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Pore modulation of metal–organic frameworks towards enhanced hydrothermal stability and acetylene uptake *via* incorporating different functional brackets

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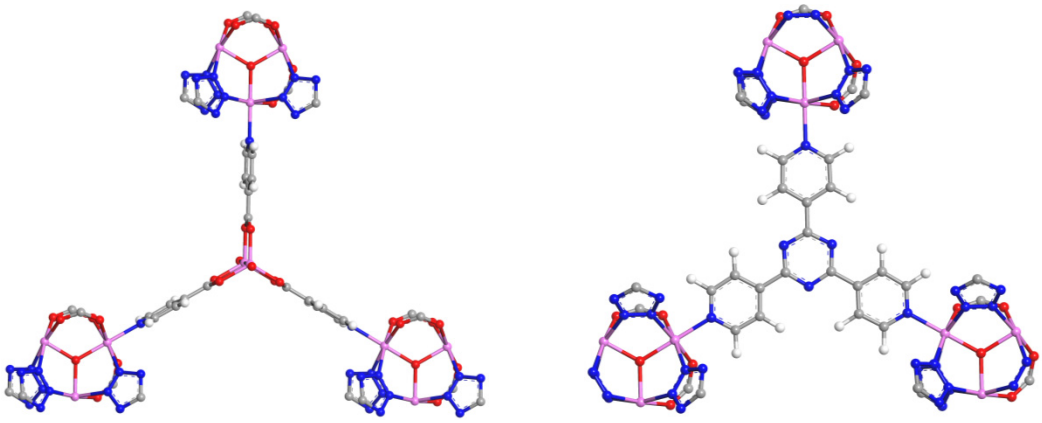

Fig. S1 View of the three-connected bracket in (left) **1** and (right) **2**.

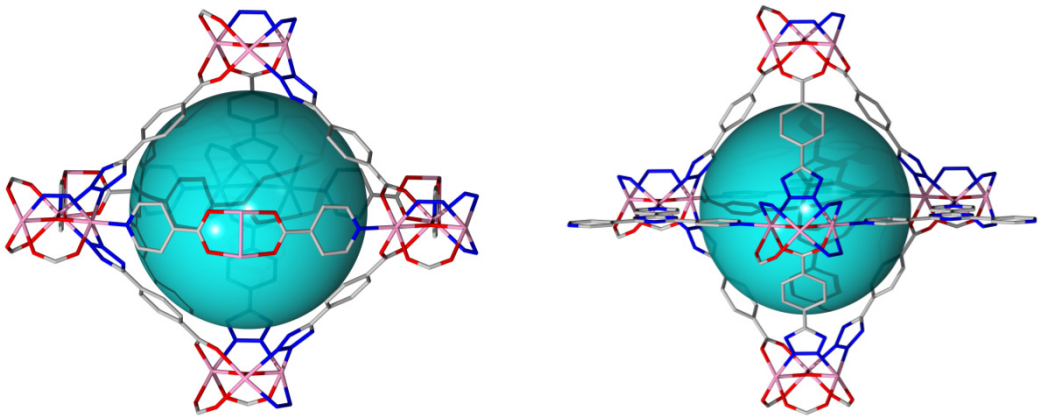

Fig. S2 View of the trigonal bipyrimidal nanocage in (left) **1** and (right) **2**.

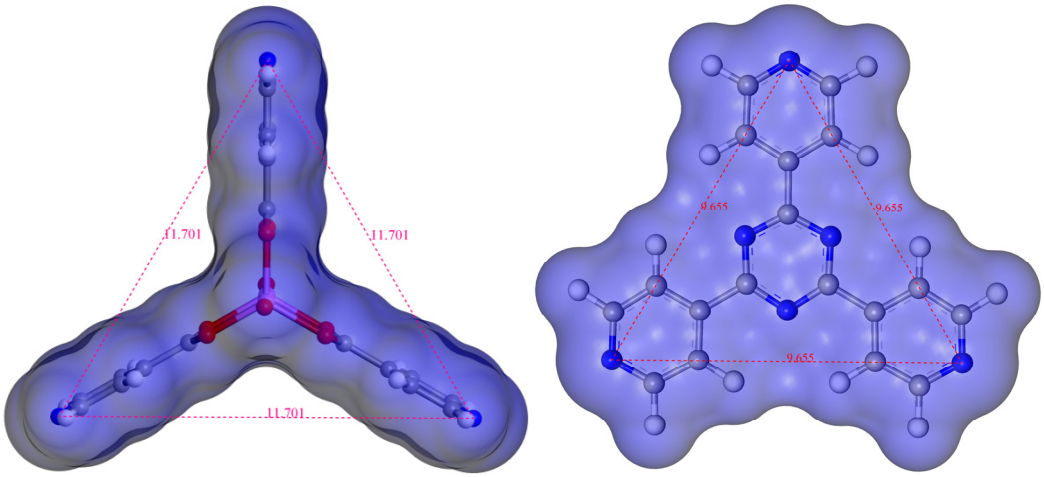

Fig. S3 Connolly surface for (left) $[Co_2(ina)_3(H_2O)_2]^+$ and (right) tpt brackets.

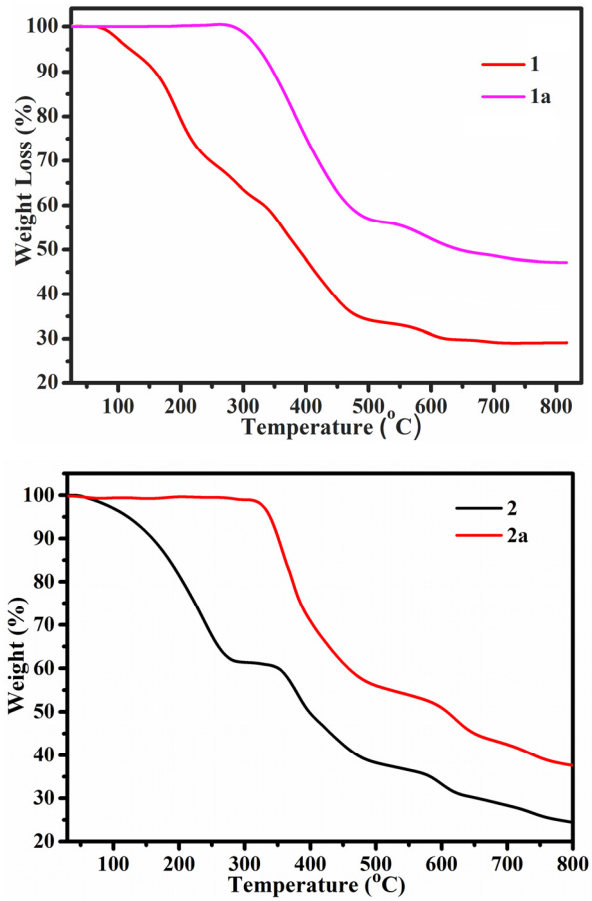

Fig. S4 TGA curves for **1**, **1a**, **2** and **2a**.

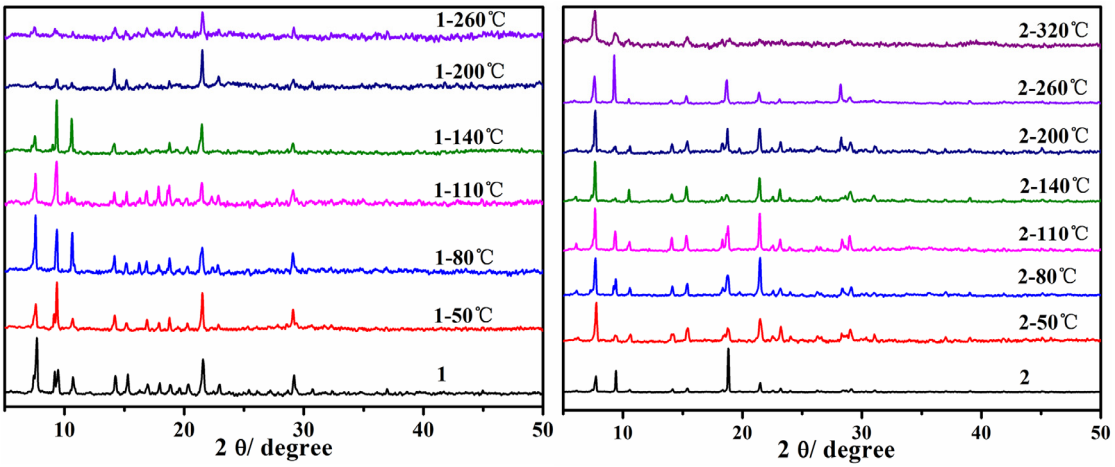

Fig. S5 VT-PXRD patterns for (left) **1** and (right) **2**.

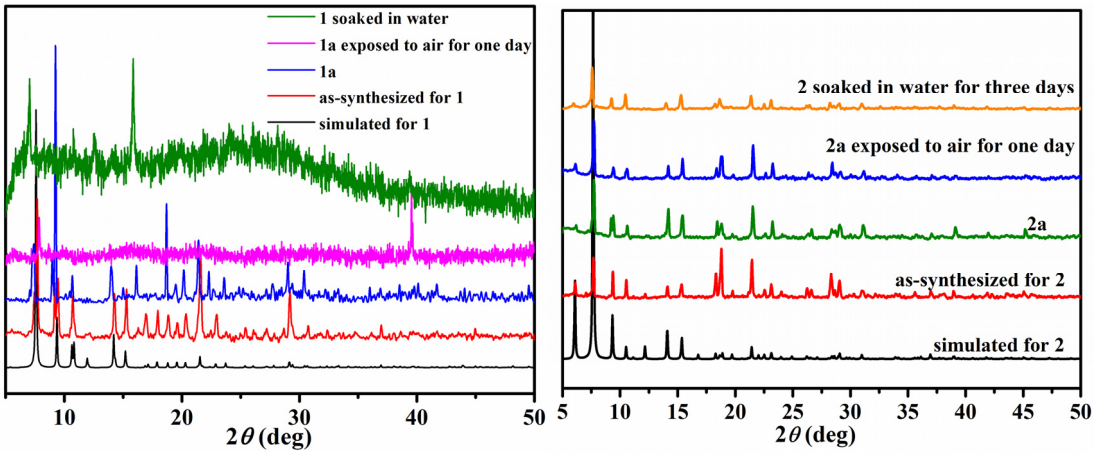

Fig. S6 PXRD patterns for (left) **1** and (right) **2** under different conditions.

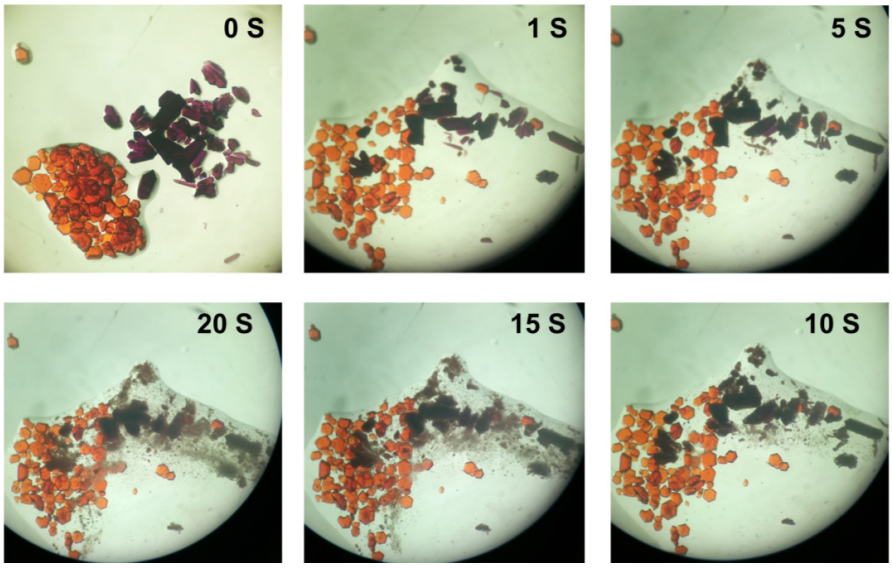

Fig. S7 The time-dependent photographs for **1** (purple crystals) and **2** (orange crystals) soaked in water.

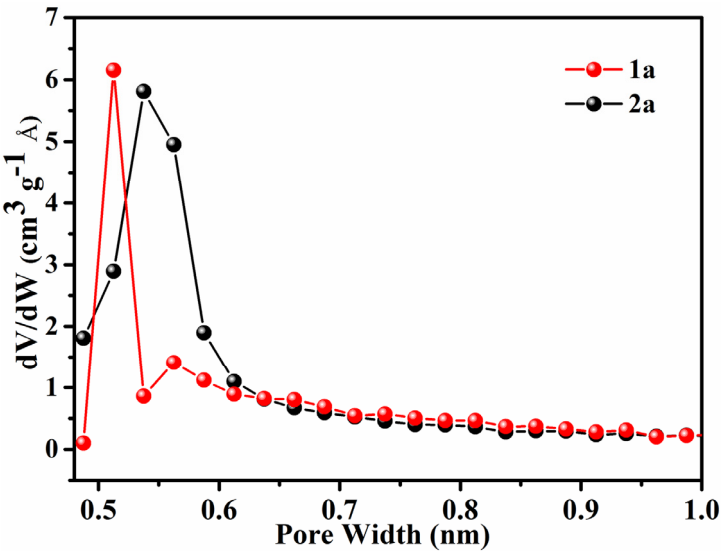

Fig. S8 Pore size distribution of **1a** and **2a** derived from N_2 sorption at 77 K using Horvath-Kawazoe method.

Calculation of sorption heat for CO_2 and C_2H_2 uptake using virial fitting

$$\ln P = \ln N + 1/T \sum_{i=0}^{m} a_i N^i + \sum_{i=0}^{n} b_i N^i \qquad Q_{st} = -R \sum_{i=0}^{m} a_i N^i$$

The above virial expression was used to fit the combined isotherm data for **1a** and **2a** at 273 and 298 K, where P is pressure, N is adsorbed amount, T is temperature, a_i and b_i are virial coefficients, and m and N are number of coefficients used to describe the isotherms. Q_{st} is the coverage-dependent enthalpy of adsorption and R is the universal gas constant.

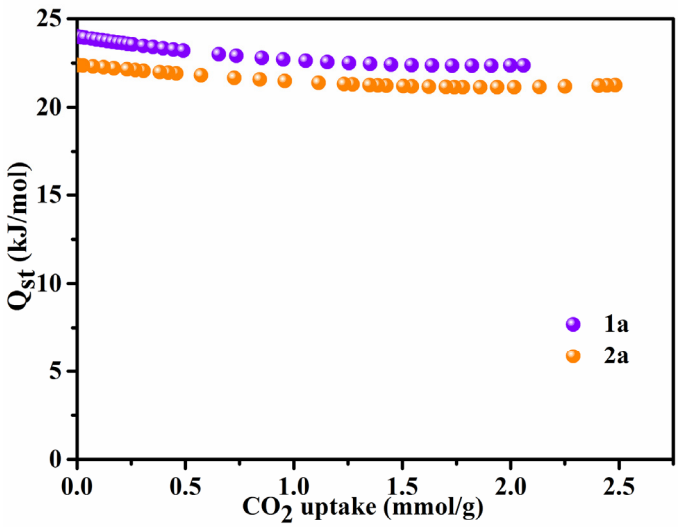

Fig. S9 CO_2 sorption heats for **1a** and **2a**.

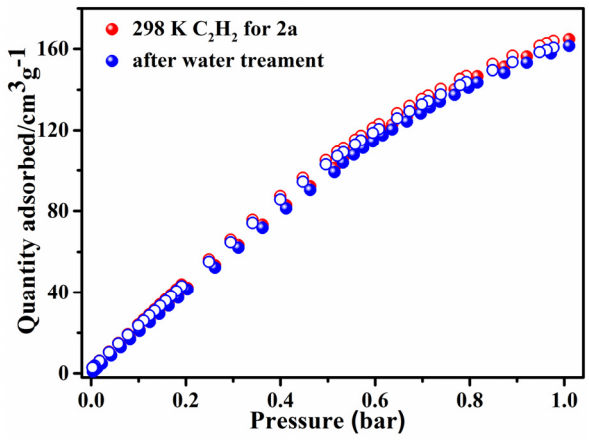

Fig. S10 C_2H_2 sorption isotherms for **2a** before and after water treatment.

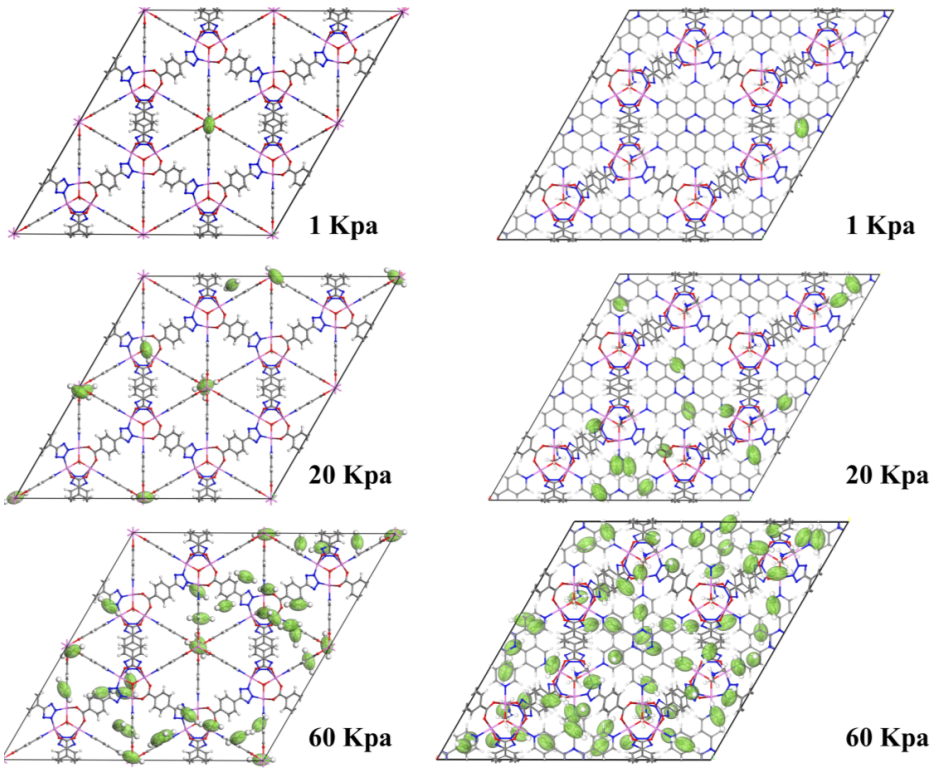

Fig. S11 Snapshots of CO_2 adsorption from GCMC simulations at various pressures

for (left) **1a** and (right) **2a**.

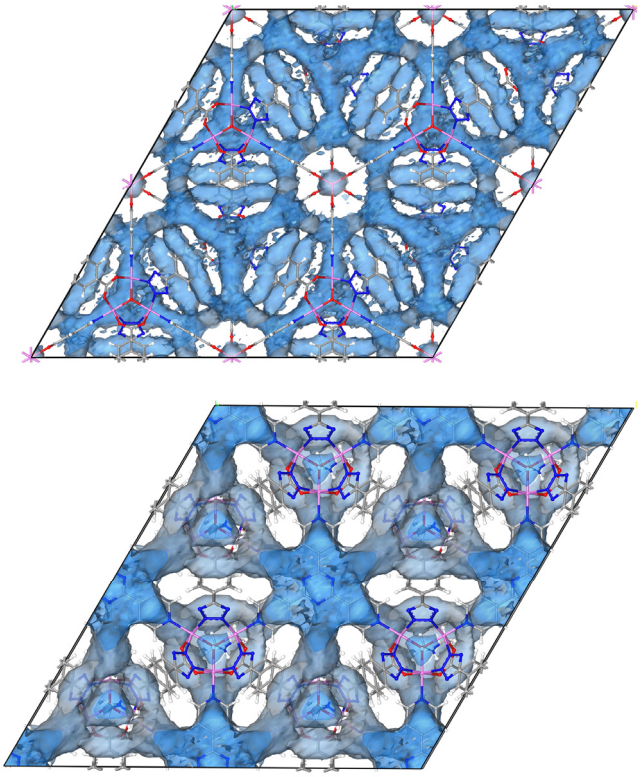

Fig. S12 Probability distribution of the C_2H_2 center of mass in (up) **1a** and (down) **2a** obtained from GCMC simulation at 298 K and 1 bar. The blue regions represent the places where C_2H_2 molecules are populated in the framework.

Table S1. Crystal data and structural refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_{42}H_{24}Co_5N_{15}O_{15}$	$C_{44}H_{32}Co_3N_{19}O_7$
Formula weight	1273.41	1115.67
Temperature/K	293(2)	293(2)
Crystal system	hexagonal	hexagonal
Space group	$P6_3/mmc$	$P6_3/mmc$
a / Å	18.8605(4)	16.7919(10)
b / Å	18.8605(4)	16.7919(10)
c / Å	16.6183(4)	18.9208(13)
α / °	90	90
β / °	90	90
γ / °	120	120
Volume / Å^3	5119.5(3)	4620.3(7)
Z	2	2
ρ_{calc} / g cm^{-3}	0.826	0.802
μ / mm^{-1}	6.561	4.484
Goodness-of-fit on F^2	1.106	1.157
Final R indexes [$I >= 2\sigma(I)$]	$R_1 = 0.0968$, w$R_2 = 0.2788$	$R_1 = 0.0518$, w$R_2 = 0.1636$
Final R indexes [all data]	$R_1 = 0.0987$, w$R_2 = 0.2881$	$R_1 = 0.0532$, w$R_2 = 0.1651$