Supporting information

Iodine-templated assembly of unprecedented 3d-4f metal-organic frameworks as photocatalysts for hydrogen generation

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S1. Materials and measurements

All chemical materials were purchased from commercial sources and used without further purification. The FT-IR spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. XRPD patterns were recorded on a Siemens D5005 diffractometer with Cu Kα (λ = 1.5418 Å) radiation in the range of 3−60° at a rate of 5°/min. The UV-Vis absorption spectra were examined on a Shimadzu UV-2550 spectrophotometer in the wavelength range of 200-800 nm. The C, H, and N elemental analyses were conducted on a Perkin-Elmer 2400CHN elemental analyzer. TG was performed on a Perkin–Elmer TG-7 analyzer heated from room temperature to 1000 ºC at a ramp rate of 5 °C/min under nitrogen.

S2. X-ray crystallography

Single-crystal X-ray diffraction data for **1–4** were recorded by using a Bruker Apex CCD diffractometer with graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å) at 293 K. Absorption corrections were applied by using a multi-scan technique. All the structures were solved by Direct Method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program within WINGX. Non-hydrogen atoms were refined with anisotropic temperature parameters.

The detailed crystallographic data and structure refinement parameters for **1−4** are summarized in Table S1.

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

	1	2	3	4
Formula	$C_{42}H_{36}Cu_5Sm_2I_8N_6O_{34}$	$C_{42}H_{36}Cu_5Eu_2I_8N_6O_{34}$	$C_{42}H_{36}Cu_5Gd_2I_8N_6O_{34}$	$C_{42}H_{36}Cu_5Tb_2I_8N_6O_{34}$
Formula weight	2802.37	2805.59	2816.17	2819.51
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*c*	*P*2(1)/*c*
a (Å)	12.3970(10)	12.380(2)	12.390(2)	12.3775(10)
b (Å)	13.5897(13)	13.575(5)	13.575(3)	13.5563(12)
c (Å)	22.542(2)	22.507(5)	22.512(5)	22.4534(19)
α (°)	90.00	90.00	90.00	90.00
β (°)	104.7390(10)	104.799(5)	104.811(3)	105.004(2)
γ (°)	90.00	90.00	90.00	90.00
V (Å^3)	3672.7(6)	3657.0(17)	3660.6(13)	3639.1(5)
Z	2	2	2	2
$D_{calcd.}$[g cm^{-3}]	2.534	2.548	2.555	2.573
F(000)	2590	2594	2598	2602
Reflections collected	17913/6465	17820/6443	17773/6422	18293/6386
R(int)	0.0400	0.0524	0.0601	0.0366
Goodness-of-fit on F^2	1.045	1.062	1.035	1.025
$R_1{}^a$ [I>2σ (I)]	0.0360	0.0397	0.0513	0.0357
$wR_2{}^b$	0.0823	0.0876	0.1219	0.0812

S3. Photocatalytic Measurements

Photocatalytic reactions were carried out in a Pyrex inner-irradiation-type reaction vessel with a magnetic stirrer at room temperature. The reactant solution was evacuated using N_2 several times to ensure complete air removal and then irradiated by using a 500 W mercury lamp. The produced H_2 was analyzed by a GC9800 instrument with a thermal conductivity detector and a 5 Å molecular sieve column (2 mm× 2 m) using N_2 as carrier gas.

S4. Synthesis of 1–4

Method 1: A mixture of H_2pydc (50 mg, 0.25 mmol), Ln_2O_3 (0.1 mmol, Ln = Sm, Eu, Gd, and Tb for **1–4**), $Cu(NO_3)_2 \cdot 6H_2O$ (60 mg, 0.2 mmol), I_2 (25.4 mg, 0.1 mmol) and H_2O (6 mL) was placed in a Teflon-lined autoclave and heated to 150 °C for three days. The autoclave was then allowed to cool naturally to room temperature. Black crystals of **1–4** had been produced, which were collected by filtration and washed repeatedly with distilled water.

Method 2: A mixture of H_2pydc (50mg, 0.25mmol), Ln_2O_3 (0.1 mmol, Ln = Sm, Eu, Gd, and Tb for **1–4**), CuI (47.5mg, 0.25mmol), HNO_3 (5 drops), and H_2O (6 mL) was placed in a Teflon-lined autoclave and heated to 150 °C for three days. The autoclave was then allowed to cool naturally to room temperature. Black crystals of **1–4** had been produced, which were collected by filtration and washed repeatedly with distilled water.

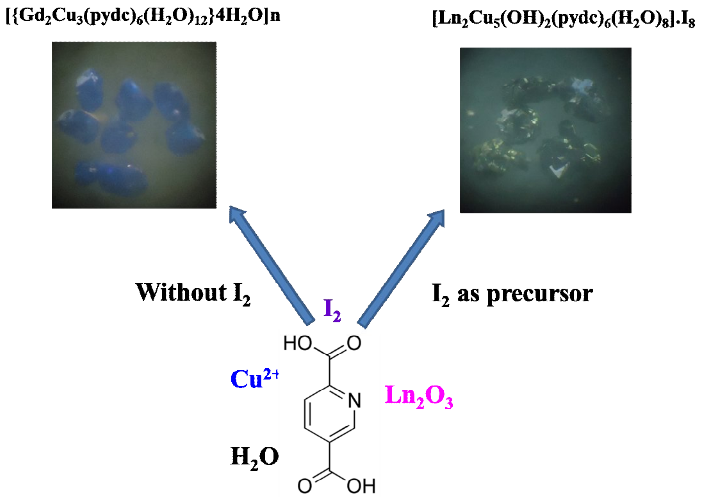
Anal. Calcd for $C_{42}H_{36}Cu_5Sm_2I_8N_6O_{34}$: C, 18.00; H, 1.29; N, 3.00. Found: C, 17.87; H, 1.36; N, 3.12.

Anal. Calcd for $C_{42}H_{36}Cu_5Eu_2I_8N_6O_{34}$: C, 17.98; H, 1.29; N, 3.00. Found: C, 17.91; H, 1.22; N, 3.07.

Anal. Calcd for $C_{42}H_{36}Cu_5Gd_2I_8N_6O_{34}$: C, 17.91; H, 1.29; N, 2.98. Found: C, 17.79; H, 1.22; N, 3.12.

Anal. Calcd for $C_{42}H_{36}Cu_5Tb_2I_8N_6O_{34}$: C, 17.89; H, 1.29; N, 2.98. Found: C, 17.81; H, 1.33; N, 2.89.

IR (cm^{-1}): 1154.20 (w), 1047.26 (w), 458.20 (w), 1488.75 (w), 683.19 (m), 847.71 (m), 1287.27 (m), 537.97 (m), 760.43 (m), 1599.99 (s), 1426.59 (s), 3385.01 (s), 1393.74 (s), 1363.39 (s), 1591.22 (s), 1612.74 (s).



Scheme S1 Schematic presentation of the preparation of **1−4** using iodine as the precursor template.

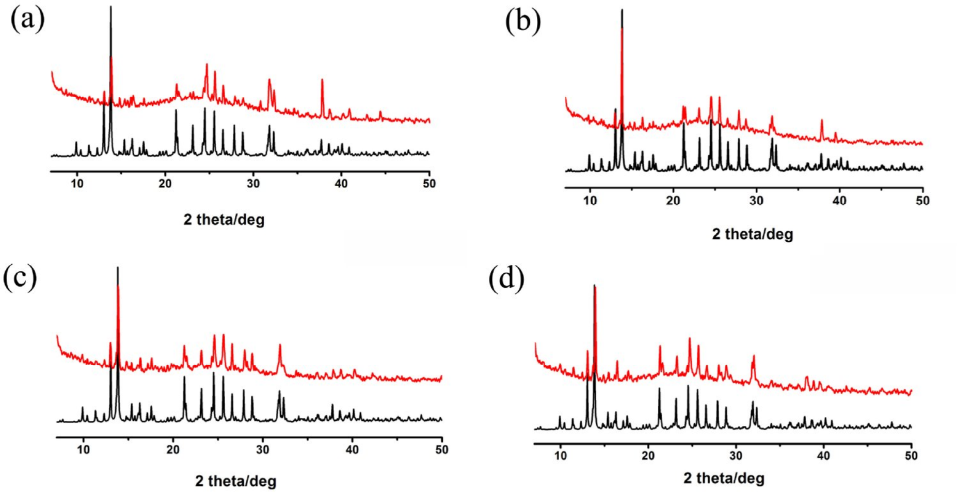


Fig. S1 X-ray powder diffraction patterns of as-synthesized (red) and simulated (black) **1** (a), **2** (b), **3** (c) and **4** (d).

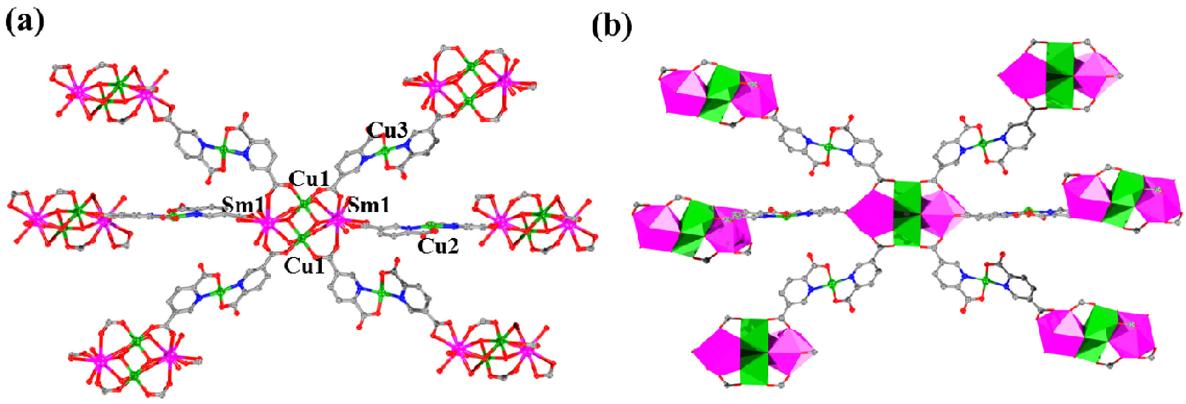


Fig. S2 (a) Coordination environment of Cu, Sm atoms in **1** (the H atoms are not shown for clarity). (b) The SBU can be viewed as a six-connected node.

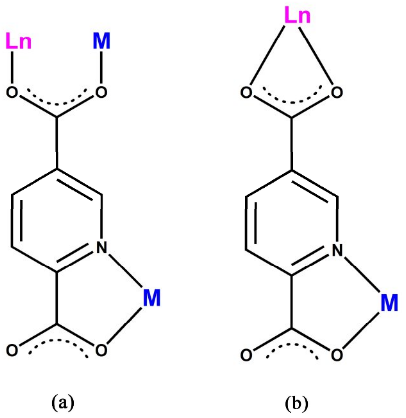


Fig. S3 Coordination modes of the pydc ligands found in **1**.

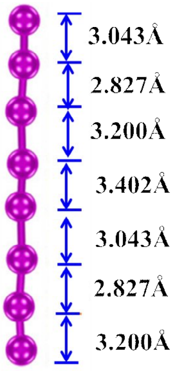


Fig. S4 The iodine–iodine distances of the repeated unit I(1)–I(2)–I(3)–I(4)–I(5)–I(6)–I(7)–I(8).

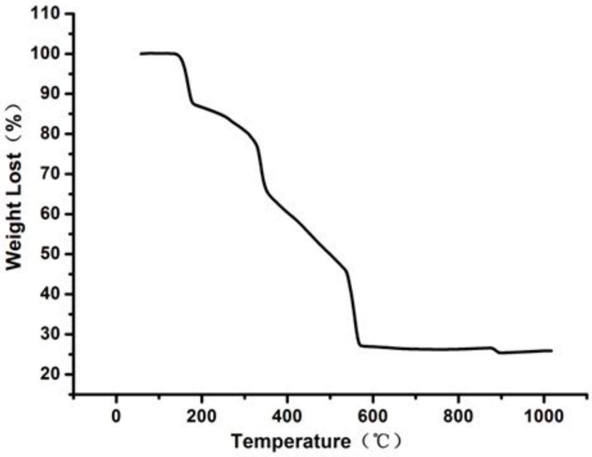


Fig. S5 TG curve of **2**. The TG curve of compound **2** shows the first weight loss of 9.05% in the range 25-176 °C, which corresponds to the partial loss of polyiodide molecules. The second weight loss of 20.6% in the range 176-330 °C is confirmed to the loss of the coordinated water molecules and the further decomposition of polyiodide molecules. The mass loss was obtained above 330 °C because of complete collapse of the coordination network with decomposition of the pydc ligands. The final weight, 26.7% suggests that the residue was probably mainly composed of Eu_2O_3 and CuO.

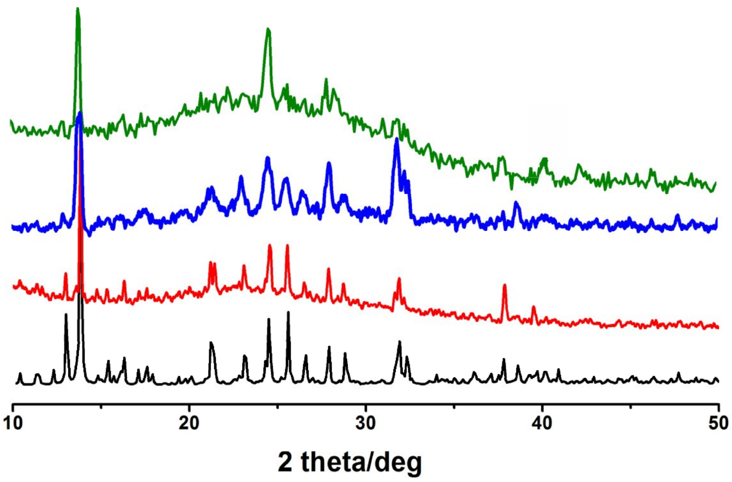


Fig. S6 XRPD patterns of **2** after treated in boiling water for 3 days (green) and exposed it to air for 3 months (blue).

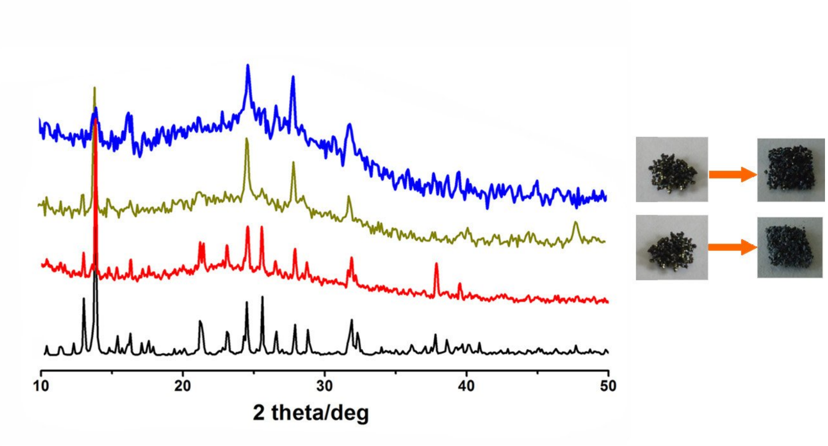


Fig. S7 XRPD patterns of **2** after soaking in acid (pH = 2, yellow) and base solutions (pH = 12, blue). The photos of the crystals before and after soaking in acid solutions and base solutions are shown in the right side of each spectrum, respectively.

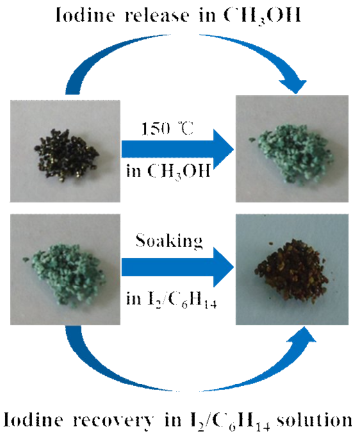


Fig. S8 The photographs of **2** for releasing I_2 in methanol at 150°C and **2a** for adsorbing I_2 in hexane.

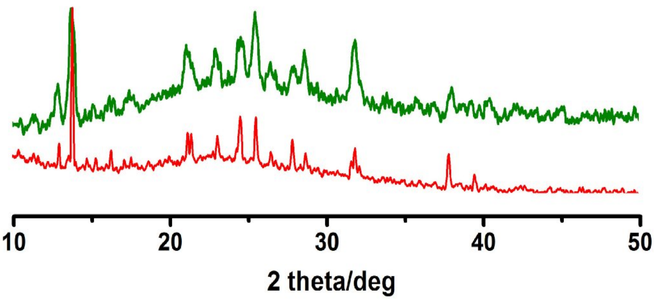


Fig. S9 XRPD patterns of as-synthesized **2** (red) and after releasing I_2 of **2** (green).

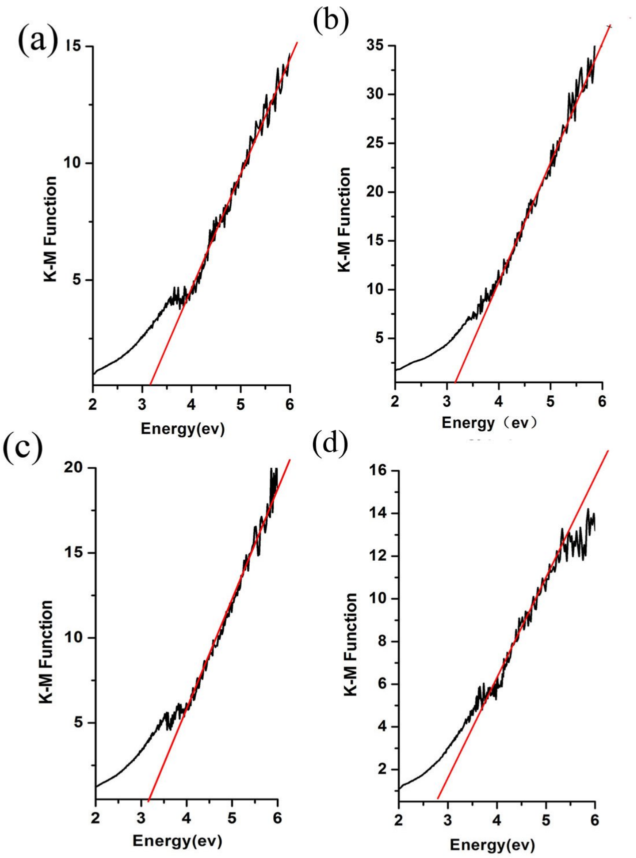


Fig. S10 The diffuse reflectance UV-vis-NIR spectra of K-M function vs. energy (eV) of compounds **1** (a), **2** (b), **3** (c), **4** (d).

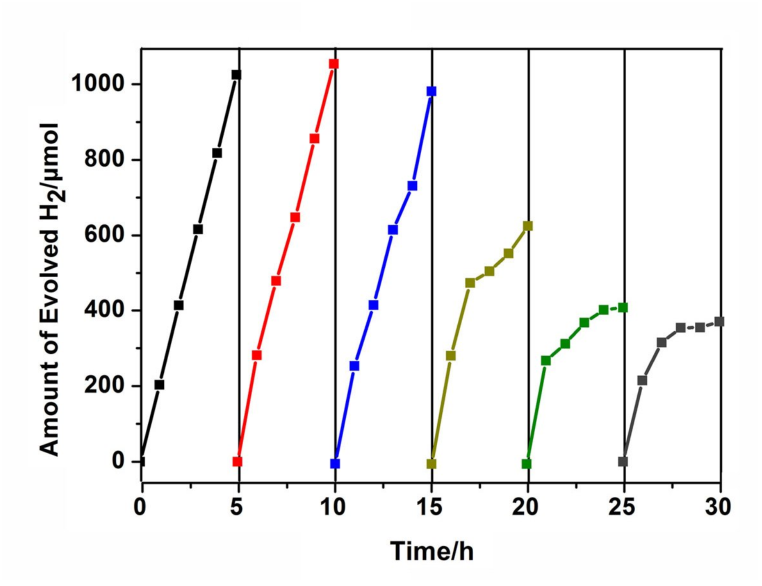


Fig. S11 Time course of H_2 evolution from compound **3** dissolved in 100 mL of 10% methanol solution under UV irradiation using a 500 W mercury lamp.

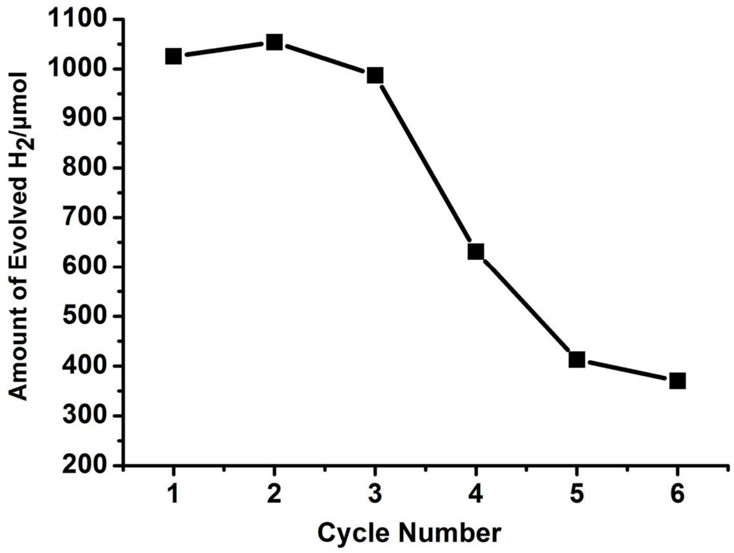


Fig. S12 The hydrogen evolution cycle property in compound **3**.

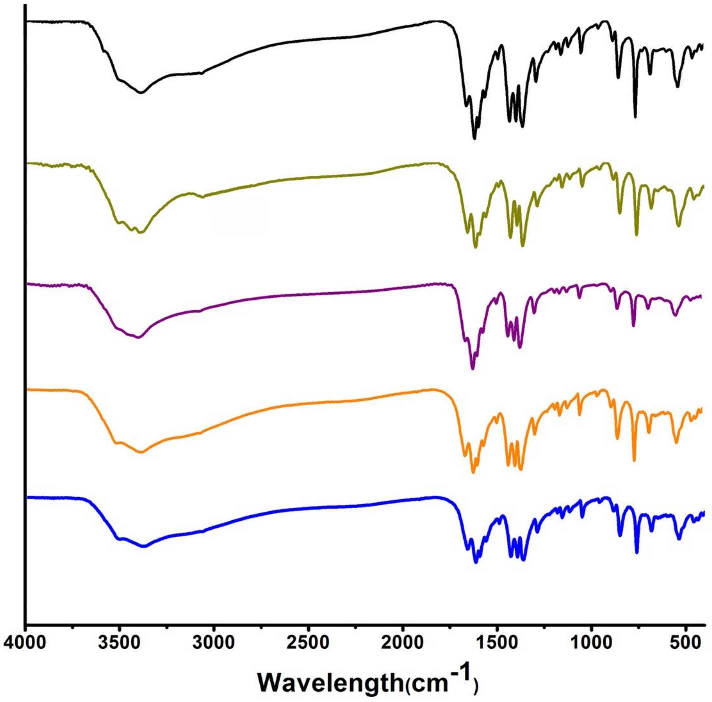


Fig. S13 FT-IR spectra of as-synthesized **2** (black) and the samples **1** (dark yellow), **2** (purple), **3** (light yellow), **4** (blue) after photocatalytic hydrogen generation.