

Electronic Supplementary Information

**2D Metal-Organic Frameworks Bearing Butterfly-shaped Metal-bis(dithiolene) Linkers from Dithiol-functionalized Benzenedicarboxylic Acid**

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## Experimental details

**General procedure.** Elemental analysis was obtained with a Vario Micro CUBE CHN elemental analyzer. Powder X-ray diffraction (PXRD) patterns were collected on a Rigaku Smart lab diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5418 \text{ \AA}$ ) at room temperature. The Xray tube operated at a voltage of 40 kV and a current of 15 mA. Fourier-transform infrared (FT-IR) spectra in the range 400–4000  $\text{cm}^{-1}$  were recorded on a Nicolet Avatar 360 FT-IR spectrophotometer. Thermogravimetric analysis (TGA) were carried out in a PerkinElmer thermal analysis equipment. The porosity and surface area analysis were performed using a Quantachrome Autosorb iQ gas sorption analyzer. The sample was outgassed at 0.03 torr with a 5  $^{\circ}\text{C}/\text{min}$  ramp to 130  $^{\circ}\text{C}$  and held at 130  $^{\circ}\text{C}$  for 12 h. The proportion of metal atoms was determined by the atomic absorption spectrophotometer (SHIMADZU). X-ray photoelectron spectroscopy (XPS) was carried out by a Scanning Auger/X-ray Photoelectron Spectroscopy System (PHI 5802). The morphology of the samples was investigated using scanning electron microscopy (SEM, SIGMA 500, ZEISS, Germany) and a transmission electron microscope (Hitach-SU8010 field emission). Photoelectrochemistry was carried out at CH Instruments Electrochemical Workstation CHI760E and DH Instruments Electrochemical Workstation DH7003. UV–Vis absorption spectra were recorded by SHIMADZU model UV-3600 Plus instruments using  $\text{BaSO}_4$  as a reference. The resulting spectra were used for computing Tauc plot to determine the optical bandgap. The photocatalytic experiments were performed by a multichannel photochemical reaction system (PCX-50C, Beijing Perfectlight Co., Ltd, China) equipped with a visible-light LED source ( $\lambda \geq 420 \text{ nm}$ ). Hydrogen was measured by gas chromatography (Fuli GC9790Plus, argon, Ar, as a carrier gas) using a thermal conductivity detector (TCD).

### Single crystal X-ray crystallography.

The X-ray diffraction data of crystals **Ni-dcbdt**, **Co-dcbdt**, **Fe-dcbdt** and metallolinker [NiS<sub>4</sub>] were determined using the BrukerAPEX-II CCD single crystal diffractometer (graphite monochromatic Cu K $\alpha$  radiation,  $\lambda = 1.54184 \text{ \AA}$ ) by collecting data through scanning along with Lp factor correction as well as empirical absorption correction. The space group was assigned and the structure was solved by direct methods using XPREP within the SHELXTL<sup>1</sup> suite of programs and refined by full matrix least squares against  $F^2$  with all reflections using Shelxl2018<sup>2</sup> using the graphical interface Olex2<sup>3</sup>, which yielded the positions of all non-hydrogen atoms, and they were refined anisotropically. Hydrogen atoms were placed in calculated positions with fixed isotropic thermal parameters and included in the structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL system of computer programs. These structures were deposited on Cambridge Crystallographic Data Centre and published as CSD communication.<sup>4</sup> Detailed parameters are shown in Table S1. **Co-dcbdt** and **Fe-dcbdt** are isomorphous with **Ni-dcbdt** and their structural representations (See Fig. 1a–1c in main manuscript) are not repeated here.

### Preparation of H<sub>2</sub>dcbdt.

H<sub>2</sub>dcbdt was synthesized according to the literature.<sup>5</sup>

### Preparation of M-dcbdt and metallolinkers.

**Self-assembly of M-dcbdt (Ni, Co, Fe).** Taking **Ni-dcbdt** as an example, H<sub>2</sub>dcbdt (2.5 mg, 0.01 mmol) and Ni(OOCCH<sub>3</sub>)<sub>2</sub>•4H<sub>2</sub>O (2 mg, 0.008 mmol) were added into 8-mm diameter glass tubes followed by addition of *N,N*-dimethylacetamide (DMA)/H<sub>2</sub>O mixture (0.35 mL, v:v = 4:3) and CH<sub>3</sub>COOH (50  $\mu$ L). The tube was then filled with N<sub>2</sub>, sealed up and allowed to stay in oven at 120 °C for 48 hours to generate black blocks which were collected, washed with DMF and acetone for thrice and then dried at 60 °C

for 10 hours to harvest **Ni-dcbdt** as black blocks (yield: 73%). **Co-dcbdt** (yield: 66%) and **Fe-dcbdt** (yield: 48%) were prepared analogously by replacing Ni(OOCCH<sub>3</sub>)<sub>2</sub>•4H<sub>2</sub>O with same mole of Co(OOCCH<sub>3</sub>)<sub>2</sub>•4H<sub>2</sub>O or FeCl<sub>3</sub>•6H<sub>2</sub>O respectively. Notably, their metallolinkers were prepared under the same conditions with shorter reaction duration (say 24 hours).

#### **Photocatalytic Hydrogen Evolution of M-dcbdt.**

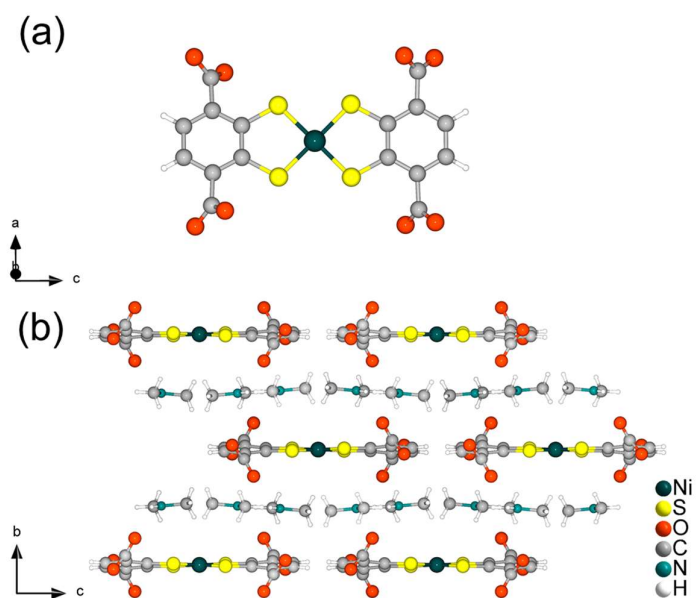
The photocatalytic tests were conducted under sealed conditions, using a multi-channel photochemical reaction system with visible LED ( $\lambda \geq 420\text{nm}$ ) as light source, and H<sub>2</sub> generated was analyzed by gas chromatograph through manual sampling. 1 mg of catalyst was weighed in a centrifuge tube and then 2.5 mL of DMF was added. Afterwards, the mixture was ultrasonically dispersed and added to the reactor. Then, the mixture was added 3 mg of photosensitizer, [Ru(bpy)<sub>3</sub>]Cl<sub>2</sub>, 2.5 mL of H<sub>2</sub>O, and 1 mL of sacrificial agent *N,N*-dimethylaniline. Subsequently, the set-up was sealed up and the mixture was deoxygenated for 30 minutes by bubbling N<sub>2</sub>. Upon completion of degassing, the photocatalytic reaction was carried out.

#### **Photoelectrochemical measurements.**

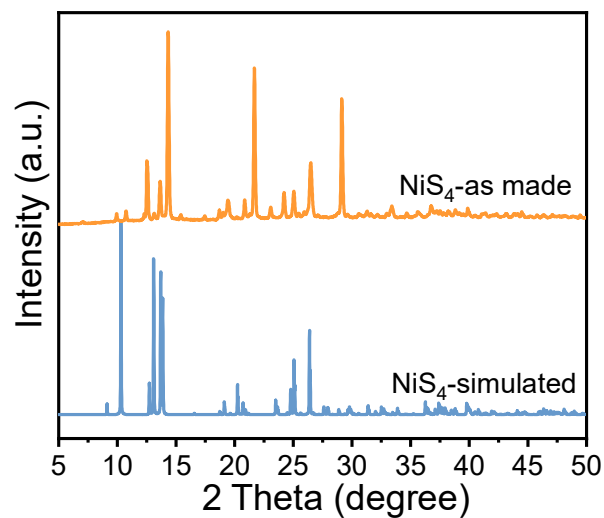
Photocurrent measurements were performed using the CHI760E Electrochemical Workstation. The samples (2 mg) were dispersed in a mixed solution of 10  $\mu\text{L}$  Nafion and 1 mL EtOH. The working electrodes were prepared by dropping the suspension (150  $\mu\text{L}$ ) onto the surface of ITO plate. The working electrodes were dried at room temperature. The electrochemical impedance spectroscopy (EIS) was performed in frequency range from 0.1 to 10<sup>5</sup> Hz without bias potential. Measurements were performed in a three-electrode system, with the Pt filament as the counter electrode and Ag/AgCl as the reference electrode. The photocurrent signal of the sample was measured under chopping light with a bias potential of 0.3 V. The sampling interval was 0.1 seconds, with occlusion of the light source every 40 seconds and running

duration of 440 seconds. Mott-Schottky plots were obtained using the same three-electrode system in 0.2 M Na<sub>2</sub>SO<sub>4</sub> aqueous solution. 500 Hz and 1000 Hz were selected as the applied alternating current (AC) frequency.

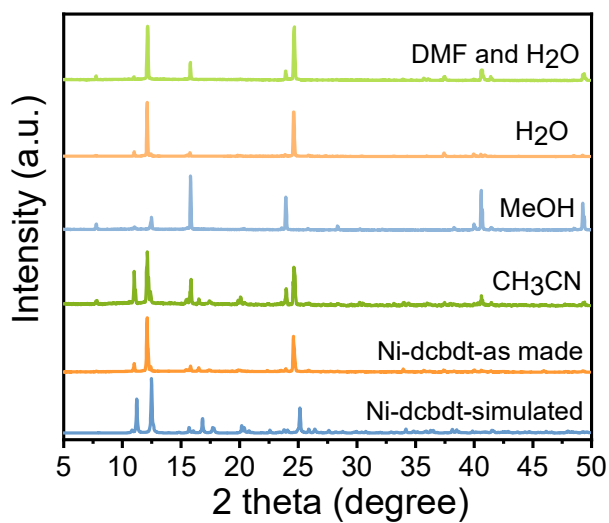
## Figures and Tables



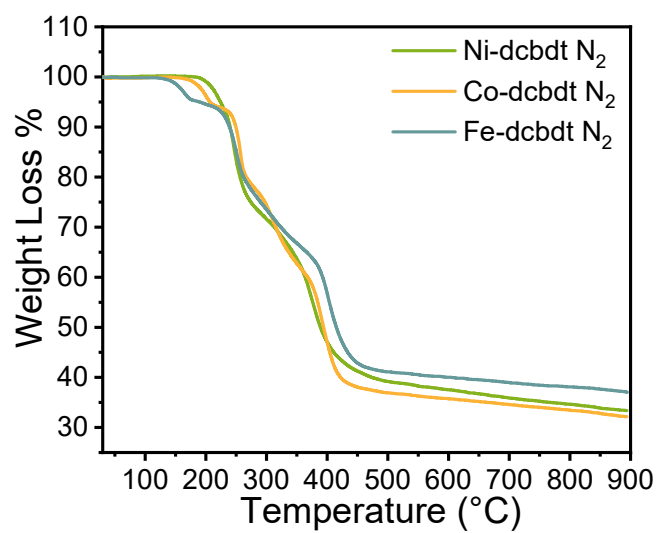
**Fig. S1** The single-crystal structure of metallolinker [NiS<sub>4</sub>]: (a) coordination environment of Ni-bis(dithiolene) unit, (b) packing of metallolinker [NiS<sub>4</sub>] viewed along *a* axis.



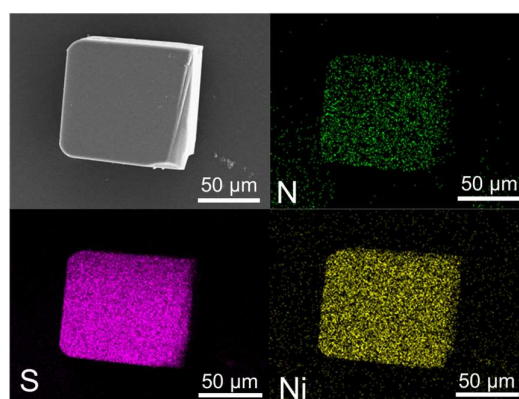
**Fig. S2** PXRd patterns of as made metallolinkers [NiS<sub>4</sub>] and single crystal structure of metallolinkers [NiS<sub>4</sub>].



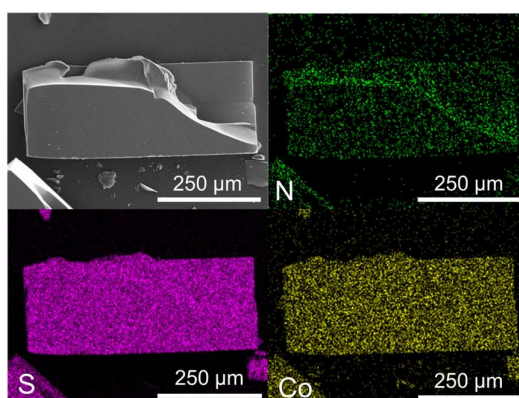
**Fig. S3** PXRd patterns of **Ni-dcbdt** at different solvent media.



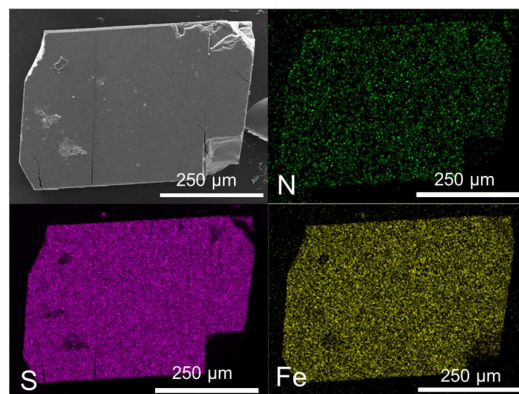
**Fig. S4** The TG plots of **M-dcbdt** under N<sub>2</sub> atmosphere.



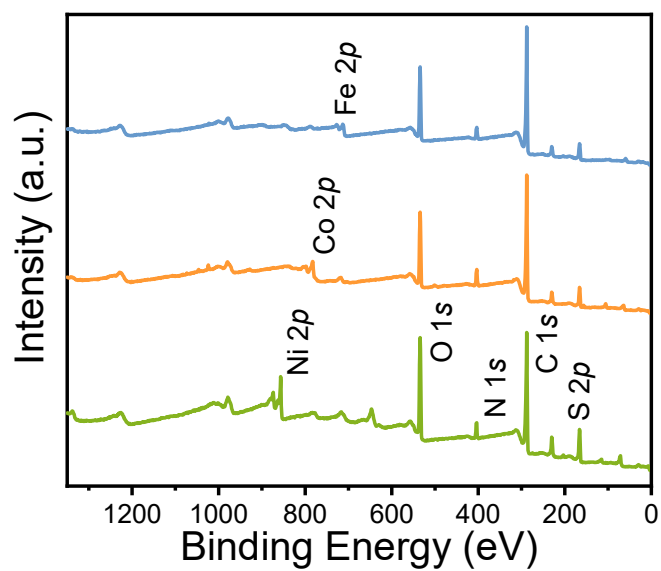
**Fig. S5** The SEM image and elemental mappings of **Ni-dcbdt**.



**Fig. S6** The SEM image and elemental mappings of **Co-dcbdt**.

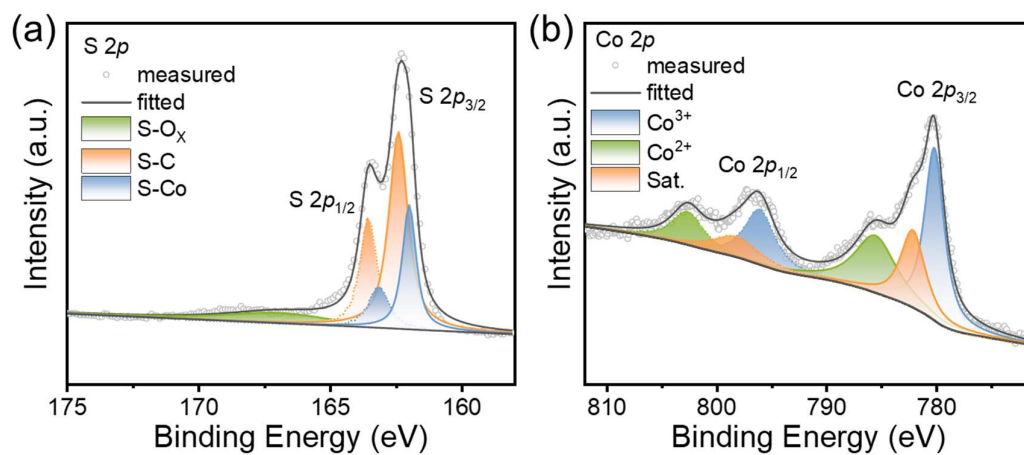


**Fig. S7** The SEM image and elemental mappings of **Fe-dcbdt**.

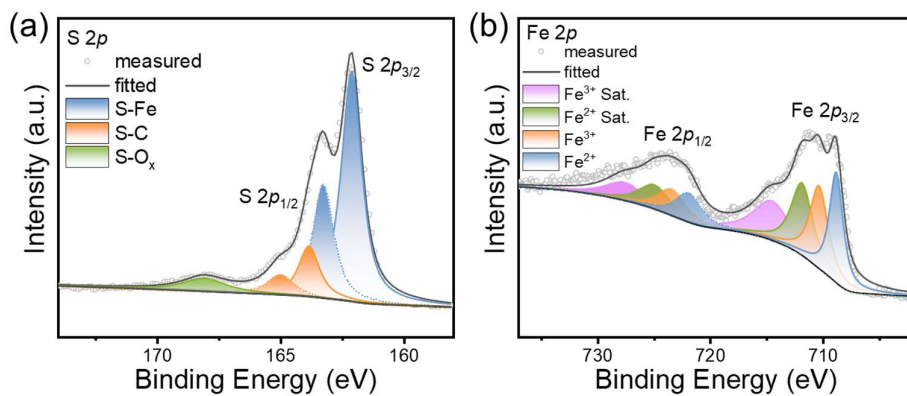


**Fig. S8** The XPS survey spectra of **M-dcbdt** (green: **Ni-dcbdt**; orange: **Co-dcbdt**; blue: **Fe-dcbdt**).

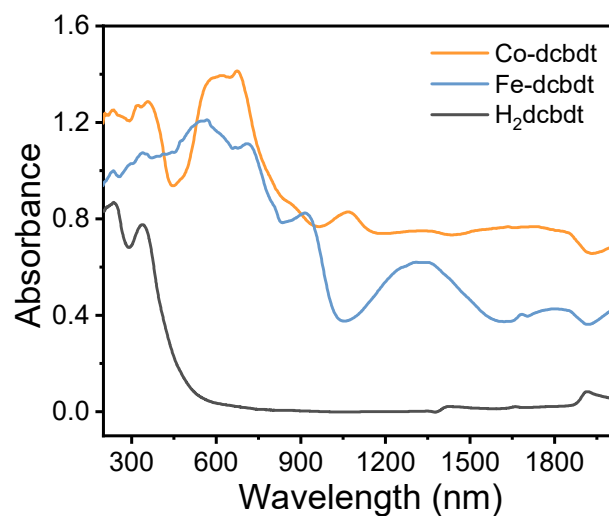




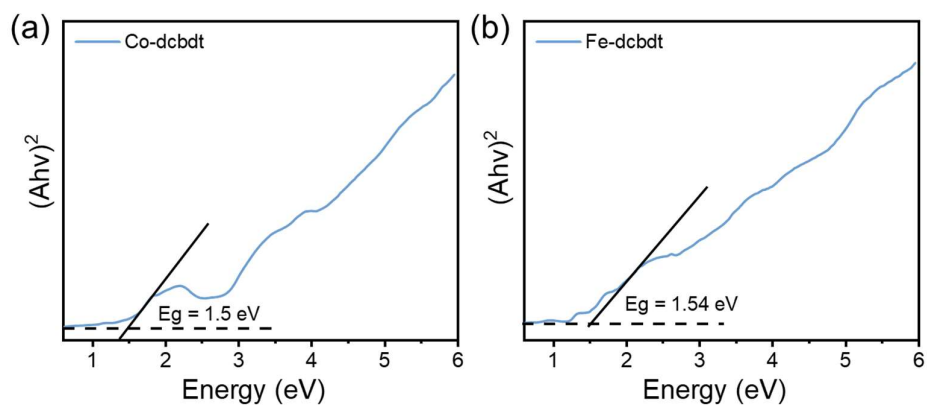
**Fig. S9** The XPS (a) S 2*p* and (b) Co 2*p* spectra of **Co-dcbdt**.



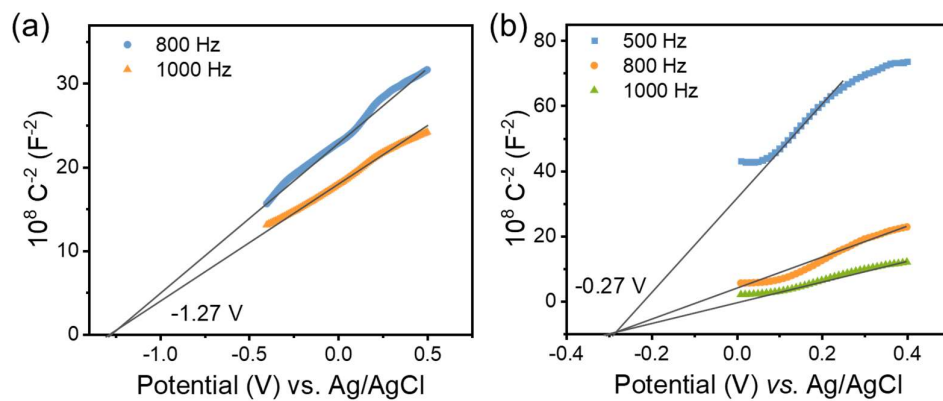
**Fig. S10** The XPS (a) S 2*p* and (b) Fe 2*p* spectra of **Fe-dcbdt**.



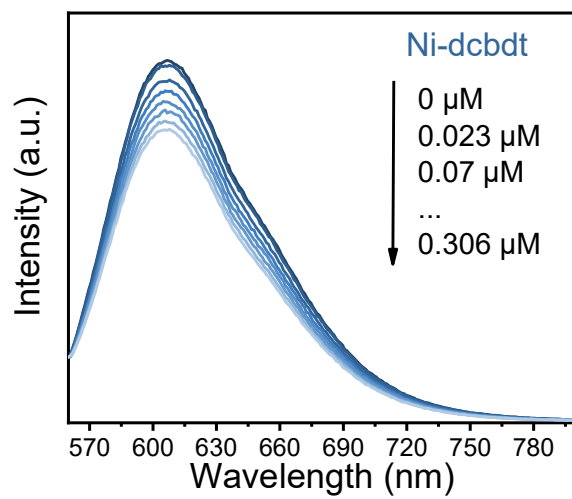
**Fig. S11** UV-vis absorption spectra of **Co-dcbdt**, **Fe-dcbdt** and **H<sub>2</sub>dcbdt**.



**Fig. S12** Tauc plots of (a) **Co-dcbdt** and (b) **Fe-dcbdt**.



**Fig. S13** Mott-Schottky plots and band structures of (a) **Co-dcbdt** and (b) **Fe-dcbdt**.



**Fig. S14** Steady-state PL spectral change ( $\lambda_{\text{ex}} = 550 \text{ nm}$ ) of  $[\text{Ru}(\text{bpy})_3]\text{Cl}_2$  upon addition of **Ni-dcbdt**.

**Table S1** Crystallographic refinement parameters and results of **M-dcbdt**.

Compound	Ni-dcbdt	Co-dcbdt	Fe-dcbdt
Chemical formula	C <sub>28</sub> H <sub>45</sub> N <sub>3</sub> Ni <sub>2</sub> O <sub>10</sub> S <sub>4</sub>	C <sub>28</sub> H <sub>45</sub> N <sub>3</sub> Co <sub>2</sub> O <sub>10</sub> S <sub>4</sub>	C <sub>28</sub> H <sub>45</sub> Fe <sub>2</sub> N <sub>3</sub> O <sub>10</sub> S <sub>4</sub>
Formula weight	829.33	829.79	823.61
Crystal system	<i>orthorhombic</i>	<i>orthorhombic</i>	<i>orthorhombic</i>
Space group	<i>Pbcn</i>	<i>Pbcn</i>	<i>Pbcn</i>
<i>a</i> /Å	22.0141(2)	22.1038(3)	22.2191(2)
<i>b</i> /Å	22.3831(3)	22.5058(3)	22.6288(2)
<i>c</i> /Å	14.1276(10)	14.2421(2)	14.4544(10)
$\alpha$ /°	90	90	90
$\beta$ /°	90	90	90
$\gamma$ /°	90	90	90
<i>V</i> /Å <sup>3</sup>	6961.29(12)	7084.93(17)	7267.55(10)
<i>Z</i>	8	8	8
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.583	1.554	1.423
<i>F</i> (000)	3472.0	3424.0	3081.0
Reflections collected	33167	35968	37858
GOF	1.052	1.070	1.042
<i>R</i> <sub>1</sub> <sup>a</sup> [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0577, <i>wR</i> <sub>2</sub> = 0.1584	<i>R</i> <sub>1</sub> = 0.0906, <i>wR</i> <sub>2</sub> = 0.2595	<i>R</i> <sub>1</sub> = 0.0348, <i>wR</i> <sub>2</sub> = 0.1032
<i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	<i>R</i> <sub>1</sub> = 0.0671, <i>wR</i> <sub>2</sub> = 0.1632	<i>R</i> <sub>1</sub> = 0.1047, <i>wR</i> <sub>2</sub> = 0.2776	<i>R</i> <sub>1</sub> = 0.0431, <i>wR</i> <sub>2</sub> = 0.1093

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

**Table S2** Crystallographic refinement parameters and results of [NiS<sub>4</sub>].

Compound	[NiS <sub>4</sub> ]
Chemical formula	C <sub>24</sub> H <sub>32</sub> N <sub>4</sub> NiO <sub>8</sub> S <sub>4</sub>
Formula weight	691.48
Crystal system	<i>orthorhombic</i>
Space group	<i>Fddd</i>
<i>a</i> /Å	9.5425 (4)
<i>b</i> /Å	26.9470(10)
<i>c</i> /Å	27.7314(11)
$\alpha$ /°	90
$\beta$ /°	90
$\gamma$ /°	90
<i>V</i> /Å <sup>3</sup>	7130.9(5)
<i>Z</i>	8
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.288
<i>F</i> (000)	2880.0
Reflections collected	12297
GOF	1.087
$R_1^a$ [ <i>I</i> >2σ( <i>I</i> )]	$R_1 = 0.0322, wR_2 = 0.0984$
$wR_2^b$ (all data)	$R_1 = 0.0357, wR_2 = 0.1010$

<sup>a</sup>  $R_1 = \sum(|F_o| - |F_c|) / \sum|F_o|$ ; <sup>b</sup>  $wR_2 = (\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2)^{1/2}$

**Table S3** Electrical conductivities of **M-dcbdt**.

Samples	Electrical conductivity (S cm <sup>-1</sup> )
<b>Ni-dcbdt</b>	$1.01 \times 10^{-6}$
<b>Co-dcbdt</b>	$2.22 \times 10^{-8}$
<b>Fe-dcbdt</b>	$1.1 \times 10^{-8}$

**References:**

- [1] G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112-122.
- [2] G. M. Sheldrick, *Acta Cryst.* **2015**, *C71*, 3-8.
- [3] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Cryst.* **2009**, *42*, 339-341.
- [4] Single crystal data were documented in CSD Communication as Experimental Crystal Structure Determination: **Ni-dcbdt** (DOI: 10.5517/ccdc.csd.cc2jy7zq); **Co-dcbdt** (DOI: 10.5517/ccdc.csd.cc2jy7yp); **Fe-dcbdt** (DOI: 10.5517/ccdc.csd.cc2jy7xn); **NiS<sub>4</sub>** molecule (DOI: 10.5517/ccdc.csd.cc2jy9qj)
- [5] H. Zhong, S. Chen, Z. Jiang, J. Hu, J. Dong, L.-H. Chung, Q.-C. Lin, W. Ou, L. Yu, J. He, *Small* **2023**, *19*, 2207266.