Electronic Supplementary Information

Two novel nickel cluster substituted polyoxometalates: syntheses, structures and their photocatalytic activities, magnetic behaviors, and ion-conduction properties

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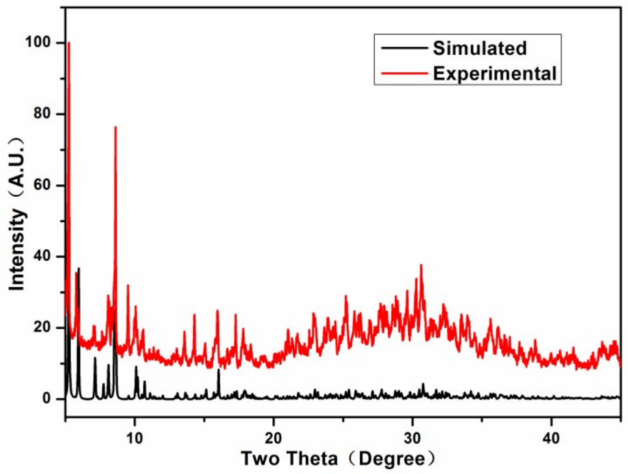


Fig. S1 Simulated and experimental PXRD patterns of **1.**

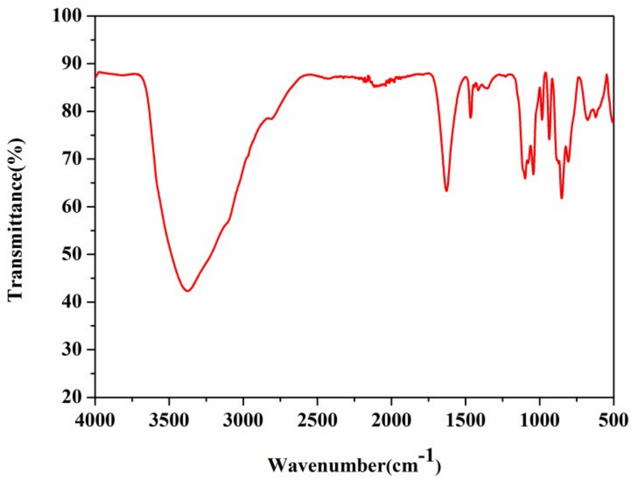


Fig. S2 IR spectrum of **1.**

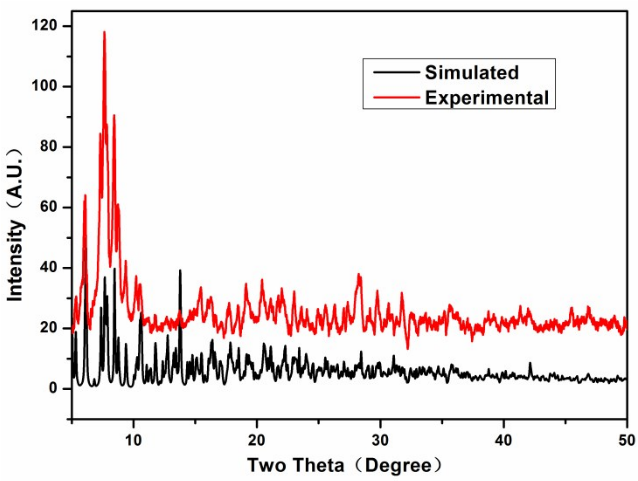


Fig. S3 Simulated and experimental PXRD patterns of **2.**

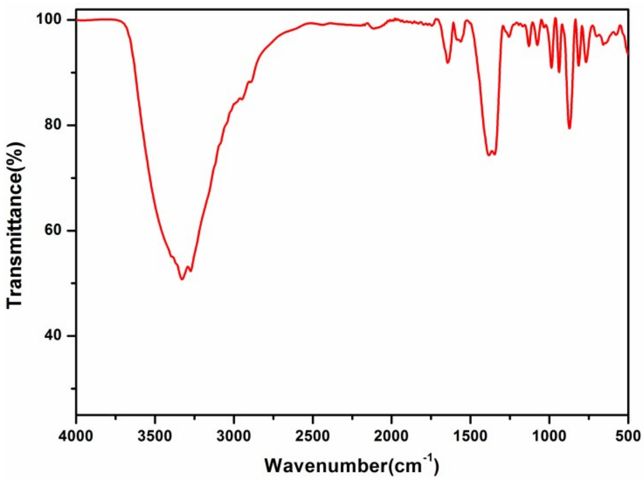


Fig. S4 IR spectrum of **2.**

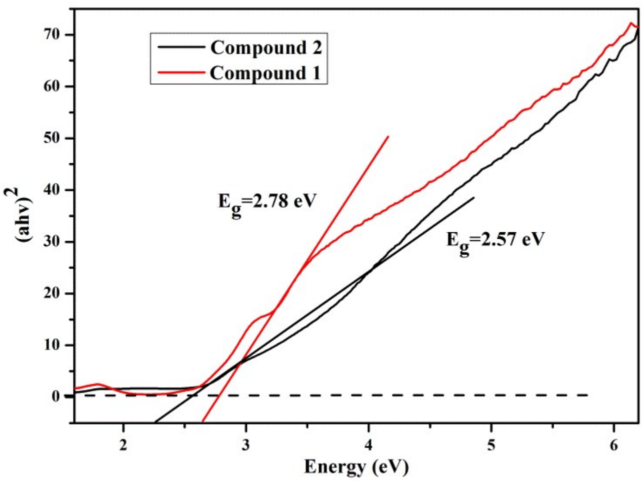


Fig. S5 Tauc plots of **1** and **2**.

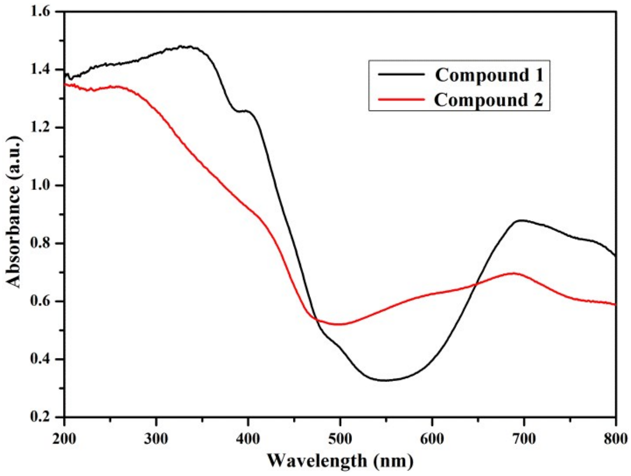


Fig. S6 UV-Vis spectra of **1** and **2**.

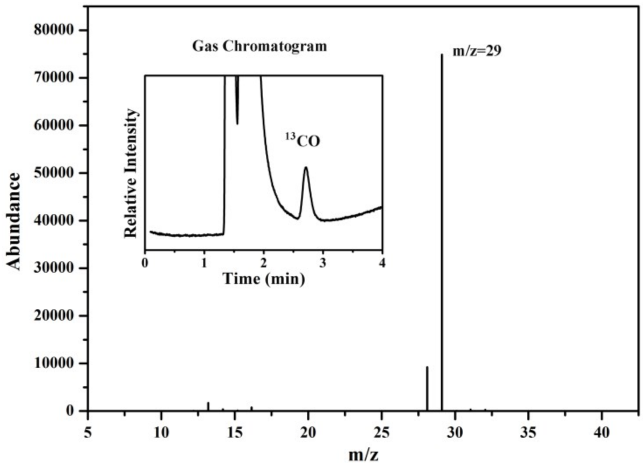


Fig. S7 Gas chromatogram and mass spectrum analysis of the carbon source of the evolved CO in the photocatalytic reduction of $^{13}CO_2$ by **2**.

The peak at 2.7 min with m/z = 29 is assigned to the generated ^{13}CO, confirming that the produced and detected CO originates from CO_2.

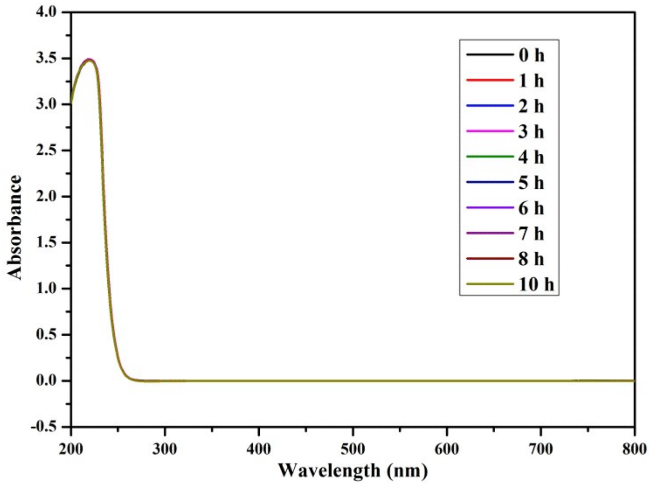


Fig. S8 Time-dependent UV-Vis spectrum of **2** (1.7×10^{-5} M) in the solution (MeCN : TEOA : H_2O = 4 : 1 : 1, v : v : v). The UV-Vis curves remained unchanged with time.

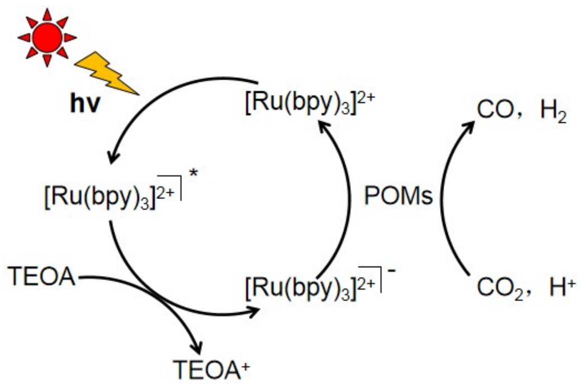


Fig. S9 Proposed mechanism for the photoreduction of CO_2.

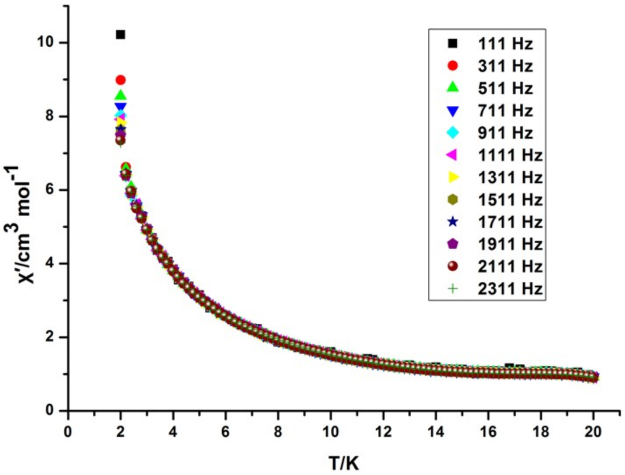


Fig. S10 Frequency dependence of real χ_m' component in the temperature range of 2-20 K for **1.**

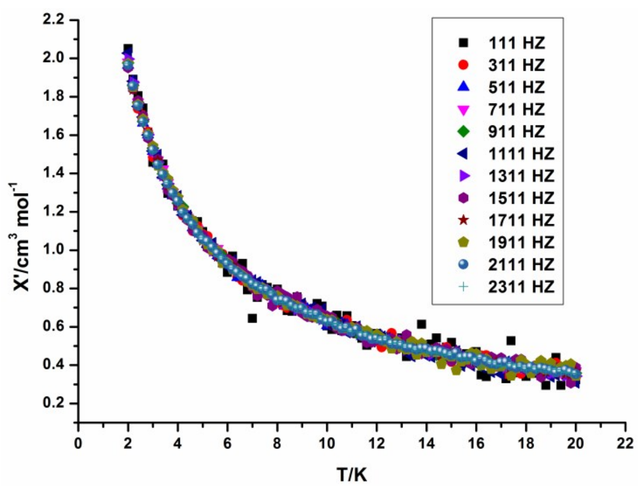
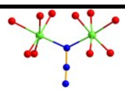
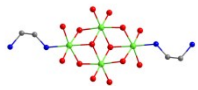
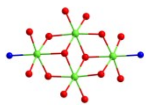
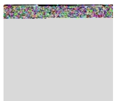
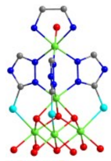
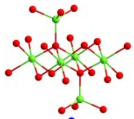
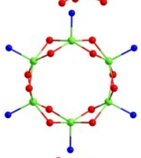
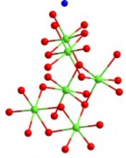
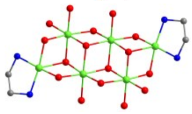
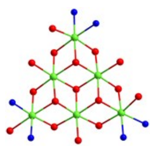


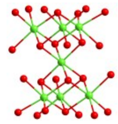
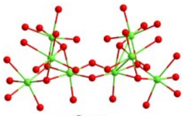
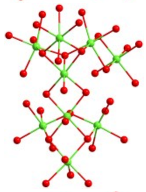
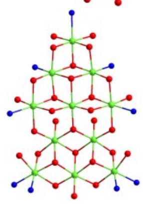
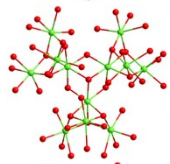
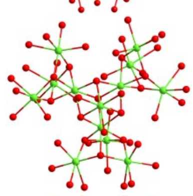
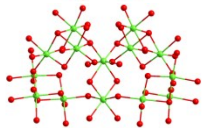
Fig. S11 Frequency dependence of real χ_m' component in the temperature range of 2-20 K for **2**.

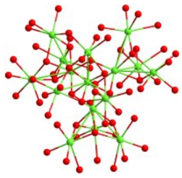
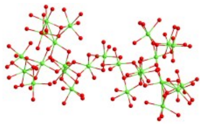
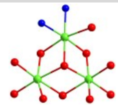
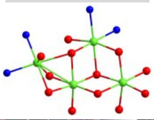
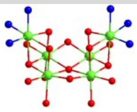
2. Additional Tables

Table S1. Summary of reported nickel cluster-substituted POMs

Fomula	TM core type[a]	Diagram	lacunary POM fragments	ref
$[(Ni(H_2O))_2N_3(PW_{10}O_{37})]^{6-}$	{Ni_2}		{$PW_{10}O_{37}$}	1
$[Li_2Ni_2(PW_9O_{34})_2]^{12-}$	{Ni_2}		{PW_9O_{34}}	2
$[M_2(B\text{-}\beta\text{-}SiW_8O_{31})_2]^{16-}$	{Ni_2}		{$B\text{-}\beta\text{-}SiW_8O_{31}$}	3
$[Na_2(H_2O)_2Ni_2(As_2W_{15}O_{56})_2]^{18-}$	{Ni_2}		{$As_2W_{15}O_{56}$}	4
$[M^{II}_2(P_2W_{15}O_{56})_2]^{20-}$ (M = Mn, Co, or Ni)	{Ni_2}		{$P_2W_{15}O_{56}$}	5
$[Ni_3Na(H_2O)_2(AsW_9O_{34})_2]^{11-}$	{Ni_3}		{AsW_9O_{34}}	6
$[Ni_3Na(H_2O)_2(PW_9O_{34})_2]^{11-}$	{Ni_3}		{PW_9O_{34}}	7
$[NaNi_3(H_2O)_2(P_2W_{15}O_{56})_2]^{17-}$	{Ni_3}		{$P_2W_{15}O_{56}$}	8
$[Ni_3(OH)_3(H_2O)_3P_2W_{16}O_{59}]^{9-}$	{Ni_3}		{$P_2W_{16}O_{59}$}	9
$[Ni_6As_3W_{24}O_{94}(H_2O)_2]^{17-}$	2{Ni_3}		{AsW_9O_{34}} {AsW_6O_{16}}	6
$[Na_3(H_2O)_8\{Ni_3(H_2O)(PW_9O_{34})(PW_8O_{31})\}_2]^{21-}$	2{Ni_3}		{PW_9O_{34}} {PW_8O_{31}}	10
$[\{Ni(Hen)\}_2Ni_2(GeW_9O_{34})_2]^{10-}$	{Ni_4}		{GeW_9O_{34}}	11
$[Na\{(A\text{-}\alpha\text{-}SiW_9O_{34})Ni_4(CH_3COO)_3(OH)_3\}_2]^{15-}$	{Ni_4}		{$A\text{-}\alpha\text{-}SiW_9O_{34}$}	12
$[(SiW_9O_{34})KNi_4(OH)_3((SC_4H_3)CH_2COO)_3]^{7-}$	{Ni_4}		{SiW_9O_{34}}	13
$[Na\{(A\text{-}\alpha\text{-}SiW_9O_{34})Ni_4(CH_3COO)_3(OH)_3\}_2]^{15-}$	{Ni_4}		{$A\text{-}\alpha\text{-}SiW_9O_{34}$}	14
$[(SiW_9O_{34})(OH)_3Ni_4(C_6H_{13}NO_2)_3]^{5-}$	{Ni_4}		{SiW_9O_{34}}	15
$[Ni_4(Hdap)_2(HXW_9O_{34})_2]^{8-}$ (X= Si or Ge)	{Ni_4}		{XW_9O_{34}} (X= Si or Ge)	16
$[Ni_4(H_2O)_2(\alpha\text{-}B\text{-}PW_9O_{34})_2]^{1-}$	{Ni_4}		{$\alpha\text{-}B\text{-}PW_9O_{34}$}	17
$\{Ni_4[H_4N_2(CH_2)_6]_2(H_2PW_9O_{34})_2\}^{2-}$	{Ni_4}		{PW_9O_{34}}	18
$\{[Ni(enMe)_2]_2[Ni(enMe)_2(H_2O)]_2[As_2W_{18}Ni_4(enMe)_2O_{68}]\}$	{Ni_4}		{$As_2W_{18}O_{68}$}	19
$[\{\beta\text{-}GeNi_2W_{10}O_{36}(OH)_2(H_2O)\}_2]^{12-}$	{Ni_4}		{$\beta\text{-}GeW_{10}O_{36}$}	20
$[Ni_4(H_2O)_2(\alpha\text{-}GeW_9O_{34})_2]^{2-}$	{Ni_4}		{$\alpha\text{-}GeW_9O_{34}$}	21
$[Ni(en)_2]_2[\{(\alpha\text{-}B\text{-}PW_9O_{34})_2Ni_4(H_2O)_2\}\{Ni(en)_2(H_2O)\}_2]^{2-}$	{Ni_4}		{$\alpha\text{-}B\text{-}PW_9O_{34}$}	22
$\{P_2^VW_{18}^{VI}Ni_4(H_2O)_2O_{68}[Ni(en)_2(H_2O)_2[Ni(en)_3]_2[Ni(en)_2(H_2O)_2]$	{Ni_4}		{$P_2^VW_{18}^{VI}O_{68}$}	23
$[Ni_4(H_2O)_2(B\text{-}\alpha\text{-}AsW_9O_{34})_2]^{10-}$	{Ni_4}		{$B\text{-}\alpha\text{-}AsW_9O_{34}$}	24
$\{Ni_4(H_2O)_2(B\text{-}\alpha\text{-}XW_9O_{34})_2\}^{n-}$	{Ni_4}		{$B\text{-}\alpha\text{-}XW_9O_{34}$}	25
$\{(GeW_9O_{34})_2Ni_4(Hen)_2\}^{10-}$	{Ni_4}		{GeW_9O_{34}}	26
$[Ni_4(AsW_9O_{34})_2(H_2O)_2]^{10-}$	{Ni_4}		{AsW_9O_{34}}	27
$[Ni(en)_2]_2[\{Ni_3(en)_6(H_2O)_2Ni_4(H_2O)_2(\alpha\text{-}PW_9O_{34})_2\}]$	{Ni_4}		{$\alpha\text{-}PW_9O_{34}$}	28

$[Ni_4(OH_2)_2(AsW_9O_{34})_2]^{10-}$	{Ni_4}		{AsW_9O_{34}}	29
$\{[Ni(dien)]_2Ni_4(H_2O)_2(GeW_9O_{34})_2\}^{6-}$	{Ni_4}		{GeW_9O_{34}}	30
$\{[Ni_4(Hen)_2][B\text{-}\alpha\text{-}AsW_9O_{34}]_2\}^{8-}$	{Ni_4}		{B-α-AsW_9O_{34}}	31
$[Ni_4(H_2O)_2(\alpha\text{-}B\text{-}HPW_9O_{34})_2]^{10-}$	{Ni_4}		{α-B-HPW_9O_{34}}	32
$[Na\{(A\text{-}\alpha\text{-}SiW_9O_{34})Ni_4(CH_3COO)_3(OH)_2(N_3)\}_2]^{15-}$	2{Ni_4}		{A-α-SiW_9O_{34}}	12
$[\{(SiW_9O_{34})Ni_4(OH)_3\}_4(OOC(CH_2)_3COO)_6]^{32-}$	4{Ni_4}		{SiW_9O_{34}}	13
$[\{Ni_5(H_2O)_5(OH)_3(SiW_9O_{34})(SiW_8O_{31})\}]^{13-}$	{Ni_5}		{SiW_9O_{34}} {SiW_8O_{31}}	33
$[Ni_5(OH)_6(OH_2)_3(Si_2W_{18}O_{66})]^{12-}$	{Ni_5}		{$Si_2W_{18}O_{66}$}	34
$\{[Ni_5(OH)_3(H_2O)_4(CH_3CO_2)][Si_2W_{18}O_{66}]\}^{2-}$	{Ni_5}		{$Si_2W_{18}O_{66}$}	35
$[Ni_5(OH)_3(trzS)_3(en)(H_2O)(B\text{-}\alpha\text{-}PW_9O_{34})]^{8-}$	{Ni_5}		{B-α-PW_9O_{34}}	36
$[Ni_4(H_2O)_2(\alpha\text{-}NiW_9O_{34})_2]^{16-}$	{Ni_6}		{α-NiW_9O_{34}}	37
$[Ni_6(imi)_6(H_3AsW_9O_{33})_2]$	{Ni_6}		{AsW_9O_{33}}	38
$[\{Ni_6(H_2O)_4(\mu_2\text{-}H_2O)_4(\mu_3\text{-}OH)_2\}(x\text{-}SiW_9O_{34})_2]^{10-}$	{Ni_6}		{SiW_9O_{34}}	39
$\{[Ni_6(en)_2(H_2O)_2][B\text{-}\alpha\text{-}GeW_9O_{34}]_2\}^{6-}$	{Ni_6}		{B-α-GeW_9O_{34}}	40
$[\{Ni_6(OH)_3(en)_3(H_2O)_6\}(GeW_9O_{34})]^{-}$	{Ni_6}		{GeW_9O_{34}}	41
$[Ni_6(OH)_3(H_2O)_6(dap)_3(XW_9O_{34})]^{-}$ (X= Si or P)	{Ni_6}		{XW_9O_{34}} (X= Si or P)	42
$[Ni_6(en)_3(H_2O)_6P_2W_{15}]^{3-}$	{Ni_6}		{$P_2W_{15}O_{56}$}	43
$[\{Ni_6(\mu_3\text{-}OH)_3(en)_3(H_2O)_6\}(B\text{-}\alpha\text{-}PW_9O_{34})]$	{Ni_6}		{B-α-PW_9O_{34}}	44
$[Ni_6(\mu_3\text{-}OH)_3(H_2O)_6L_3(B\text{-}\alpha\text{-}PW_9O_{34})]$	{Ni_6}		{B-α-PW_9O_{34}}	45
$\{[Ni_3(dap)(H_2O)_2]_2(H_2W_4O_{16})\}\{(\alpha\text{-}H_2AsW_6O_{26})[Ni_6(OH)_2(H_2O)(dap)_2](B\text{-}\alpha\text{-}HAsW_9O_{34})\}^{4-}$	{Ni_6}		{B-α-$HAsW_9O_{34}$}	46
$[Ni_6(\mu_3\text{-}OH)_3(H_2O)_6(en)_3(B\text{-}\alpha\text{-}PW_9O_{34})]$	{Ni_6}		{B-α-PW_9O_{34}}	47
$[Ni_6(enMe)_3(OH)_3PW_9O_{34}]$	{Ni_6}		{PW_9O_{34}}	48
$[HNi_{20}X_4W_{34}\text{-}(OH)_4O_{136}(H_2O)_6(enMe)_8]^{13-}$	{Ni_6}		{X_4W_{34}}	49
$\{[Ni_6(\mu_3\text{-}OH)_3(H_2O)_4(en)(CH_3COO)(IN)(B\text{-}PW_9O_{34})]\}^{2-}$	{Ni_6}		{B-PW_9O_{34}}	50
$[H_2Ni_{24}P_4W_{36}(OH)_{12}O_{136}(enMe)_{12}(OAc)_4(H_2O)_{12}]^{2-}$	{Ni_6}		{P_4W_{36}}	51
$\{[Ni_6(OH)_3(H_2O)_2(en)_3(Im)_2](B\text{-}\alpha\text{-}PW_9O_{34})\}$	{Ni_6}		{B-α-PW_9O_{34}}	52

$[\{Ni_6(\mu_3\text{-}OH)_3en(H_2O)_{10}\}(H_2P_2W_{15}O_{56})]^-$	$\{Ni_6\}$		$\{H_2P_2W_{15}O_{56}\}$	53
$[Ni_6(\mu_3\text{-}OH)_3(oeen)_3(H_2O)_3(B\text{-}\alpha\text{-}PW_9O_{34})]$	$\{Ni_6\}$		$\{B\text{-}\alpha\text{-}PW_9O_{34}\}$	54
$[(SiW_8O_{31})_2Ni_7(H_2O)_4(OH)_6]^{12-}$	$\{Ni_7\}$		$\{SiW_8O_{31}\}$	33
$[Ni_7(OH)_4(H_2O)(CO_3)_2(HCO_3)(A\text{-}\alpha\text{-}SiW_9O_{34})(\beta\text{-}SiW_{10}O_{37})]^{10-}$	$\{Ni_7\}$		$\{A\text{-}\alpha\text{-}SiW_9O_{34}\}$ $\{\beta\text{-}SiW_{10}O_{37}\}$	39
$[\{B\text{-}PW_9O_{34})Ni_3(OH)(H_2O)_2(O_3PC(O)(C_3H_6NH_3)(PO_3)\}_2Ni]^{14-}$	$\{Ni_7\}$		$\{B\text{-}PW_9O_{34}\}$	55
$[(PW_9O_{34})_2(OH)_2(H_2O)_4M_7(O_3PC(O)(C_3H_6NH_2CH_2C_4H_3S)PO_3)_2]^{14-}$ [M = Ni, Co]	$\{Ni_7\}$		$\{PW_9O_{34}\}$	56
$[H_{12}Ni_8P_4W_{28}O_{120}]^{16-}$	$\{Ni_8\}$		$\{P_4W_{28}O_{120}\}$	57
$[(BO_3)_2(B_2O_4(OH)_2)_2Ni_8O_4(SiW_9O_{34})_2]^{26-}$	$\{Ni_8\}$		$\{SiW_9O_{34}\}$	58
$[(A\text{-}\alpha\text{-}SiW_9O_{34})2Ni_9(OH)_6(H_2O)_6(CO_3)_3]^{14-}$	$\{Ni_9\}$		$\{A\text{-}\alpha\text{-}SiW_9O_{34}\}$	12
$[Ni_9(OH)_3(H_2O)_6(HPO_4)_2(PW_9O_{34})_3]^{16-}$	$\{Ni_9\}$		$\{PW_9O_{34}\}$	59
$[Ni_{11}(PW_9O_{34})_2(IDA)_3(en)_2(Hen)_2(OH)_6]$	$\{Ni_{11}\}$		$\{PW_9O_{34}\}$	60
$[Ni_{12}(OH)_9WO_4(W_7O_{26}(OH))(PW_9O_{34})_3]^{25-}$	$\{Ni_{12}\}$		$\{PW_9O_{34}\}$	61
$[(BO_3)_3PO_4Ni_{12}O_9(SiW_9O_{34})_3]^{36-}$	$\{Ni_{12}\}$		$\{SiW_9O_{34}\}$	58
$[Ni_{12}(OH)_9(CO_3)_3(PO_4)(SiW_9O_{34})_3]^{24-}$	$\{Ni_{12}\}$		$\{SiW_9O_{34}\}$	62
$[Ni_{13}(H_2O)_3(OH)_9(PO_4)_4(SiW_9O_{34})_3]^{25-}$	$\{Ni_{13}\}$		$\{SiW_9O_{34}\}$	62
$[Ni_{14}(OH)_6(H_2O)_{10}(HPO_4)_4(P_2W_{15}O_{56})_4]^{34-}$	$\{Ni_{14}\}$		$\{P_2W_{15}O_{56}\}$	64
$[\{Ni_4(OH)_3AsO_4\}_4(B\text{-}\alpha\text{-}PW_9O_{34})_4]^{28-}$	$\{Ni_{16}\}$		$\{B\text{-}\alpha\text{-}PW_9O_{34}\}$	65

$[\{Ni_4(OH)_3(PO_4)\}_4(A\text{-}PW_9O_{34})_4]^{28-}$	$\{Ni_{16}\}$		$\{A\text{-}PW_9O_{34}\}$	66
$[\{Ni_4(OH)_3(PO4)\}_4(A\text{-}PW_9O_{34})_2(B\text{-}PW_9O_{34})_2]^{28-}$	$\{Ni_{16}\}$		$\{A\text{-}PW_9O_{34}\}$ $\{B\text{-}PW_9O_{34}\}$	66
$[\{Ni_4(OH)_3(VO_4)\}_4(B\text{-}PW_9O_{34})_4]^{28-}$	$\{Ni_{16}\}$		$\{B\text{-}PW_9O_{34}\}$	66
$[Ni_{25}(H_2O)_2OH)_{18}(CO_3)_2(PO_4)_6(SiW_9O_{34})_6]^{50-}$	$\{Ni_{25}\}$		$\{SiW_9O_{34}\}$	62
$[\{(AsW_6O_{26})Ni_6(OH)_2(H_2O)_3(en)(AsW_9O_{34})\}_2^{-}$	$2\{Ni_6\}+2\{Ni_3\}$	 	$\{AsW_6O_{26}\}$ $\{AsW_9O_{34}\}$	67
$[\{(AsW_6O_{26})Ni_6(OH)_2(en)_{2.5}(AsW_9O_{34})\}_2H_4[W_4O_{16}]^{-}$	$2\{Ni_6\}+2\{Ni_4\}$		$\{AsW_6O_{26}\}$ $\{AsW_9O_{34}\}$	67
$[H_6Ni_{20}P_4W_{34}(OH)_4O_{136}(enMe)_8(H_2O)_6]^{6-}$	$2\{Ni_6\}+2\{Ni_4\}$		$\{B\text{-}\alpha\text{-}PW_9O_{34}\}$	68
$[Ni_{12}O_9(PO_4)_6(SiW_9O_{34})(Si_2W_{22}O_{79})]^{40-}$	$\{Ni_{12}\}$		$\{SiW_9O_{34}\}$ $\{Si_2W_{22}O_{79}\}$	This work
$\{[Ni(C_4N_3H_{13})]_4[Ni_8(OH)_2][B_4O_4(H_2O)_8](SiW_{10}O_{37})_4\}^{14-}$	$\{Ni_6\}$		$\{SiW_{10}O_{37}\}$	

m and n refer to the number of metal cores within a polyanion and the number of metals within a core, respectively. Ni: green balls, O: red balls, N: dark blue balls, C: gray balls, S: azure balls.

Table S2 Bond valence sum calculations of the O in $Ni_{12}(OH)_9$

Atom Code	Bond Valence	Valence state	Atom Code	Bond Valence	Valence state	Atom Code	Bond Valence	Valence state
O_{26}	1.28369	1	O_{42}	1.30941	1	O_{79}	1.32438	1
O_{35}	0.81522	1	O_{58}	1.29452	1			

Table S3 Bond valence sum calculations of the O in $W_4O_{10}(OH)$

Atom Code	Bond Valence	Valence state	Atom Code	Bond Valence	Valence state	Atom Code	Bond Valence	Valence state
O_6	1.60623	2	O_{15}	1.62147	2	O_{56}	1.01455	1
O_{12}	1.54068	2	O_{48}	1.56701	2	O_{76}	1.88242	2

Table S4 Bond valence sum calculations of the O in $P_4O_2(OH)_2$

Atom Code	Bond Valence	Valence state	Atom Code	Bond Valence	Valence state	Atom Code	Bond Valence	Valence state
O_{27}	1.39794	1	O_{39}	1.15283	1	O_{40}	1.71397	2
O_{49}	1.75081	2						

Table S5 Bond valence sum calculations of the O in $Ni_6(OH)$

Atom Code	Bond Valence	Valence state	Atom Code	Bond Valence	Valence state
O_{21}	1.19507	1	O_{60}	1.17714	1

Table S6 Various experimental conditions of **2**

Entry	**2** TON_{CO}[a]	**2** TON_{CH4}[b]	**2** TON_{H2}[c]	**2** TON[d]
1	69.88	0	13.15	83.03
2_e	0.13	0.01	0.09	0.23
3_f	0	1	0	1
4_g	0	0	0	0
5_h	0	0	0	0
6_i	0	0.20	0	0.20
7_j	2	0	0	2
8_k	8.02	0.04	0	8.06
9[l]	0	0	0	0
10[m]	0.13	0	0	0.13

Reaction conditions: compounds (0.1 μmol), $[Ru(bpy)_3]Cl_2·6H_2O$ (0.01 mmol) triethanolamine (TEOA, 1 mL), H_2O (1 mL) and acetonitrile (MeCN, 4 mL). The reaction setup was alternately vacuum degassed and purged with CO_2 three times, after which high-purity CO_2 was purged again for 30 min, λ ≥ 420 nm, 30 °C, 1 h.

a. Turnover number ($n_{CO}/n_{Compound}$). b. Turnover number ($n_{CH4}/n_{Compound}$). c. Turnover number ($n_{H2}/n_{Compound}$). d. Turnover number [$(n_{CO} + n_{CH4} + n_{H2})/n_{Compound}$]. e. Without **2**. f. Without $[Ru(bpy)_3]Cl_2·6H_2O$. g. Without TEOA. h. Using N_2 to replace CO_2. i. In the dark. j. Using $Na_{10}[A\text{-}\alpha\text{-}SiW_9O_{34}]$ (0.4 μmol) to replace **2**. k. Using $Ni(Ac)_2·4H_2O$ (1.37 μmol) to replace **2**. l. Using $K_2B_{10}O_{16}·8H_2O$ (1.96 μmol) to replace **2**. m. Using DETA (9.29 μmol) to replace **2**.

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