Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Electronic Supplementary Information

Open Metal Sites Dangled on Cobalt Trigonal Prismatic Clusters within Porous MOF for CO_2 Capture

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Synthesis of 1

A mixture of H_8tdcppy (8.0 mg), $Co(NO_3)_2\cdot 6H_2O$ (15.0 mg), 3 drop of tetrafluoroboric acid (48 wt. % in H_2O), 3.2 mL dimethylformamide (DMF), 0.8 mL methanol (MeOH) and 0.8 mL water (H_2O) was put in a 7 mL scintillation vial and heated to 120 ^{o}C for 36 hours. The resulting purple block-shaped crystals were obtained (~15.0 mg). IR (cm^{-1}):1582(s); 1415(m); 1358(vs); 1019(w); 781(m); 711(vs).

General methods

Commercially available reagents were purchased as high purity from Fisher Scientific and used without further purification. 1,3,6,8-tetra(3,5-dicarboxyphenyl)pyrene (H_8tdcppy) was synthesized using the similar procedures as reported.[1] Thermogravimetric analysis (TGA) was performed under nitrogen on a TA Instrument TGA 2950 Hi-Res from 25^{o}C to 700 ^{o}C at the speed of 10 ^{o}C/min. Gas adsorption isotherms of **1** were collected using the surface area analyzer ASAP-2020. Before the measurements, the freshly prepared samples were exchanged with HPLC-grade methanol for 3 days, and then activated with the "degas" port under the vacuum at 65 ^{o}C overnight. CO_2 gas adsorption isotherms were collected at 273K using a water-ice bath and at 298K with a water bath. The N_2 adsorption isotherm was measured at 77K using a liquid nitrogen bath.

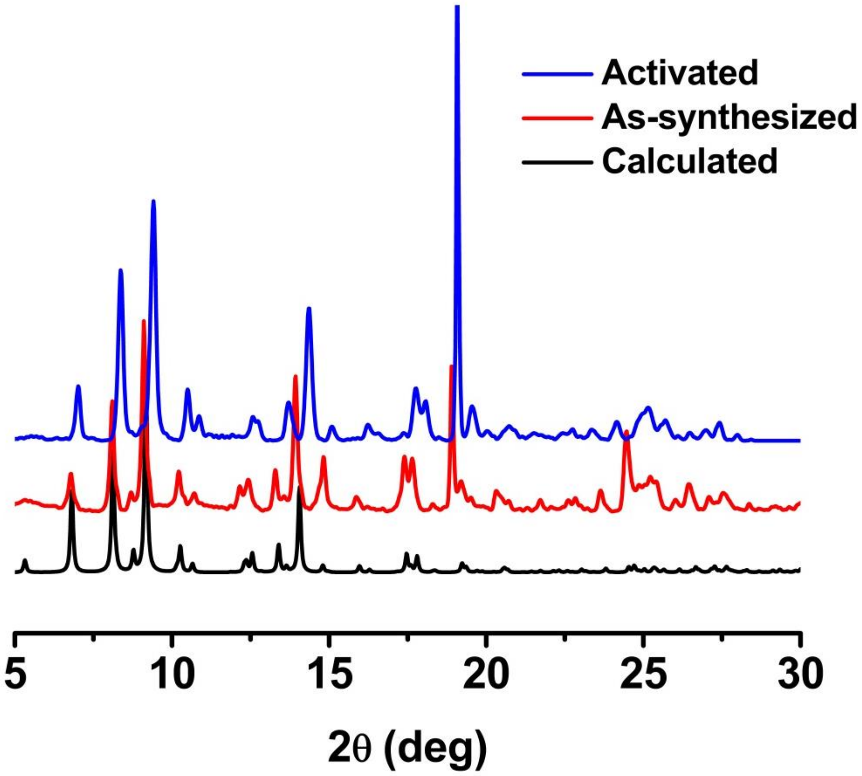


Fig. S1 Powder X-ray diffraction patterns of **1**.

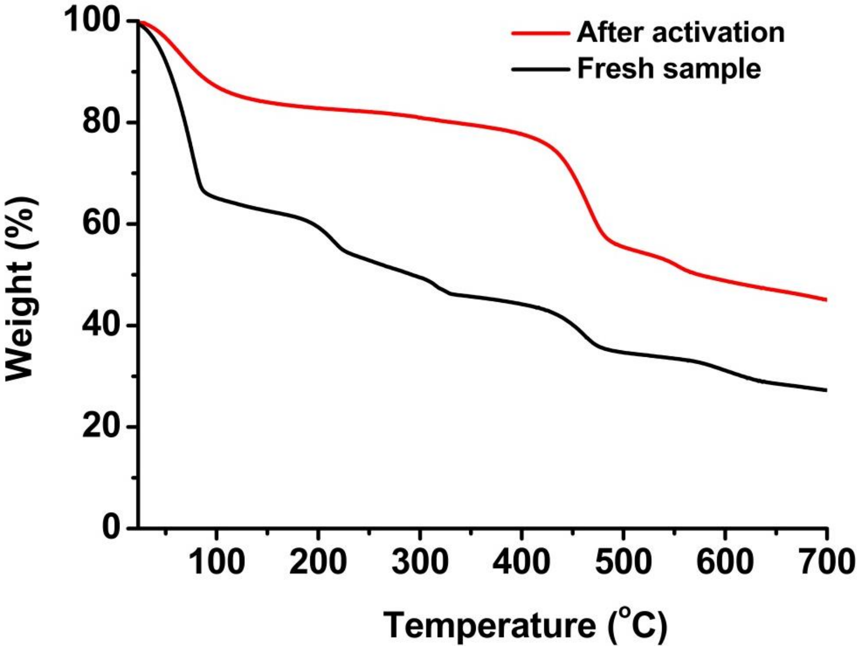


Fig. S2 TGA plots of the fresh and activated samples of **1**.

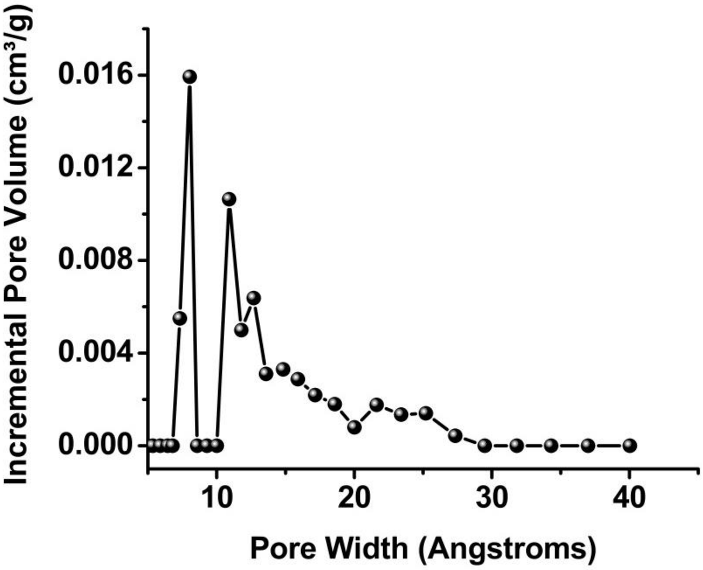


Fig. S3 Density functional theory (DFT) pore size distribution analysis based on the N_2 adsorption data of **1** at 77 K.

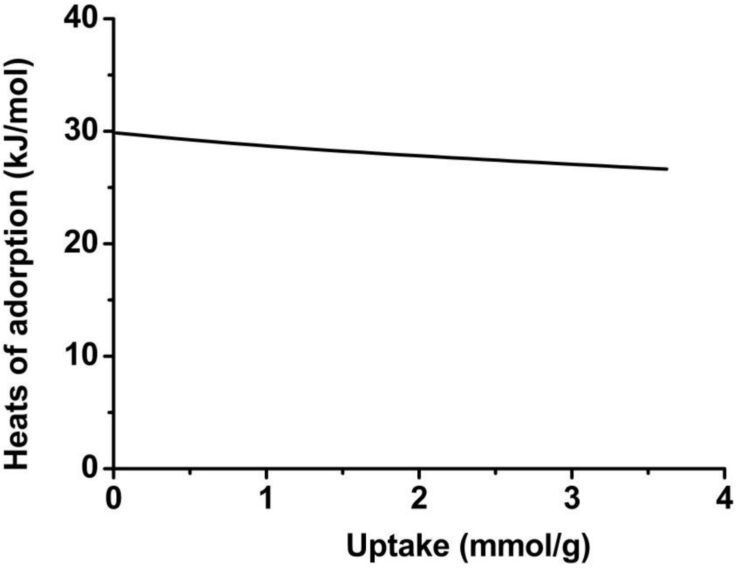


Fig. S4 Heats of adsorption of CO_2 of **1** using the virial method.

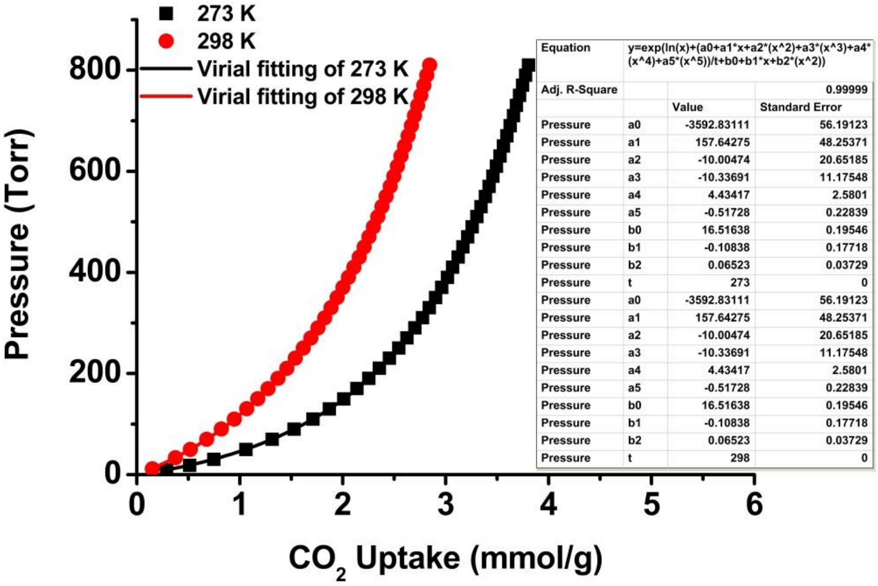
Calculations of Heats of Adsorption (Q_{st})

The virial equation of the form given in Equation (1) was employed to calculate the enthalpies of adsorption for CO_2 on **1**.

$$\ln P = \ln \mathrm{N} + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad (1)$$

where P is the pressure expressed in Torr, N is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_i are virial coefficients, and m and n represent the number of coefficients required to adequately describe the isotherms. The equation was fitted by using the the least-squares method; m and n were gradually increased until the contribution of a and b coefficients toward the overall fitting is statistically trivial, as determined by the t-test. The values of the virial coefficients $a_0 \ldots a_m$ were then used to calculate the isosteric heat of adsorption by the following expression:

$$\mathrm{Q}_{st} = -R \sum_{i=0}^{m} a_i N^i \qquad (2)$$



Equation	y=exp(ln(x)+(a0+a1*x+a2*(x^2)+a3*(x^3)+a4*(x^4)+a5*(x^5))/t+b0+b1*x+b2*(x^2))		
Adj. R-Square			0.99999
		Value	Standard Error
Pressure	a0	-3592.83111	56.19123
Pressure	a1	157.64275	48.25371
Pressure	a2	-10.00474	20.65185
Pressure	a3	-10.33691	11.17548
Pressure	a4	4.43417	2.5801
Pressure	a5	-0.51728	0.22839
Pressure	b0	16.51638	0.19546
Pressure	b1	-0.10838	0.17718
Pressure	b2	0.06523	0.03729
Pressure	t	273	0
Pressure	a0	-3592.83111	56.19123
Pressure	a1	157.64275	48.25371
Pressure	a2	-10.00474	20.65185
Pressure	a3	-10.33691	11.17548
Pressure	a4	4.43417	2.5801
Pressure	a5	-0.51728	0.22839
Pressure	b0	16.51638	0.19546
Pressure	b1	-0.10838	0.17718
Pressure	b2	0.06523	0.03729
Pressure	t	298	0

Fig. S5 The plots of virial equation of **1**.

Single-Crystal X-ray Diffraction for 1

The X-ray diffraction data for **1** were measured using synchrotron radiation (λ=0.41328Å) at Advanced Photon Source in Argonne National Laboratory (Beamline 15-ID-B,C,D). Indexing was performed using *APEX2*[2] (Difference Vectors method). Data integration and reduction were performed using SaintPlus 6.01.[3] Absorption correction was performed by multi-scan method implemented in SADABS.[4] Space groups were determined using XPREP implemented in APEX2.[2] The structure was solved using SHELXS-97 (direct methods) and refined using SHELXL-2013 (full-matrix least-squares on F^2) contained in WinGX[5,6,7,8] and OLEX2 programs.[9]

All framework non-hydrogen atoms were refined anisotropically. Partially occupied, disordered DMF and methanol molecules have been refined using restraints and in most of the cases with isotropic approximation. The occupancy of disordered Co has been restraints to be 1 as suggested by initial free refinement. All hydrogen atoms were placed in geometrically calculated positions and included in the refinement process using riding model with isotropic thermal parameters: Uiso(H) = 1.2Ueq(-CH) Crystal data and refinement conditions are shown in Table S1.

Table S1. Crystal data and structure refinement for 1.

Identification code	Co_Pyrene_1
Empirical formula	$C_{56.15}H_{18}Co_4N_{2.65}O_{24.68}$
Formula weight	1360.22
Temperature/K	100(2)
Crystal system	orthorhombic
Space group	*Pnma*
a/Å	33.152(2)
b/Å	14.4302(10)
c/Å	14.0799(10)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	6735.6(8)
Z	4
ρ_{calc}g/cm^3	1.341

μ/mm^{-1}	0.208
F(000)	2716.0
Crystal size/mm^3	0.03 × 0.03 × 0.02
Radiation	Synchrotron (λ = 0.41328)
2Θ range for data collection/°	2.724 to 28.482
Index ranges	$-39 \le h \le 39$, $-17 \le k \le 16$, $-16 \le l \le 16$
Reflections collected	108920
Independent reflections	6143 [R_{int} = 0.1844, R_{sigma} = 0.0628]
Data/restraints/parameters	6143/56/514
Goodness-of-fit on F^2	1.070
Final R indexes [I>=2σ (I)]	R_1 = 0.0705, wR_2 = 0.1955
Final R indexes [all data]	R_1 = 0.1009, wR_2 = 0.2175
Largest diff. peak/hole / e Å^{-3}	0.91/-0.81

Fluorescence Analysis

A sample of H_8tdcppy was dissolved in ethanol. Crystals of **1** were removed from the mother liquor, washed repeatedly with ethanol and sonicated in ethanol. UV/Vis absorption spectra were collected on a Shimadzu UV-2401PC spectrophotometer. Steady state emission measurements were performed using an ISS PC1 single-photon counting spectrofluorometer. The optical density (OD) of both samples was 0.60 at the emission excitation wavelength of 375nm

The solution of H_8tdcppy in ethanol has an absorption maximum at 379 nm and emission maximum at 422 nm (Fig. S6, left). The H_8tdcppy was luminescent with a 375 nm excitation. When H_8tdcppy incorporated in **1**, emission was quenched by the open-shelled Co ions (Fig. S6, right).

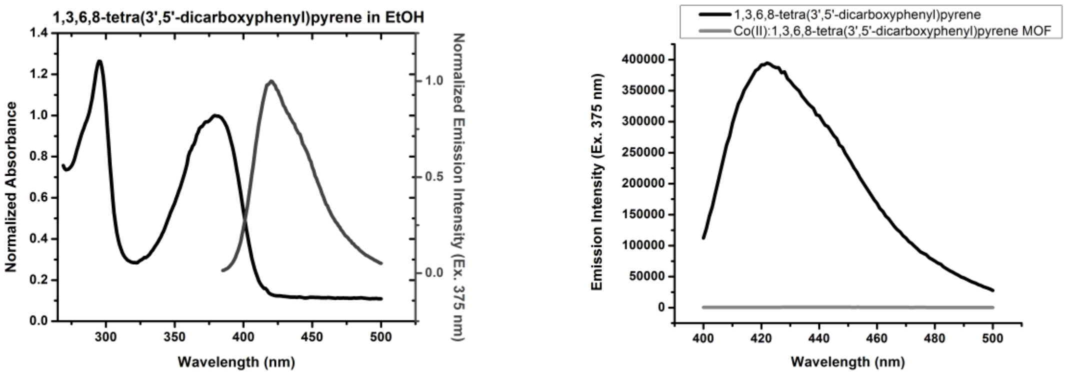


Fig. S6 Normalized absorption and emission spectra of H_8tdcppy in ethanol (left); Emission spectra of H_8tdcppy and **1** in ethanol (Excitation wavelength 375 nm).

References.

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