles (°) of **1**

Table S6 Selected bond angles (°) of **1**

O(1)-Mo(1)-O(2)	103.8(3)	O(1)-Mo(1)-O(4)	166.2(2)	O(5)-Mo(1)-O(6)	73.85(18)
O(7)-Mo(2)-O(8)	103.8(3)	O(7)-Mo(2)-O(6)	166.0(2)	O(5)-Mo(2)-O(6)	73.6(18)
O(12)-Mo(3)-O(11)	102.9(3)	O(12)-Mo(3)-O(14)	167.3(3)	O(13)-Mo(3)-O(15)	72.65(18)
O(16)-Mo(4)-O(17)	103.9(3)	O(16)-Mo(4)-O(15)	166.4(2)	O(18)-Mo(4)-O(19)	74.75(17)
O(21)-Mo(5)-O(20)	102.5(3)	O(20)-Mo(5)-O(24)	166.1(2)	O(18)-Mo(5)-O(23)	74.21(17)
O(25)-Mo(6)-O(3)	102.8(3)	O(26)-Mo(6)-O(27)	167.7(2)	O(22)-Mo(6)-O(24)	72.09(18)
O(32)-Ni(1)-O(29)	92.41(19)	O(32)-Ni(1)-N(1)	82.1(2)	O(29)-Ni(1)-N(1)	87.5(2)
O(34)-Ni(2)-O(30)	95.5(2)	O(34)-Ni(2)-N(2)	81.7(2)	O(30)-Ni(2)-N(2)	88.8(2)
O(38)-Ni(3)-O(30)	166.8(2)	O(38)-Ni(3)-O(39)	87.32(19)	O(30)-Ni(3)-O(39)	100.92(18)
O(40)-Ni(4)-O(39)	87.3(2)	O(19A)-Ni(4)-O(39)	101.52(18)	O(18A)-Ni(4)-O(39)	176.17(19)

Section8. Some structural figures

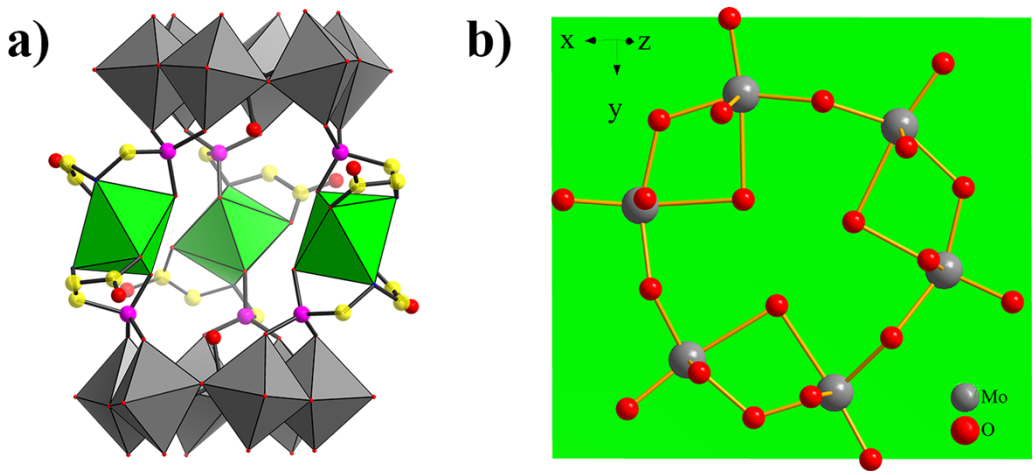

Fig. S6 (a) Polyhedral / ball-and-stick representation of $\{(PMo_6O_{22})_2(NiL_2)_3\}$ (L = $OOCCH_2NHCH_2PO_3$); (b) The structure representation of $\{Mo_6\}$ plane

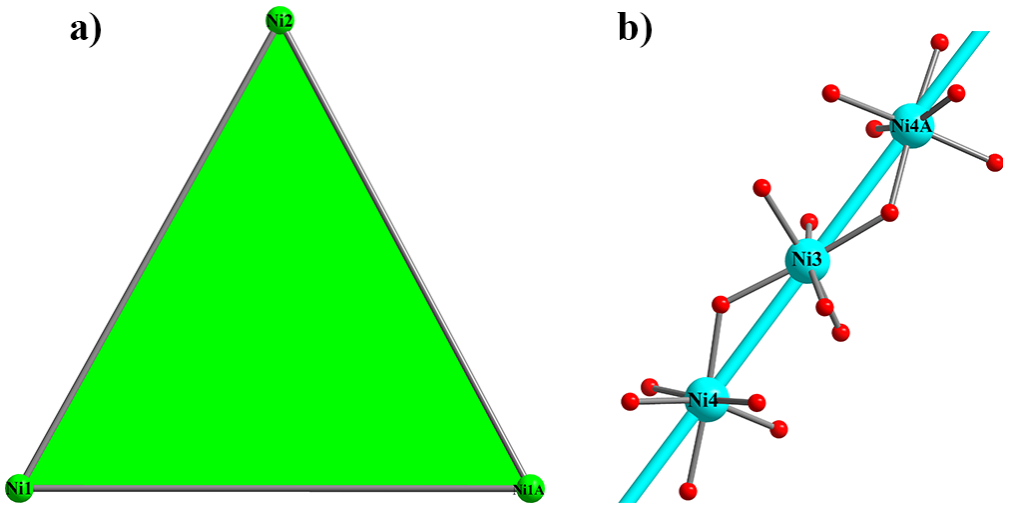

Fig. S7 (a) The normative isosceles triangle constructed by Ni1, Ni1A and Ni2 atoms; (b) The Ni4−Ni3−Ni4A line with the angle of 174.96°

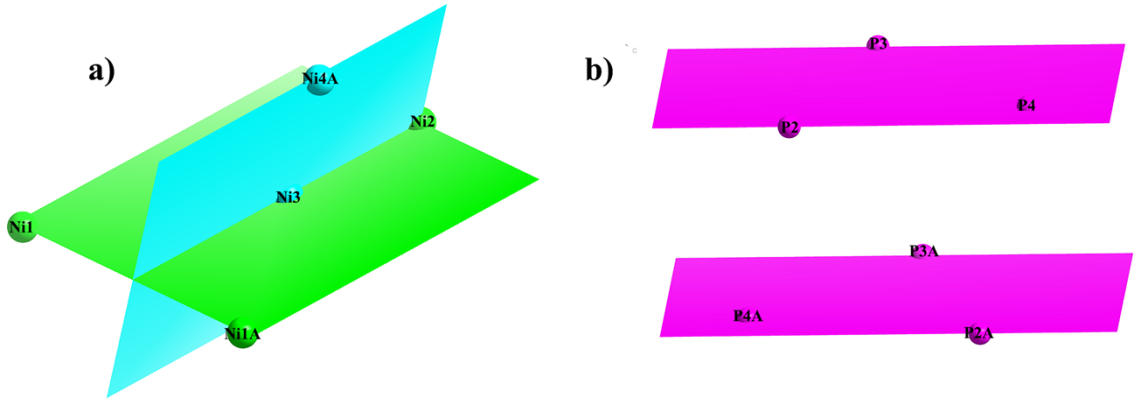

Fig. S8 (a) The dihedral plane angle 56.12° of the two planes formed by Ni1, Ni2, Ni1A and Ni3, Ni4, Ni4A; (b) The nearly paralleled planes between P2, P3, P4 and P2A, P3A, P4A with the dihedral plane angle 0.10°

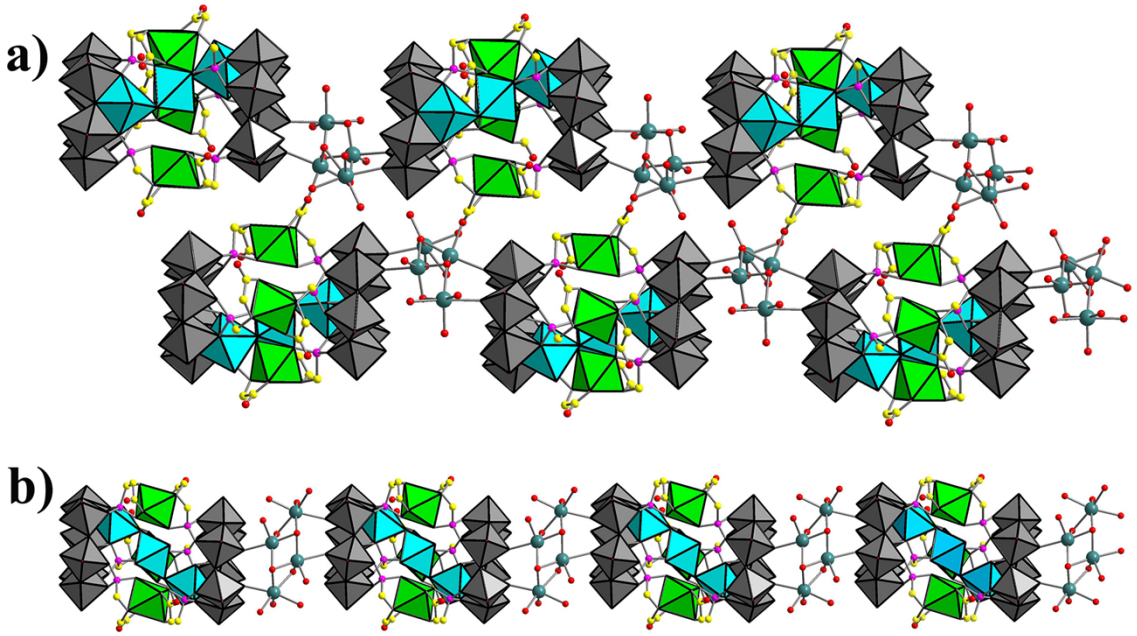

Fig. S9 (a) The 1D double-chain structure formed from $\{Na_4O_{16}\}$ bridge; (b) One branch structure of the 1D double-chain. Color code: $\{MoO_6\}$: grey octahedral; $\{NiO_4N_2\}$: green octahedral; $\{NiO_6\}$: sky blue octahedral; P: pink ball; N: blue ball; C: yellow ball; O: red ball; Na: teal ball; The H atoms are omitted for clarity.

Section9. Additional photocatalysis related table and figure

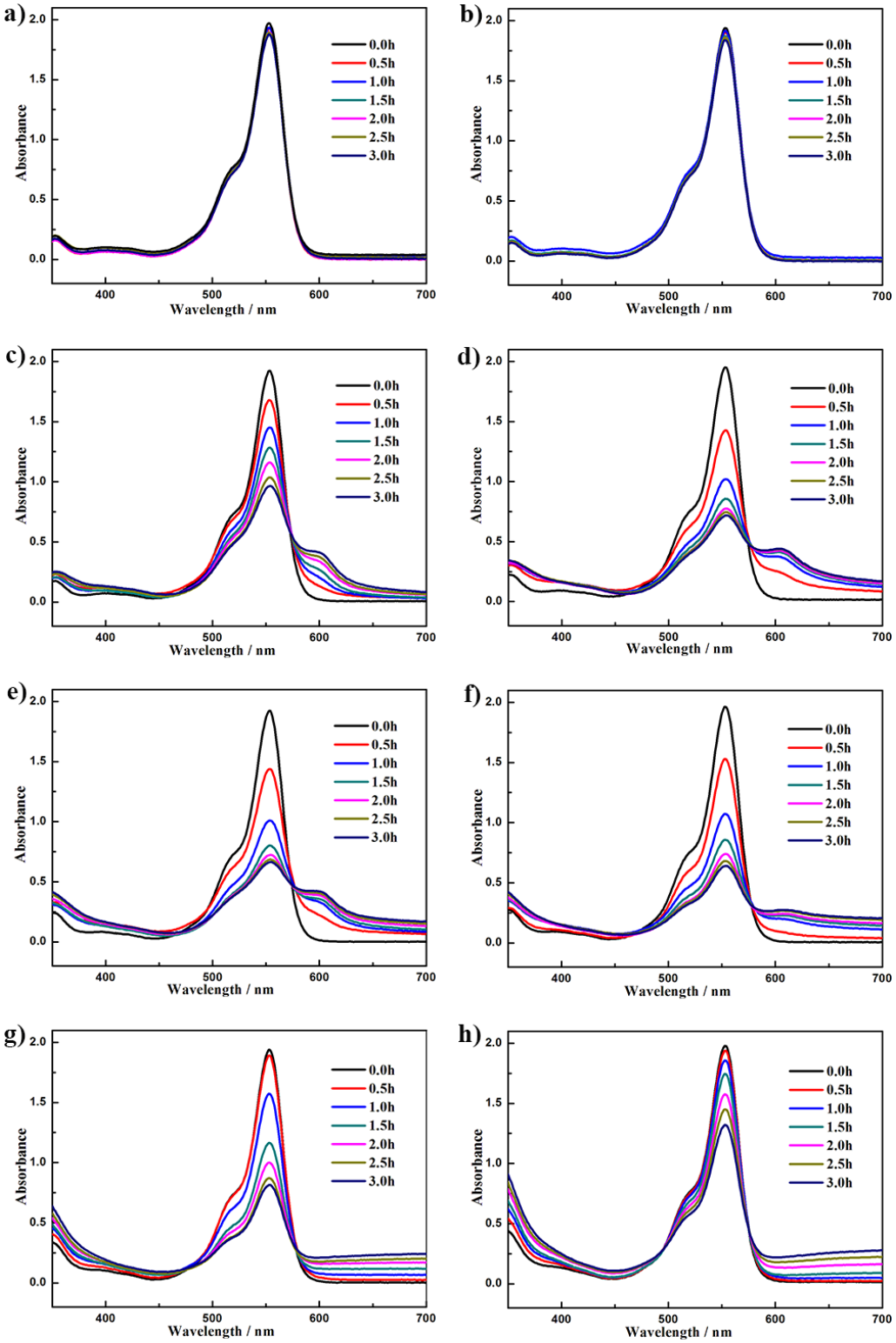

Fig. S10 Absorption spectra of the Rhodamine B (RhB) aqueous solutions (2.0×10^{-5} mol L^{-1}) during the photodegradation under 500 W Xe-lamp irradiation in the presence of **1** with 0 (a); 6.4×10^{-7} (b); 1.28×10^{-6} (c); 2.56×10^{-6} (d); 3.84×10^{-6} (e); 5.12×10^{-6} (f); 1.02×10^{-5} (g) and 2.05×10^{-5} mol (h).

Table S7 The photocatalytic degradation rates for RhB aqueous solutions of **1**

The usage amount of **1** (10^{-6} mol)	0	0.64	1.28	2.56
Degradation rate (%)	3.14	5.15	49.91	63.20
The usage amount of **1** (10^{-6} mol)	3.84	5.12	10.2	20.5
Degradation rate (%)	65.52	67.41	58.01	33.15