

Supporting Information

Synergic Coordination of Multicomponents for the Formation of a {Ni₃₀} Cluster Substituted Polyoxometalate and Its In-situ Assembly

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1. Materials and Characterization

The precursor Na₉PW₉ were prepared according to the published synthetic method.^[S1] All other reagents were purchased from commercial sources and used as received without further treatment. The single crystal X-ray diffraction data were collected on Oxford Diffraction / Agilent SuperNova (dual source) diffractometer using CuK α radiation. Calculations were performed with SHELXL-2018 / 1 program package, and the structures were solved by direct method and refined on F² by full-matrix least-squares method.^[S2] Thermogravimetric analyses (TGA) were performed with a TGA / DSC 1 STAR^e system under N₂ atmosphere in a temperature range of 30-900 °C. For Fourier Transform Infrared (FT-IR) spectroscopy, the samples were prepared as KBr pellets and the spectra were collected in transmission mode using a VERTEX70 infrared analyzer in a range of 4000~400 cm⁻¹. Intensities are denoted as s = strong, w = weak, m = medium, sh = sharp, br = broad. Element analyses (C, H, N) were measured with a vario MICRO analyzer. UV-VIS-NIR spectra were scanned in the wavelength range of 200~2000 nm at room temperature on a Perkin Elmer Lambda-950 UV/Vis/NIR spectrophotometer, using a powder sample with BaSO₄ as a standard (100 % reflectance). Powder X-ray diffraction (PXRD) were carried out on Rigaku desktop MiniFlex 600 diffractometer with CuK α radiation (λ = 1.54184 Å). HERs were carried out under the irradiation of a 300 W Xe lamp with a cut-off filter (λ \geq 420 nm), and the resulting H₂ amounts were determined by a gas chromatograph (GC2014C, Shimadzu Co., TCD, molecular sieve 5A column, argon carrier).

2. Experiment Details

Synthesis of 1. 0.25 g Na_9PW_9 , 0.8 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.035 g Htrz, 8 mL distilled water and 0.08 mL en were successively added into in a 25-mL PTFE container. After ultrasonic treatment for 10 min, the mixture was sealed in a stainless steel reactor that was subsequently heated at 160 °C for 3 days. After the temperature cooled down to room temperature, cyan plate crystals were yielded. CCDC number: 2093863. Anal. Calcd (%) for **1** ($\text{C}_{64}\text{H}_{670}\text{N}_{86}\text{O}_{488}\text{P}_6\text{Ni}_{43}\text{W}_{54}$): C 3.33, H 2.90, N 5.22. Found: C 3.27, H 2.24, N 4.87. FT-IR (KBr pellet): 3431 cm^{-1} (s, br), 1632 cm^{-1} (m), 1510 cm^{-1} (w, sh), 1458 cm^{-1} (w), 1287 cm^{-1} (w), 1213 cm^{-1} (w), 1165 cm^{-1} (w), 1040 cm^{-1} (s), 941 cm^{-1} (s), 803 cm^{-1} (s), 710 cm^{-1} (s). TG: the weight loss of 15.75% (calculated 17.30%) before 400 °C is attributed to the removal of lattice water. According to EA and TGA, the structure includes 222 water molecules and 4 Htrz molecules, but most of them can't be unambiguously located by X-ray single crystal diffraction. Finally, the formula of **1** is determined as $[\text{Ni}_{11}(\text{trz})_{12}(\text{en})_4(\text{H}_2\text{O})_{22}]\text{H}_4\{[\text{Ni}(\text{trz})_3(\text{H}_2\text{O})_3]_2[\text{Ni}_{30}(\mu_3\text{-OH})_{18}(\text{H}_2\text{O})_{16}(\text{en})_6(\text{PW}_9\text{O}_{34})_6]\} \cdot 4\text{Htrz} \cdot 222\text{H}_2\text{O}$.

Synthesis of 2. 0.244 g Na_9PW_9 , 0.8 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.035 g Htrz, 8 mL deionized water and 0.09 g en were successively added into in a 25-mL PTFE container. After ultrasonic treatment for 25 min, the mixture was sealed in a stainless steel reactor that was subsequently heated at 180 °C for 3 days. After the temperature cooled down to room temperature, cyan columnar crystals were yielded. CCDC number: 2093864. Anal. Calcd (%) for **2** ($\text{C}_{60}\text{H}_{430}\text{N}_{82}\text{O}_{364}\text{P}_6\text{Ni}_{46}\text{W}_{54}$): C 3.44, H 2.07, N 5.48. Found: C 3.37, H 1.55, N 5.22. FT-IR (KBr pellet): 3430 cm^{-1} (s, br), 1624 cm^{-1} (m), 1504 cm^{-1} (w, sh), 1458 cm^{-1} (w), 1283 cm^{-1} (w), 1210 cm^{-1} (w), 1155 cm^{-1} (w), 1036 cm^{-1} (s), 945 cm^{-1} (s), 799 cm^{-1} (s), 709 cm^{-1} (s). TG: the weight loss of 10.64% (calculated 8.08%) before 380 °C is attributed to the removal of lattice water. According to EA, TGA, the structure approximately includes 94 water molecules and 4 Htrz molecules, but most of them can't be unambiguously located by X-ray single crystal diffraction. Finally, the formula of **2** is determined as $[\text{Ni}_6(\text{trz})_6(\mu_3\text{-OH})(\text{en})(\text{H}_2\text{O})_{10}]_2\text{H}_8\{[\text{Ni}(\text{trz})_3(\text{H}_2\text{O})_3]_2[\text{Ni}_{30+2}(\mu_3\text{-OH})_{18}(\text{O})_4(\text{H}_2\text{O})_{16}(\text{en})_6(\text{PW}_9\text{O}_{34})_6]\} \cdot 4\text{Htrz} \cdot 94\text{H}_2\text{O}$.

Synthesis of 4. 0.35 g Na_9PW_9 , 0.8 g $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, 0.035 g Htrz, 10 mL deionized water and 0.1 g en were successively added into in a 25-mL PTFE container. After ultrasonic treatment for 10 min, the mixture was sealed in a stainless steel reactor that was subsequently heated at 140 °C for 3 days. After the temperature cooled down to room temperature, cyan prism crystals were yielded. CCDC number: 2093865. Anal. Calcd (%) for **4** ($\text{C}_{64}\text{H}_{624}\text{N}_{80}\text{O}_{524}\text{P}_8\text{Ni}_{52}\text{W}_{72}$): C 2.80, H 2.22, N 4.08. Found: C 2.90, H 1.85, N 3.92. FT-IR (KBr pellet): 3416 cm^{-1} (s, br), 1625 cm^{-1} (m), 1513 cm^{-1} (w, sh), 1287 cm^{-1} (w), 1214 cm^{-1} (w), 1162 cm^{-1} (w), 1038 cm^{-1} (s), 945 cm^{-1} (s), 807 cm^{-1} (s), 710 cm^{-1} (s). TG: the weight loss of 11.03% (calculated 11.41%) before 390 °C is attributed to the removal of lattice water. According to EA, TGA, the structure approximately includes 174 water molecules and 4 Htrz molecules that can't be unambiguously located by X-ray single crystal diffraction. Finally, the formula of **4** is determined as $[\text{Ni}_3(\text{trz})_3(\text{en})(\text{H}_2\text{O})_8]_2\{[\text{Ni}(\text{en})(\text{H}_2\text{O})_2]\text{H}_4[\text{Ni}_6(\mu_3\text{-OH})_3(\text{H}_2\text{O})_5(\text{en})_3(\text{PW}_9\text{O}_{34})]\}_2\{[\text{Ni}(\text{trz})_3(\text{H}_2\text{O})_3]_2[\text{Ni}_{30}(\mu_3\text{-OH})_{18}(\text{H}_2\text{O})_{16}(\text{en})_6(\text{PW}_9\text{O}_{34})_6]\} \cdot 4\text{Htrz} \cdot 174\text{H}_2\text{O}$.

Photocatalytic experiments. To a 10 ml Pyrex reaction tube charged with 15 mg ground catalyst (for **1**, **2**, and **4**) was added 4 mL acetonitrile solution of 200 μM [Ir], 0.1 M, BNAH and 0.25 M TEOA. The tube was sealed and

degassed under dark with nitrogen five times by freeze-pump-thaw-aerate cycles. Then the mixture was stirred and irradiated with a 300 W Xe lamp with a 420 nm cut-off filter. 200 μ l gas in the headspace was taken out for GC analysis every 30 minutes. The amounts of generated H₂ were quantified by gas chromatography analysis of the headspace gas in the reactor. The replenishment of [Ir] photosensitizer for the resuscitating experiment was conducted by injecting 0.1 ml acetonitrile solution of [Ir]. For recycling experiments, the catalyst was filtered out with microporous filtering film (Φ 50mm, 0.45 μ m) after reaction and washed thoroughly with water and ethanol in succession. After naturally dried, the recovered catalyst was used in the next reaction run. During the procedure, no obvious weight loss of catalysts was observed. For controlling experiments, the dosage of Ni₆POM-1 was 3 mg, equivalent to the mole of [Ni(trz)₃]₂@[Ni₃₀(H₂O)₁₆]POM.

3. Additional Tables and Figures

Table S1. Crystal data and structure refinements for **1–4**.

	1	2	3	4
Formula	C ₅₆ H ₁₇₂ N ₇₄ Ni ₄₃ O ₂₆₈ P ₆ W ₅₄	C ₅₂ H ₁₄₀ N ₇₀ Ni ₄₆ O ₂₇₃ P ₆ W ₅₄	C ₆₀ H ₂₄₀ Cl ₂ N ₇₈ Ni ₄₈ O ₂₈₁ P ₄ W ₅₄	C ₅₆ H ₂₆₄ N ₆₈ Ni ₅₂ O ₃₅₄ P ₈ W ₇₂
Formula weight	18808.92	18928.71	19492.05	24093.21
T(K)	100	100	100	100
Crystal system	Triclinic	Monoclinic	Monoclinic	Triclinic
Space group	<i>P</i> -1	<i>C</i> 2/ <i>c</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> -1
<i>a</i> (Å)	20.9289(5)	42.6584(3)	26.0749(3)	19.4435(4)
<i>b</i> (Å)	23.2751(5)	27.2039(2)	23.1535(3)	23.7706(4)
<i>c</i> (Å)	24.7121(4)	32.2228(3)	32.2661(4)	26.9875(4)
α (°)	79.0429(16)	90	90	72.326(1)
β (°)	74.1790(19)	92.9654(7)	102.9169(12)	80.482(1)
γ (°)	68.585(2)	90	90	77.460(2)
<i>V</i> (Å ³)	10727.0(4)	37343.7(5)	18986.9(4)	11534.4(4)
<i>Z</i>	1	4	2	1
<i>D</i> _x (g / cm ³)	2.912	3.367	3.409	3.469
μ (mm ⁻¹)	28.876	33.337	32.982	35.518
<i>F</i> (000)	8460.0	34000.0	17656.0	10812.0
ϑ range (°)	2.049-68.251	2.074-63.999	2.370-73.495	1.982-75.099
Limiting indices	-25 ≤ <i>h</i> ≤ 25 -26 ≤ <i>k</i> ≤ 28 -29 ≤ <i>l</i> ≤ 23	-49 ≤ <i>h</i> ≤ 49 -31 ≤ <i>k</i> ≤ 31 -36 ≤ <i>l</i> ≤ 37	-32 ≤ <i>h</i> ≤ 30 -23 ≤ <i>k</i> ≤ 28 -27 ≤ <i>l</i> ≤ 40	-24 ≤ <i>h</i> ≤ 23 -29 ≤ <i>k</i> ≤ 29 -21 ≤ <i>l</i> ≤ 32
Reflections collected / unique	74805 / 39183	202375 / 31003	78016 / 37291	89352 / 46199
<i>R</i> (int)	0.0581	0.0671	0.0450	0.0409
<i>S</i>	1.043	1.099	1.030	1.023
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0494, 0.1350	0.0947, 0.2213	0.0387, 0.0931	0.0366, 0.0899
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0623, 0.1454	0.1040, 0.2248	0.0462, 0.0979	0.0425, 0.0936
CCDC	2093863	2093864	2106591	2093865

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

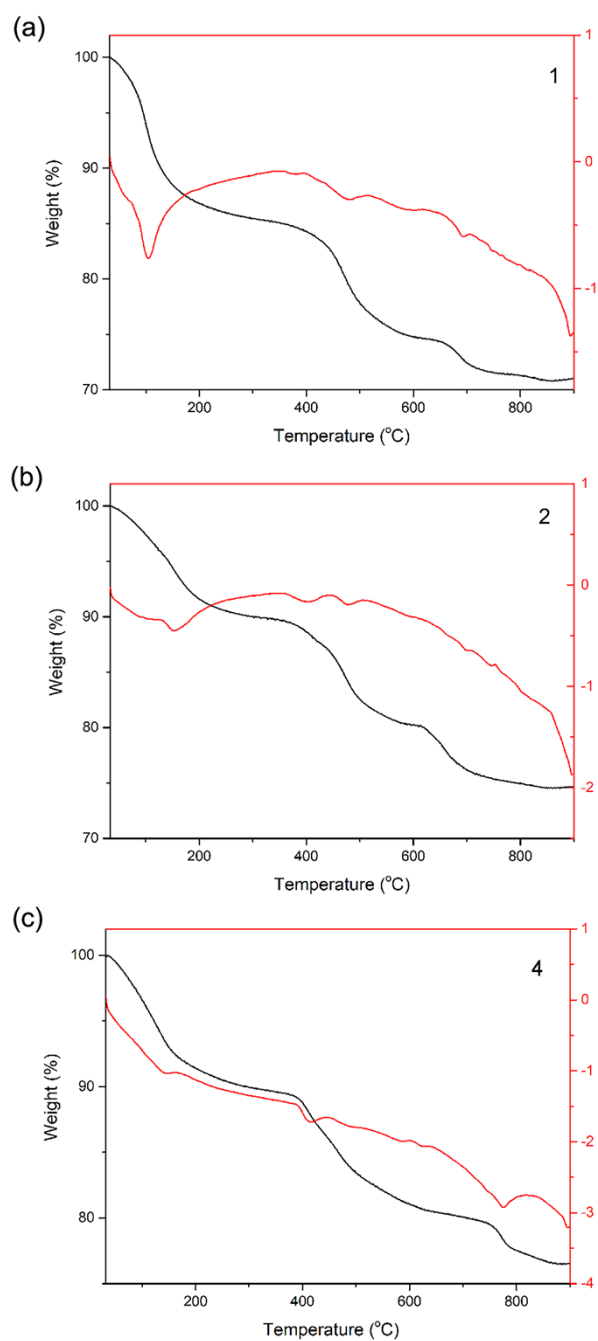


Fig. S1 TG curves of **1**, **2**, and **4**.

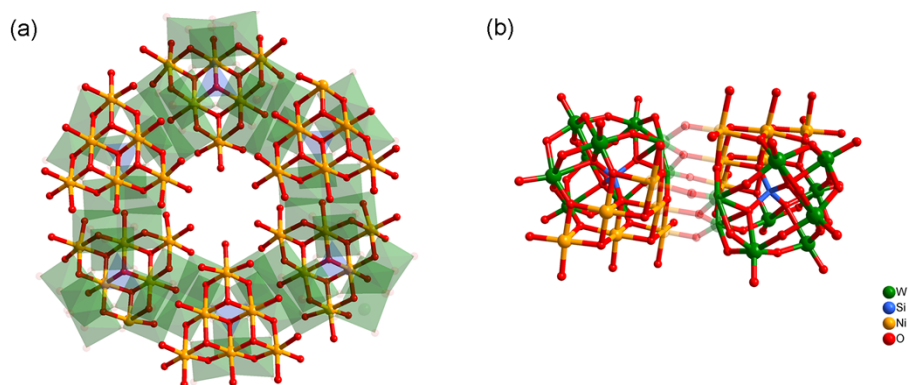


Fig. S2 (a) Structure of the reported $[\text{Ni}_6\text{POM}]_6$ by Kortz; (b) Connecting mode of neighbouring Ni_6POM fragments in $[\text{Ni}_6\text{POM}]_6$.

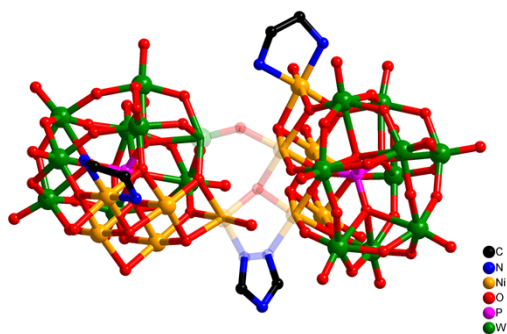


Fig. S3 Connecting mode of neighbouring Ni₅POM fragments in [Ni(trz)₃]₂@[Ni₃₀(H₂O)₁₆]POM.

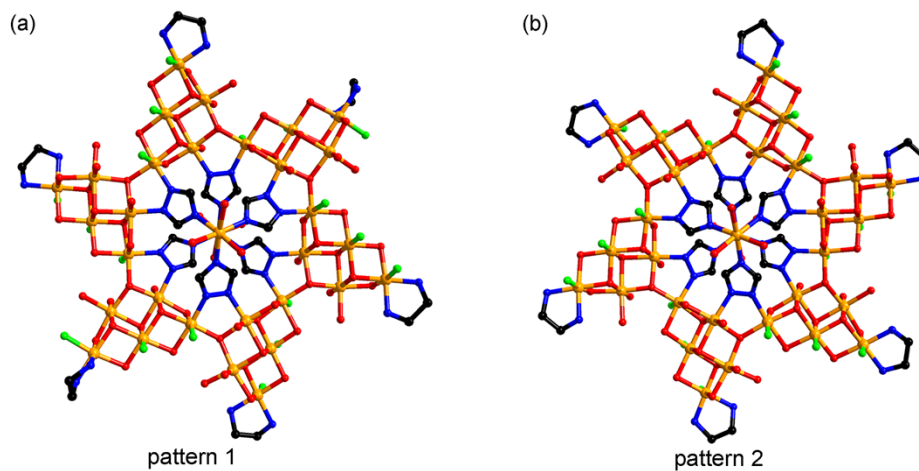


Fig. S4 Illustration of the deduced {Ni₃₀} cluster with 18 coordinating water (two patterns). (color code: green O from coordinating water; red O; orange Ni; blue N; black C).

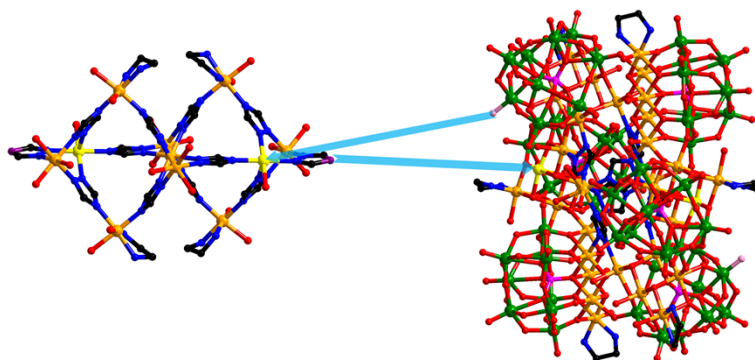


Fig. S5 [Ni₁₁(trz)₁₂] fragment (left) and SBU (right) in **1** (color code: red O; pink coordinating terminal O; orange Ni; yellow coordinating Ni; blue N; dark purple coordinating N; purple P; black C).

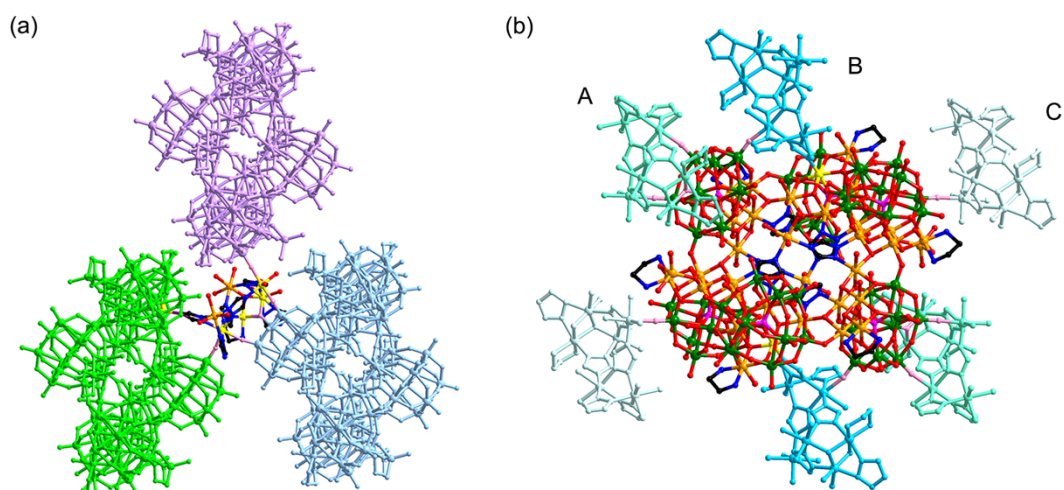


Fig. S6 (a) Three SBUs connected by one $[\text{Ni}_6(\text{trz})_6]$ bridges; (b) six $[\text{Ni}_6(\text{trz})_6]$ bridges bound by one SBU in **2**. (color code: red O; pink coordinating terminal O; orange Ni; yellow coordinating Ni; purple P; blue N; dark purple coordinating N; black C).

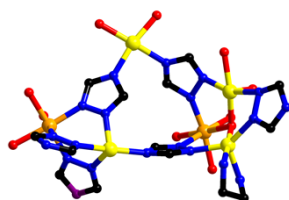


Fig. S7 Coordinating sites of $[\text{Ni}_6(\text{trz})_6]$ bridge in **2**. (color code: red O; orange Ni; yellow coordinating Ni; blue N; dark purple coordinating N; black C).

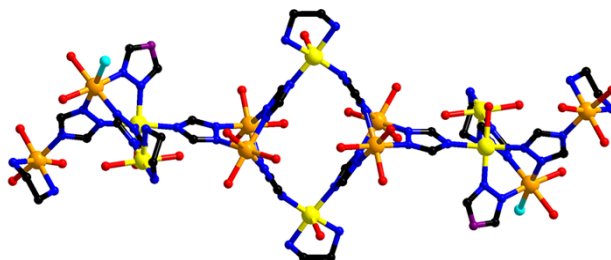


Fig. S8 Coordinating sites of $[\text{Ni}_{14}(\text{trz})_{12}]$ bridge in **3**. (color code: red O; orange Ni; yellow coordinating Ni; blue N; dark purple coordinating N; black C; cyan Cl).

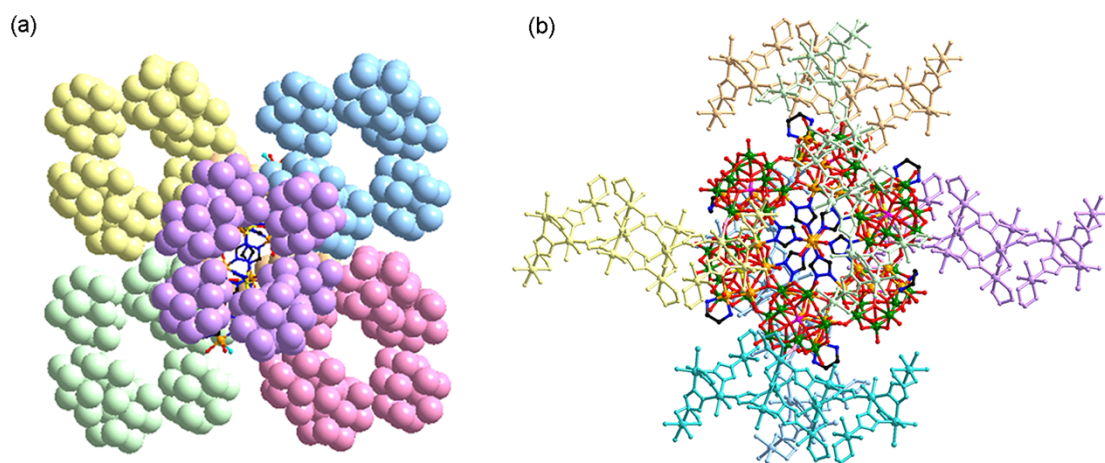


Fig. S9 Crystallographic illustration of the six $[\text{Ni}(\text{trz})_3]_2@[\text{Ni}_{30}(\text{H}_2\text{O})_{16}]$ POM linked by a $[\text{Ni}_{14}(\text{trz})_{12}]$ bridge in **3**. (color code: red O; pink coordinating terminal O; orange Ni; yellow coordinating Ni; purple P; blue N; dark purple coordinating N; black C; cyan Cl). In the space-filling mode, C, N, O and the Ni atoms locating at the center of $[\text{Ni}(\text{trz})_3]_2@[\text{Ni}_{30}(\text{H}_2\text{O})_{16}]$ POM have been omitted for clarity.

Table S2. The relationship of the dimension of frameworks **1–3** and the coordinating sites provided by $[\text{Ni}_x(\text{trz})_y]$ bridges in them.

Framework	dimension	bridge	Ni coordinating sites	N coordinating sites	Total number of coordinating sites
1	1	$[\text{Ni}_{11}(\text{trz})_{12}]$	2	2	4
2	2	$[\text{Ni}_6(\text{trz})_6]$	4	1	5
3	3	$[\text{Ni}_{14}(\text{trz})_{12}]$	6	2	8

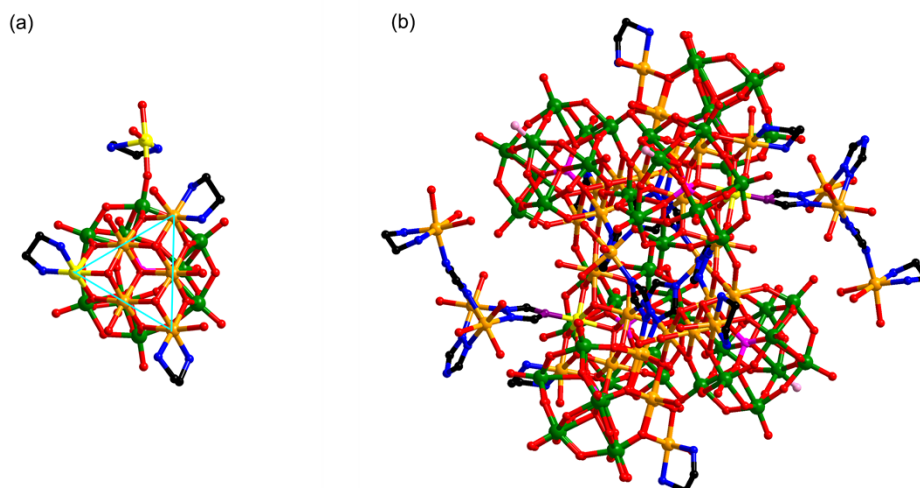


Fig. S10 (a) Bridge of **4**; (b) decorated SBU of **4** (color code: red O; pink coordinating terminal O; orange Ni; yellow coordinating Ni; purple P; blue N; dark purple coordinating N; black C).

Table S3. Photocatalytic activities of other POM compounds for H_2 evolution.

Catalyst	PS/ED	Medium/ PD	TON	Time (h)	Ref.
$\text{K}_4\{[\text{Cu}_{29}(\text{OH})_7(\text{H}_2\text{O})_2(\text{en})_8(\text{trz})_{21}][\text{Nb}_{24}\text{O}_{67}(\text{OH})_2(\text{H}_2\text{O})_3]_4\}$	$[\text{Ir}(\text{ppy})_2(\text{dtbbpy})][\text{PF}_6]/\text{TEOA}$	$\text{CH}_3\text{CN}/\text{DMF}/\text{H}_2\text{O}$	57.5	12	S3
$[\text{Cu}(\text{en})_2]@[\text{Cu}_2(\text{en})_2(\text{trz})_2]_6[\text{Nb}_{68}\text{O}_{188}]$	$[\text{Ir}(\text{ppy})_2(\text{dtbbpy})][\text{PF}_6]/\text{TEOA}$	$\text{CH}_3\text{CN}/\text{DMF}/\text{H}_2\text{O}$	60.0	12	S3
$\{[\text{Cu}(\text{en})_2]@[\text{Cu}_2(\text{trz})_2(\text{en})_2]_6[\text{H}_{10}\text{Nb}_{68}\text{O}_{188}]\}$	$[\text{Ir}(\text{ppy})_2(\text{dtbbpy})][\text{PF}_6]/\text{TEOA}$	$\text{CH}_3\text{CN}/\text{DMF}/\text{H}_2\text{O}$	59.0	12	S3
$[\text{M}(\text{H}_2\text{O})\text{TiW}_{11}\text{O}_{39}]^{n-}$ (M=Fe, Co, Zn)	–/PVA	PVA/ H_2O	3.2	3	S4
$[\text{Ni}_4(\text{H}_2\text{O})(\text{PW}_9\text{O}_{34})_2]^{10-}$	$[\text{Ir}(\text{ppy})_2(\text{dtbbpy})]^+/\text{TEOA}$	$\text{CH}_3\text{CN}/\text{DMF}/\text{H}_2\text{O}$	290	2.5	S5
$[\text{Mn}_4(\text{H}_2\text{O})_2(\text{VW}_9\text{O}_{34})_2]^{10-}$	$[\text{Ru}(\text{bpy})_3]^{2+}/\text{TEOA}$	$\text{DMF}/\text{H}_2\text{O}$	42	5.5	S6
$[\text{H}_2\text{NiNb}_9\text{O}_{28}]^{n-}$	–/MeOH	MeOH (20 vol.%)/ H_2O	7.5	8	S7
$[\text{Fe}_6\text{Se}_6\text{W}_{34}\text{O}_{124}(\text{OH})_{16}]^{18-}$	–/MeOH	MeOH (20 vol.%)/ H_2O	181	12	S8
$[\text{Fe}_{10}\text{Se}_8\text{W}_{62}\text{O}_{222}(\text{OH})_{18}(\text{H}_2\text{O})_4]^{28-}$	–/MeOH	MeOH (20 vol.%)/ H_2O	193	12	S8
1	$[\text{Ir}(\text{ppy})_2(\text{dtbbpy})][\text{PF}_6]/\text{BNAH}$	$\text{CH}_3\text{CN}/\text{TEOA}$	56.2	2	This work
2	$[\text{Ir}(\text{ppy})_2(\text{dtbbpy})][\text{PF}_6]/\text{BNAH}$	$\text{CH}_3\text{CN}/\text{TEOA}$	34.1	2	This work
4	$[\text{Ir}(\text{ppy})_2(\text{dtbbpy})][\text{PF}_6]/\text{BNAH}$	$\text{CH}_3\text{CN}/\text{TEOA}$	56.9	2	This work

PS = photosensitizer; ED = electron donor; PD = proton donor; PVA = polyvinyl alcohol.

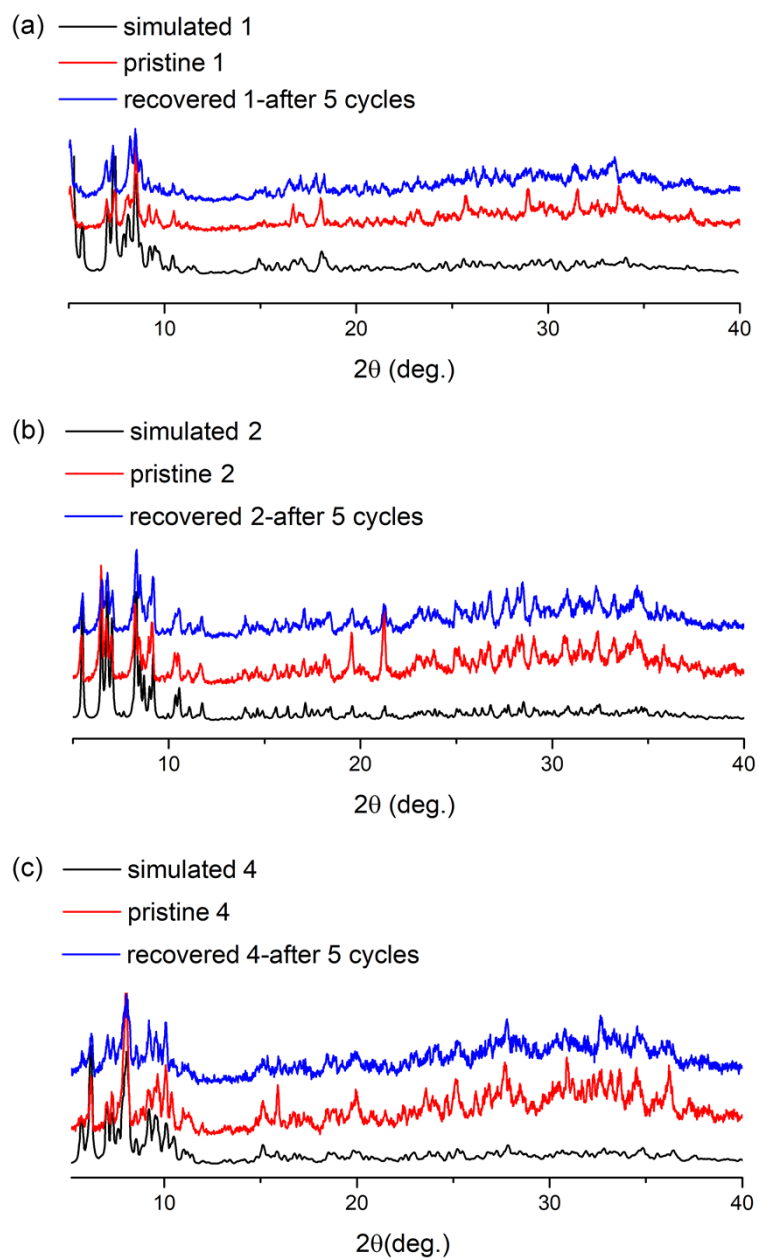


Fig. S11 PXRD patterns of simulated, pristine and recovered 1, 2, and 4.

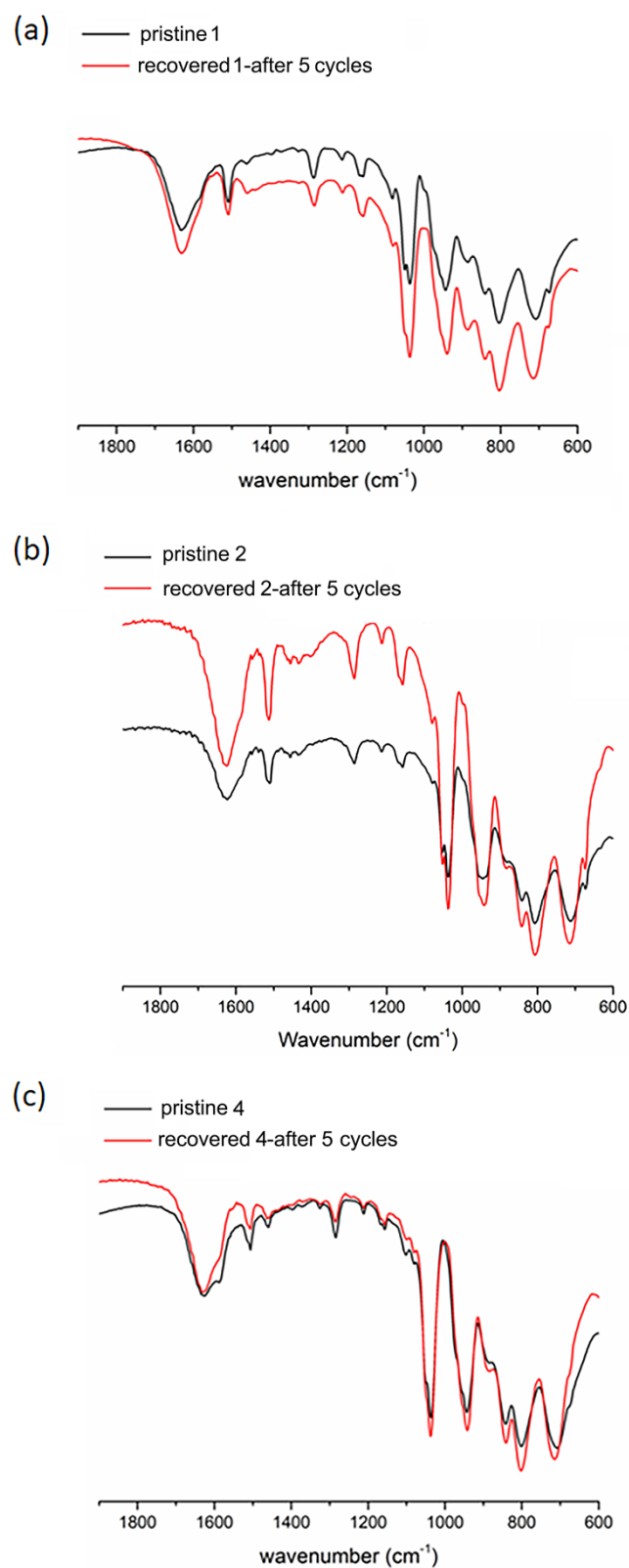


Fig. S12 FT-IR spectra of pristine and recovered **1**, **2**, and **4**.

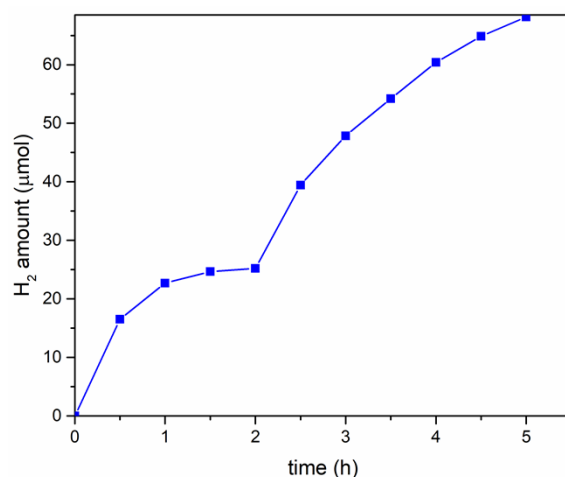


Fig. S13 The recovered H₂ evolution capacity of the reaction system with **2**.

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