

Electronic Supplementary Information

Nanorods of a Novel Highly Conductive 2D Metal-Organic Framework Based on Perthiolated Coronene for Thermoelectric Conversion

Zhijun Chen^{a,b}, Yutao Cui^{a,b}, Yigang Jin^{a,b}, Liyao Liu^c, Jie Yan^{a,b}, Yang Sun^c, Ye Zou^{a,b}, Yimeng Sun^{a,b*}, Wei Xu^{a,b*}, and Daoben Zhu^{a,b}

a. Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China. wxu@iccas.ac.cn, sunyimeng@iccas.ac.cn.

b. University of Chinese Academy of Sciences, Beijing 100049, China

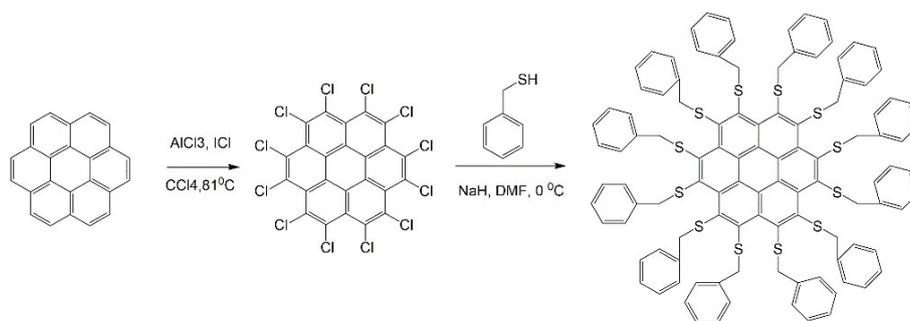
c. Institute of Chemistry Chinese Academy of Sciences Beijing 100190 (China)

General remarks

The protected PBTC is synthesized by literature method.¹ Alcohol, methanol, chlorobenzene and Ni(OAc)₂·4H₂O are purchased from Acros Organics. Boron tribromide and fluorobenzene are purchased from J&K. All the solvents are degassed with freeze-pump-thaw cycling before using.

Synthesis

Synthesis of 1,2,3,4,5,6,7,8,9,10,11,12-dodecakis(benzylthio)coronene (PBTC)

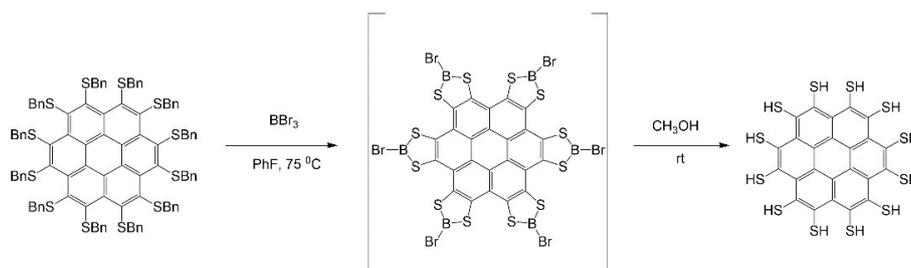


(1) 1.6 mmol (480.0 mg) of coronene, 3.2 mmol (426.0 mg) of AlCl₃, 192 mmol (15.0 g) of ICl and 40 mL of CCl₄ are put in a 100 mL flask, and then the reactants are stirred and refluxed at 81 °C for 48 h. After that, the products were poured into 50 mL methanol to quench the reaction and precipitate the products. The product as filtered was washed by methanol, hydrochloric acid (1 M), water and acetone respectively. After dried in vacuum at 60 °C overnight, 0.97 g (1.36 mmol) of 1,2,3,4,5,6,7,8,9,10,11,12-dodecakischlorocoronene (PCC) as yellow powder was obtained in a yield of 85%. HR-MS (HR-MALDI-TOF) m/z: Calcd. for C₂₄Cl₁₂: 713.6174; Found: 713.6200). Elem. Anal. calcd. for C₂₄Cl₁₂: C, 40.39; Cl, 59.61; Found: C, 40.41; Cl, 59.59.

(2) A 100 mL two-necked flask was charged with sodium hydride (120.0 mg, 5.0 mmol). Under an argon atmosphere, 10.0 mL of anhydrous DMF was injected with a syringe, and then the flask was cooled to 0 °C in an ice bath avoiding benzyl mercaptan (596.0 mg, 4.8 mmol) causing foam. After reaction mixture stirred for 30 min, PCC (143 mg, 0.2 mmol) was added and the reaction mixture was further stirred for 5 hours at 0 °C. Toluene (50 mL) and a saturated Na₂CO₃ solution (100 mL) were added, washed twice. The combined organic phases were

dried over MgSO₄ and filtered. After evaporation of the solvents, the crude product was purified by silica gel column chromatography (dichloromethane/hexane=1/1 as eluent). The last fraction was collected, and the solvent was evaporated and dried under vacuum to yield PBTC (318.0 mg) as a red amorphous air-sensitive solid in 90% yield. ¹H-NMR (300 MHz, Chloroform-d) δ 6.92 – 6.75 (m, 60H), 4.36 (s, 24H).; ¹³C-NMR (75 MHz, Chloroform-d) δ 139.65, 137.19, 132.09, 128.88, 128.09, 126.98, 122.15, 77.25, 43.93; MS (FD) m/z: 1766.8 [M]⁺; Elem. Anal. calcd. for C₁₀₈H₈₄S₁₂: C, 73.43; H, 4.79; S, 21.78; Found: C, 73.40; H, 4.77; S, 21.79

Synthesis of perthiolated coronene (PTC)



PBTC (176 mg, 0.1 mmol) is added into a 50 ml two-necked flask. Under an argon atmosphere, 10.0 mL of anhydrous fluorobenzene is injected with a syringe, and then the flask is cooled to 0 °C in an ice bath for 3 minutes, after which the reaction mixture is treated with pure BBr₃ (0.12 ml, 1.2 mmol) to induce dealkylation. The mixture is heated under reflux, and a light green precipitate after 30 minutes. After reaction for 12 h the precipitate is filtered, washed by n-hexane (3 × 30 ml) and cold fluorobenzene (2 × 20 ml).² The dithiaboroles intermediate is highly air-sensitive, because of the active B-Br bond. It is submitted to the next step without further analysis. After treated with 30 ml MeOH under an argon atmosphere, the dithiaboroles intermediate quickly turn into a red solid after stirring several minutes. Then the red powder products are filtered, washed with deoxygenated water and MeOH twice and dried in vacuum at 60 °C for 1 h. A pure air-sensitive solid (68 mg 0.1mmol, PTC) is obtained in almost quantitative yield. ¹H NMR (300 MHz, DMSO-d₆) δ 3.41 (s, 12H). ¹³C NMR (75 MHz, NaOD/Deuterium Oxide 15% w/w) δ 139.18 131.39, 116.05. Elem.Anal.calcd.for C₂₄H₁₂S₁₂: C, 42.08; H, 1.77; S, 56.16; Found: 42.25; H, 1.67; S, 56.32.

Synthesis of Ni-PTC nanorod

Ni-PTC nanorods are synthesized from the homogeneous reaction of PTC (68mg, 0.1mmol) with Ni(OAc)₂·4H₂O (75mg, 0.3mmol) in the mixture of deoxygenated chlorobenzene and ethanol (30 ml) under 80 °C for 36h. The product is collected as dark powder and washed by ethanol, water, ethyl ether and dry under vacuum at 60 °C overnight. The composition of Ni-PTC nanorods are analyzed by elements analysis (EA) and inductively coupled plasma optical emission spectrometer (ICP-oes).

Characterization Methods.

The content of C was analyzed by a Flash EA 1112 (Thermo Fisher Scientific), and the content of Ni, S was analyzed on electron probe microanalysis (EPMA; JXA-8100). The nickel content in PTC-Ni was analyzed by ICP-oes (iCAP 6300 Radial, Thermo Scientific). For ICP-oes measurements, the samples were prepared by dissolving them into fuming nitric acid. PXRD was performed on a PANalytical Empyrean II X-ray diffractometer. The measurements were employed on D/max 2500 with a Cu Kα source (λ = 1.5406 Å). Samples were observed using a 0.023° 2θ step scan from 5.0 to 50.0° with an exposure time of 30 seconds per step. Before PXRD testing, the samples should be well-grounded. SEM images were obtained using a Hitachi S4800-SEM with an acceleration voltage of 5 kV. For the pretreatment, the samples were transferred to conductive silicon substrates

and then covered with a platinum thin film with a thickness of several nanometers. TEM images were obtained by using a JOEL 2100F TEM with an accelerated voltage of 120 kV. Thermogravimetric analysis (TGA) was performed on a Shimadzu DTG 60 instrument under Ar atmosphere. XPS and UPS were performed by using AXIS Ultra-DLD ultrahigh vacuum photoemission spectroscopy system (Kratos Co.). A monochromatic magnesium Ka source (1253.8 eV) and a He I source (21.11 eV) were used for XPS and UPS, respectively. And Ni-PTC powder and a pressed pellet (thickness = ~ 0.1 mm) were used for XPS and UPS measurements, respectively. The IR spectrum of Ni-PTC was obtained at a TENSOR-27 spectrometer (Bruker). The materials were compressed into cuboid pellets (2 mm \times 5 mm \times 1 mm) under a pressure of 2 MPa to measure the electrical conductivity and Seebeck coefficient and into columned pellets ($\phi=17$ mm, $h=2$ mm) under a pressure of 25 MPa to measure the thermal conductivity. The Seebeck coefficient, electrical conductivity and thermal conductivity were measured by SB-100 Seebeck Measurement System (MMR Tech., USA), KEITHLEY 2002 Multimeter (Keithley Instrument Inc., USA) and TCI Thermal Conductivity Analyzer (C-THERM Tech., Canada). The temperature-dependent electrical conductivity was measured using four-contact probe method on the pressed pellets. The temperature of measurement environment for electrical and thermal conductivity was controlled by a CTI Cryogenics refrigerator. The electron spin-resonance (ESR) spectroscopy is obtained with JEOL JES-Fa200. The magnetic susceptibility measurements were performed in a commercial Quantum Design MPMS-XL5 SQUID magnetometer. NMR spectra were recorded at 30 MHz (Bruker). The chemical shifts were reported in parts per million (ppm) using the residual solvent signals as internal standards.

Theoretical simulation

Theoretical calculation was carried out by using the plane-wave technique as implemented in CASTEP code. An 800 eV cutoff energy was used for the plane-wave basis set, and norm conserving pseudopotentials were employed for all ions. The exchange correlation energy is described by the generalized gradient approximation (GGA) in the form of Perdew, Burke, and Ernzerhof (PBE). To eliminate the interlayer interaction, single-layer Ni-PTC is simulated by introducing a vacuum layer larger than 12 Å.

Supplementary Figures

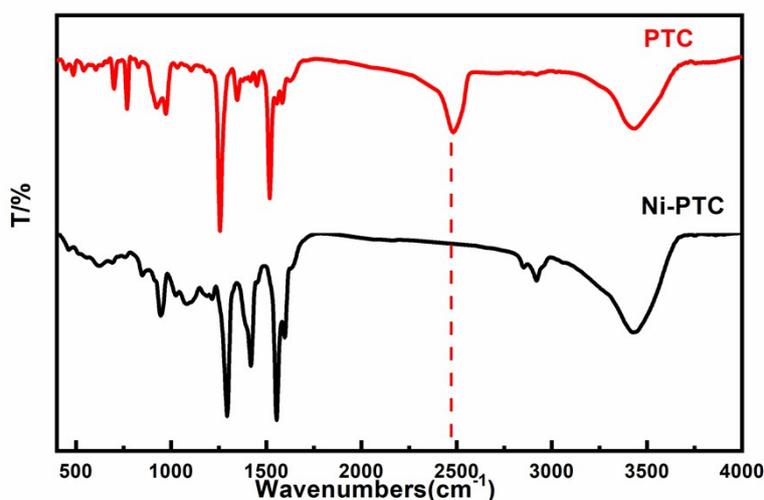


Fig. S1 FT-IR analysis of the Ni-PTC MOFs. The attenuated total reflection IR (ATR-IR) spectra of the Ni-PTC nanorods recorded on KBr pellets are compared with ligand PTC. The S-H signals at 2512 cm⁻¹ disappeared in the Ni-PTC, indicating that the thiol group in monomer PTC are efficiently coordinated to Ni ions.

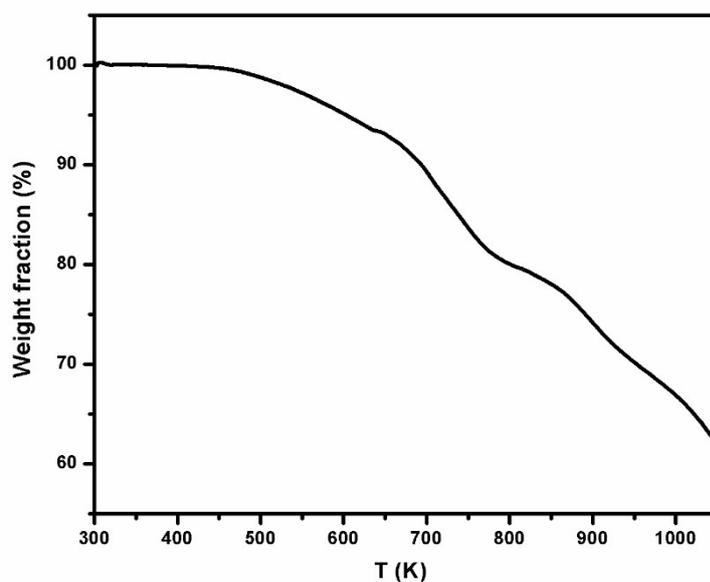


Fig. S2 TGA analysis of Ni-PTC. The MOFs begin weight loss at 460 K.

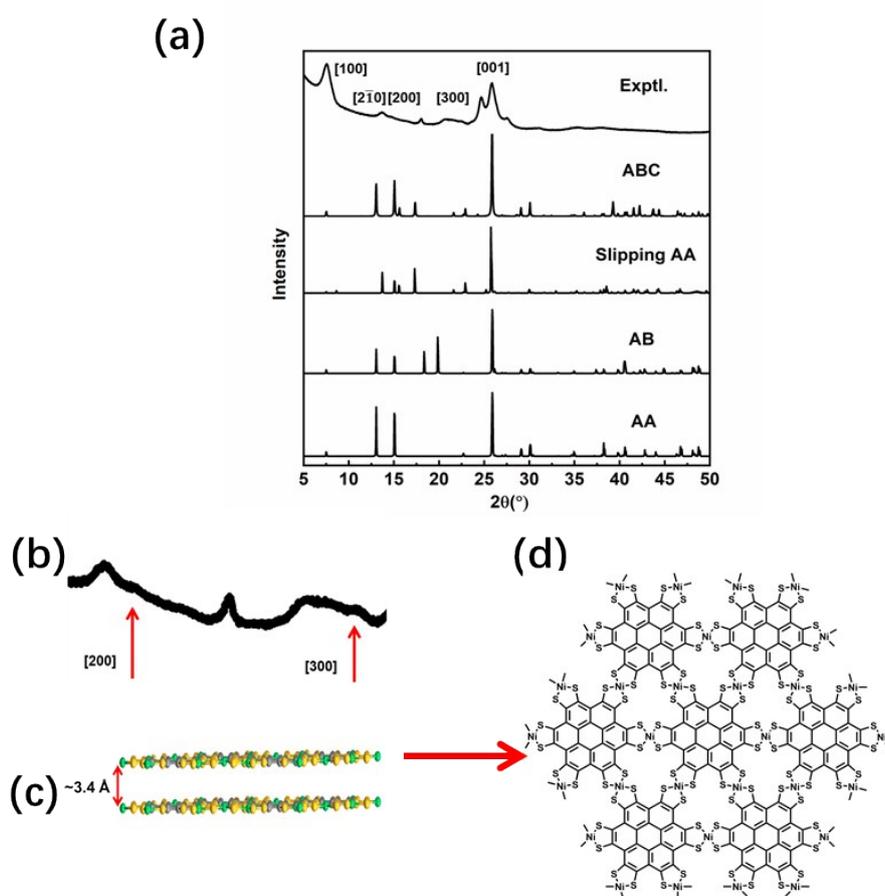


Fig. S3 Structure analysis of the Ni-PTC MOFs by powder XRD. (a) Experimental and simulated PXRD pattern. (b),

Enlarged experimental PXRD peak corresponding to (002) and (003) reflection. (c), The interlayer distance $\sim 3.4 \text{ \AA}$ from the PXRD. (d), The front schematic structure of Ni-PTC in monolayer.

Table S1. The lattice parameters of simulated stacking patterns.

Stacking Pattern	a(Å)	b(Å)	c(Å)	$\alpha(^{\circ})$	$\beta(^{\circ})$	$\gamma(^{\circ})$	Space group
AA	13.5701	13.5701	3.4400	90	90	120	P 1
AB	13.5701	23.5042	6.8800	90	90	90	Cmcm
Slipping AA	23.5042	13.5701	3.4600	90	84.2	90	C 2/m
ABC	23.5042	13.5701	10.3200	90	90	90	C 2/m

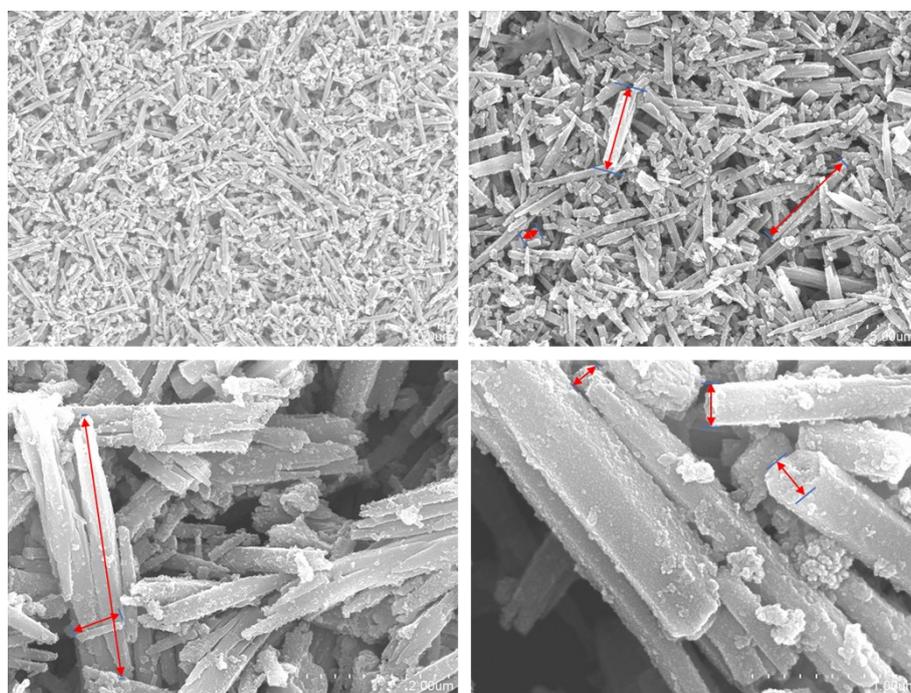


Fig. S4 Scanning electron microscopy image of Ni-PTC nanorods and a rough calculation the size.

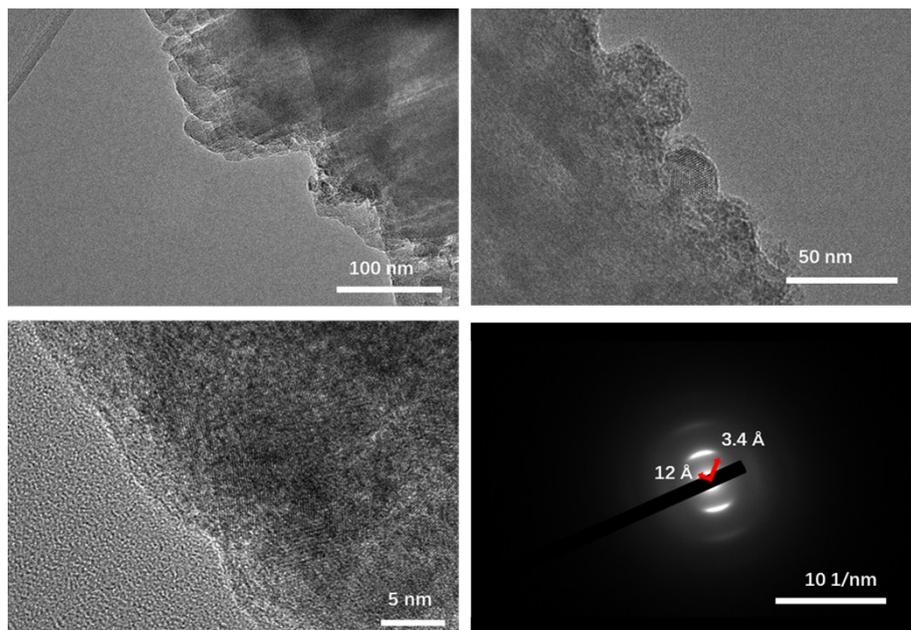


Fig. S5 Transmission electron microscopy image of Ni-PTC nanorods and Selected area electron diffraction pattern, calculating the diffraction ring corresponding to space.

Table S2. The dates of elements analysis (EA) and inductively coupled plasma optical emission spectrometer (ICP-oes)

Sample	Elemental analysis (EA)			ICP-oes
	C	H	N	Ni
Ni-PTC	33.70	<0.3	<0.3	20.29

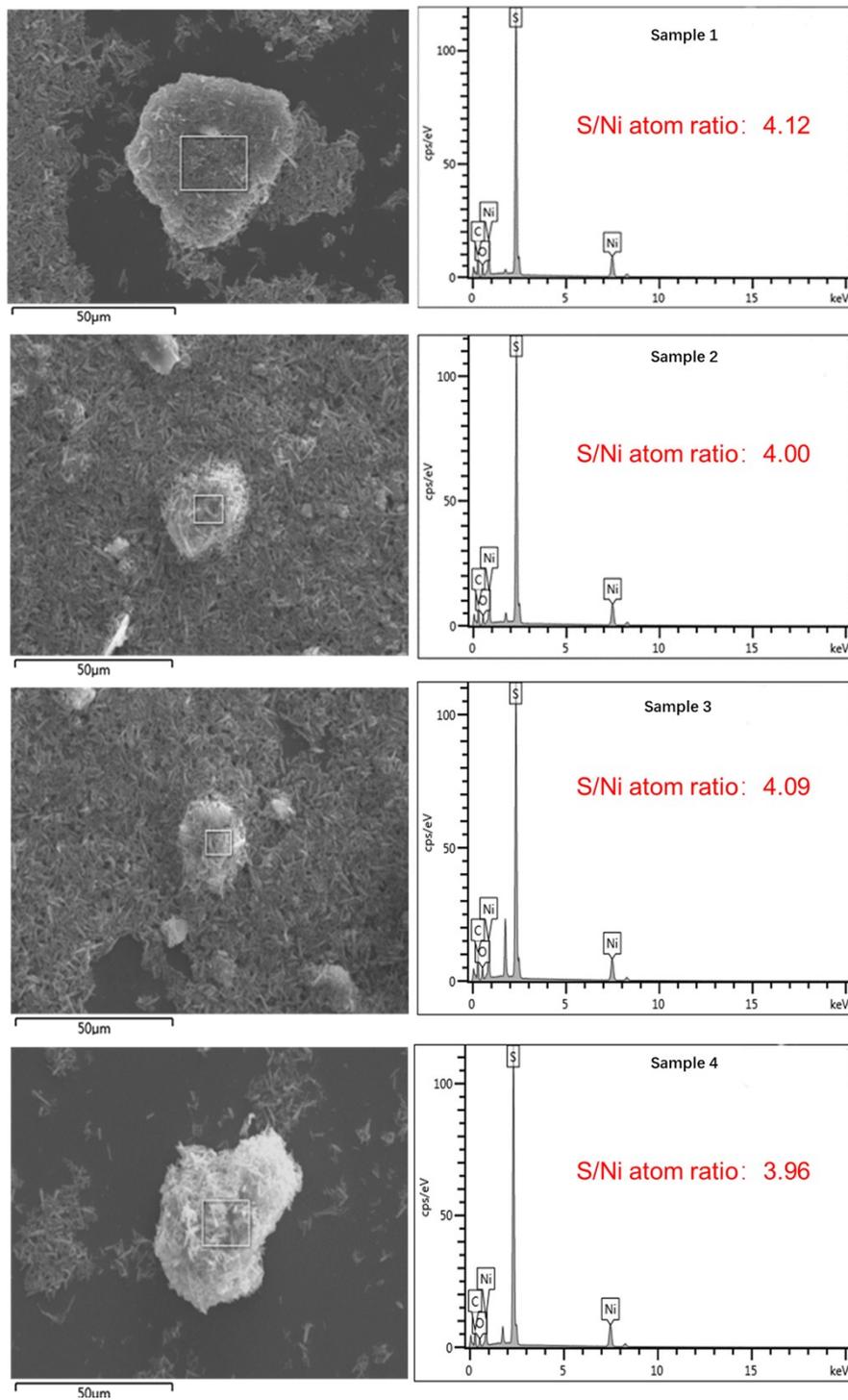


Fig. S6 EPMA Spectrum of (right) corresponding to each area of Ni-PTC sample in SEM image (left) and each sample S/Ni atom ratio.

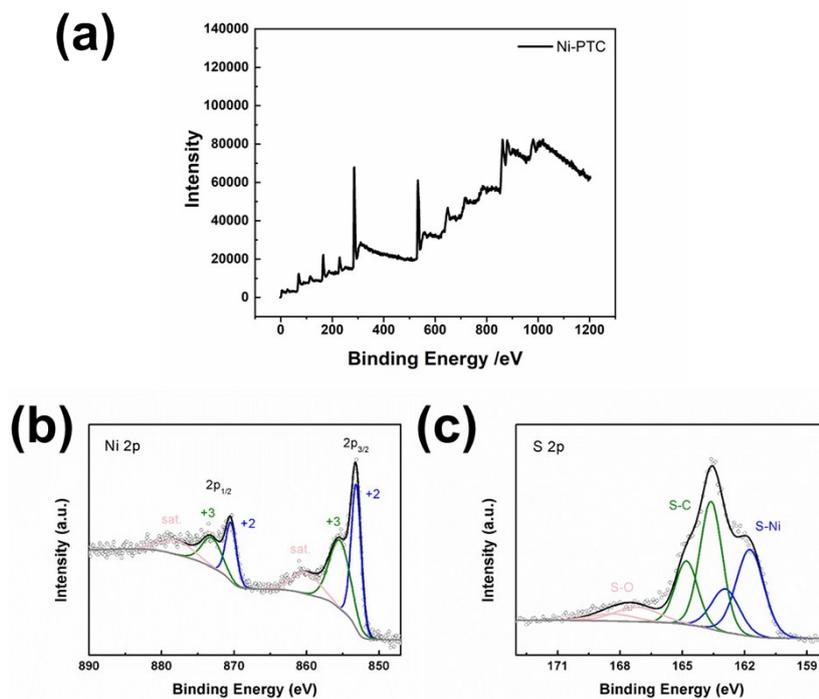


Fig. S7 XPS analysis of Ni-PTC 2D MOFs (a) XPS full spectrum of Ni-PTC detect C, S, and Ni resonance peaks. (b) In the Ni 2p region with $\text{Ni}^{2+}/\text{Ni}^{3+} \sim 1:1$, prominent Ni^{2+} $2p_{3/2}$ (binding energies 852.0 eV) and $2p_{1/2}$ (binding energies 870.1 eV) coexist with Ni^{3+} $2p_{3/2}$ (binding energies 855.7 eV) and $2p_{1/2}$ (binding energies 873.3 eV), accompanying by the obvious shake-up satellite peak. (c) The high-intensity dual peaks at 163.4 eV and 164.8 eV indeed corresponding to the -C-S- units. The major peak at 161.8 eV derive from the -Ni-S- bond, besides the weak peaks at 167.3 eV indicating the -S-O- bond.

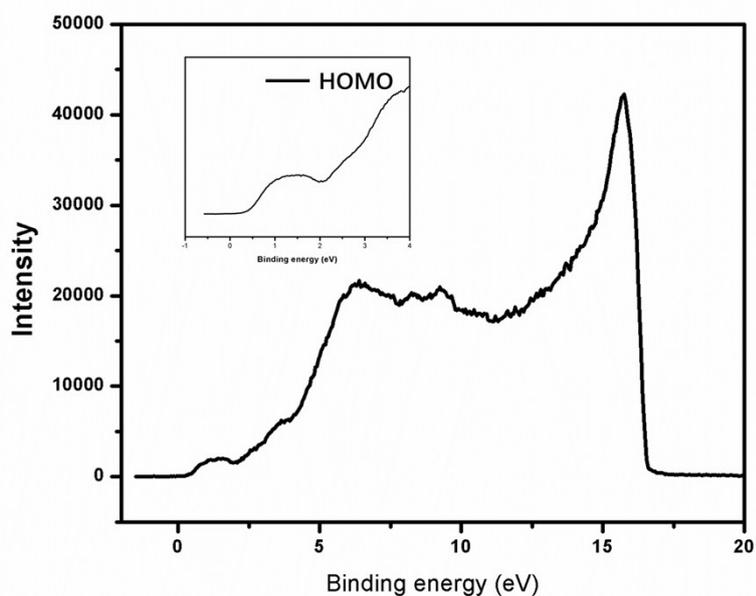


Fig. S8 The ultraviolet photoelectron spectroscopy (UPS) of Ni-PTC MOFs at 300 K and the inset is detailed UPS of the Fermi edge

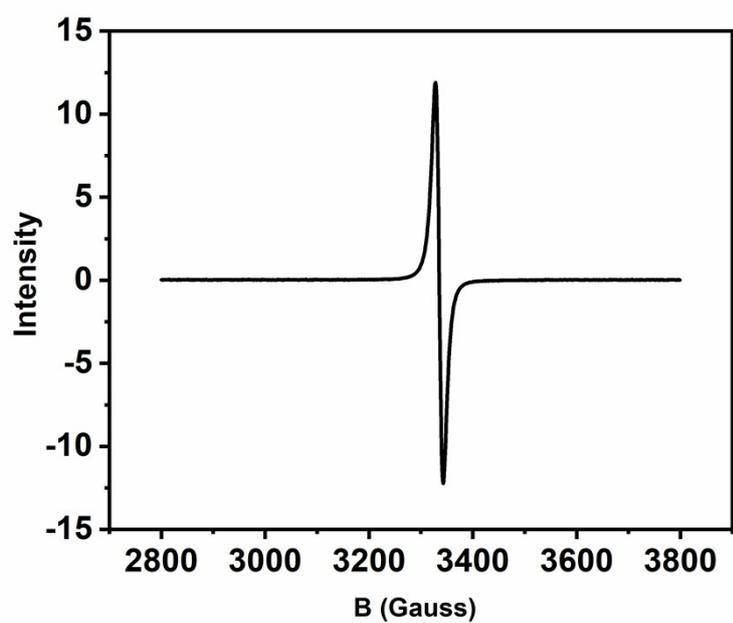


Fig. S9 ESR spectra of Ni-PTC at 10 K.³

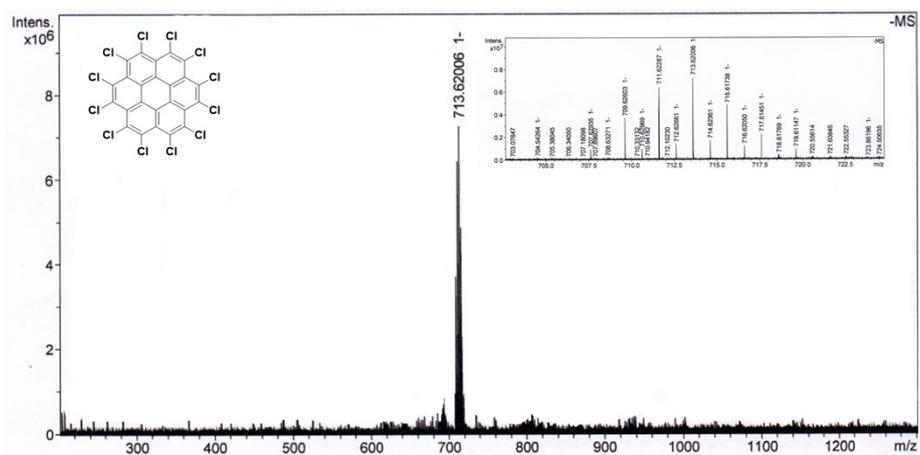


Fig. S10 HR-MS (HR-MALDI-TOF) spectrum of PCC

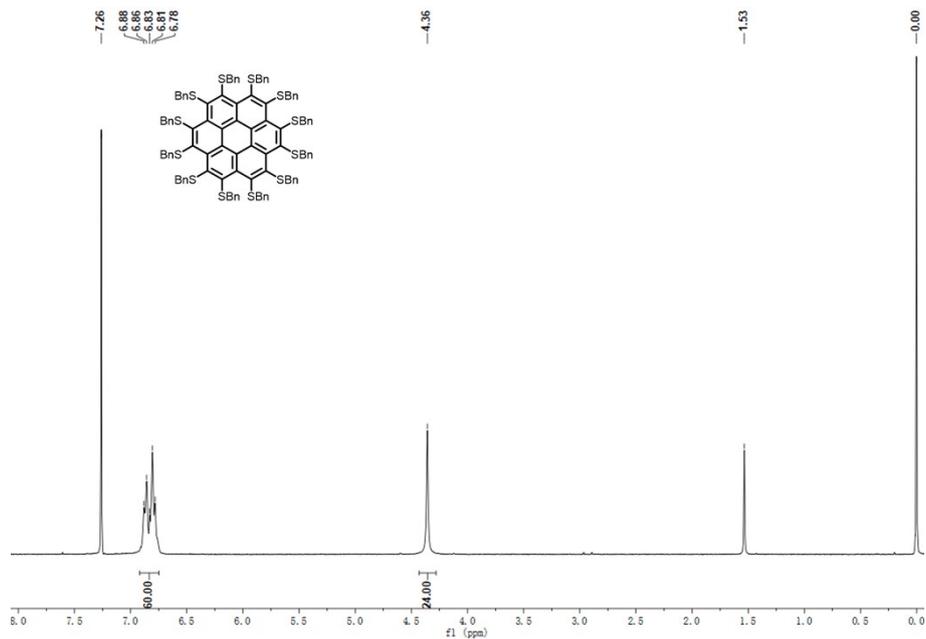


Fig. S11 ^1H -NMR (300 MHz, Chloroform-d) spectrum of PBTC

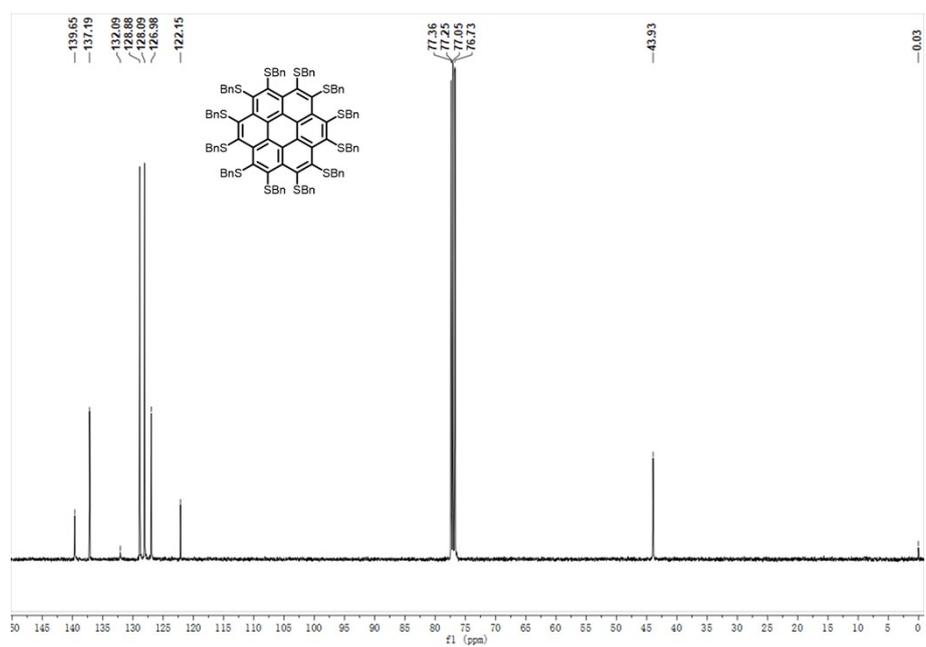


Fig. S12 ^{13}C -NMR (75 MHz, Chloroform-d) spectrum of PBTC

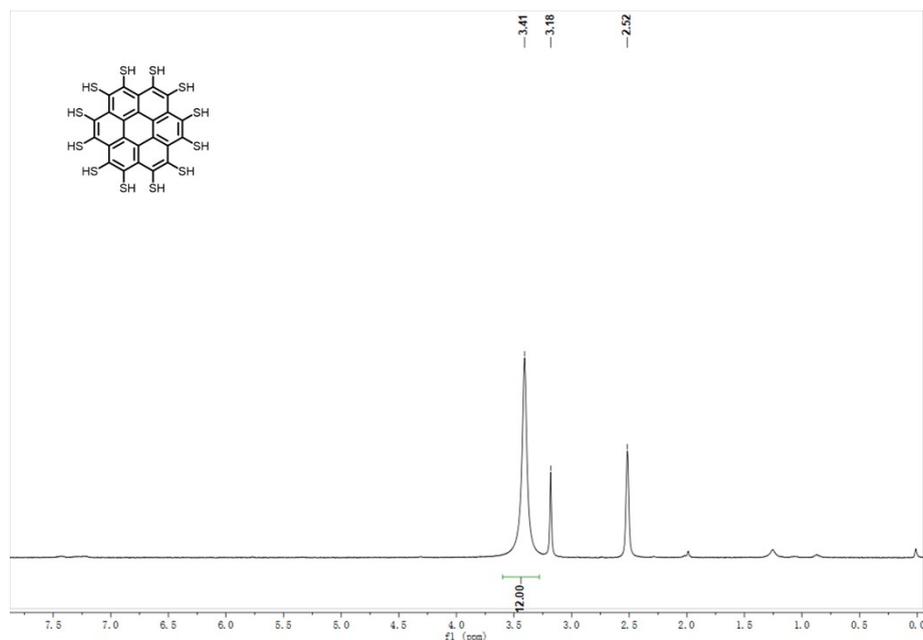


Fig. S13 ^1H NMR (300 MHz, DMSO- d_6) spectrum of PTC, a small amount of PTC is heating dissolved in deuterated DMSO under the argon atmosphere glove box, which disappeared upon further addition of D_2O , indicating the lively S-H.

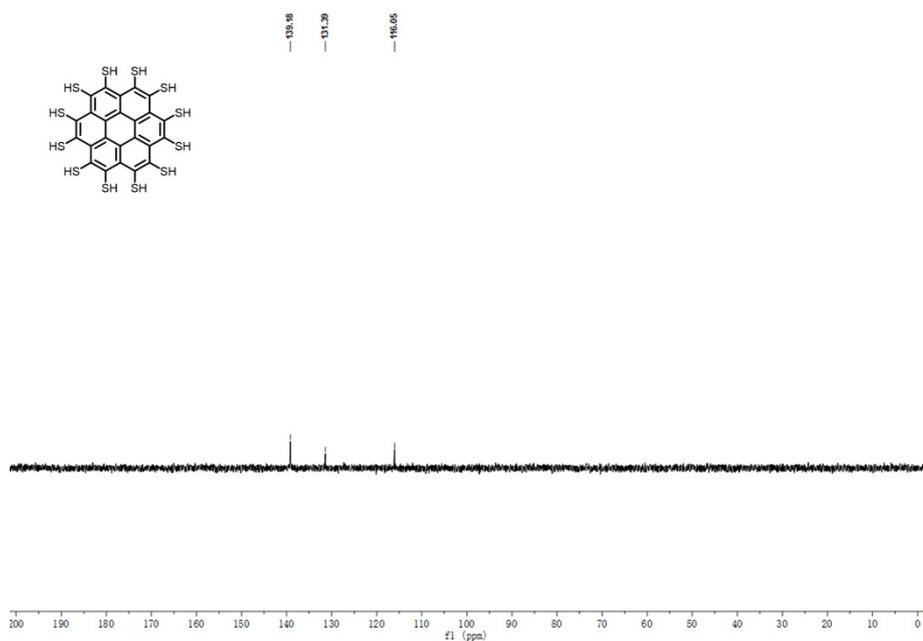


Fig. S14 ^{13}C NMR (75 MHz, NaOD/Deuterium Oxide 15% w/w). the PTC in DMSO- d_6 cannot afford ^{13}C NMR because of poor solubility and long-time instability.

Supplementary reference

1. R. Dong, M. Pfeffermann, D. Skidin, F. Wang, Y. Fu, A. Narita, M. Tommasini, F. Moresco, G. Cuniberti, R. Berger, K. Mullen and X. Feng, *J Am Chem Soc*, 2017, 139, 2168-2171.
2. S. H. Schlindwein, K. Bader, C. Sibold, W. Frey, P. Neugebauer, M. Orlita, J. Slageren and D. Gudat, *Inorg Chem*, 2016, 55, 6186-6194.
3. P. Ravat, O. Blacque and M. Juricek, *J Org Chem*, 2019, DOI: 10.1021/acs.joc.9b02163.