Supplemental Information

Molecular engineering in a family of pillared-layered metal-organic frameworks for tuning gas adsorption behavior

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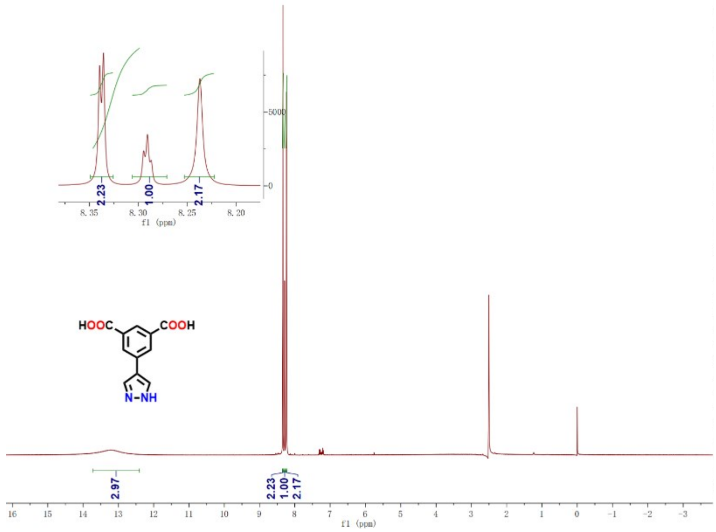


Fig. S1 NMR spectrum of H_3L.

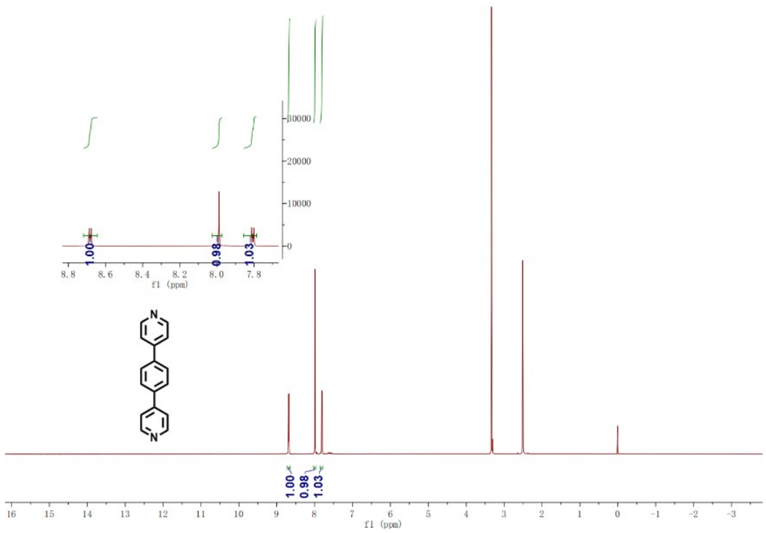


Fig. S2 NMR spectrum of dpb.

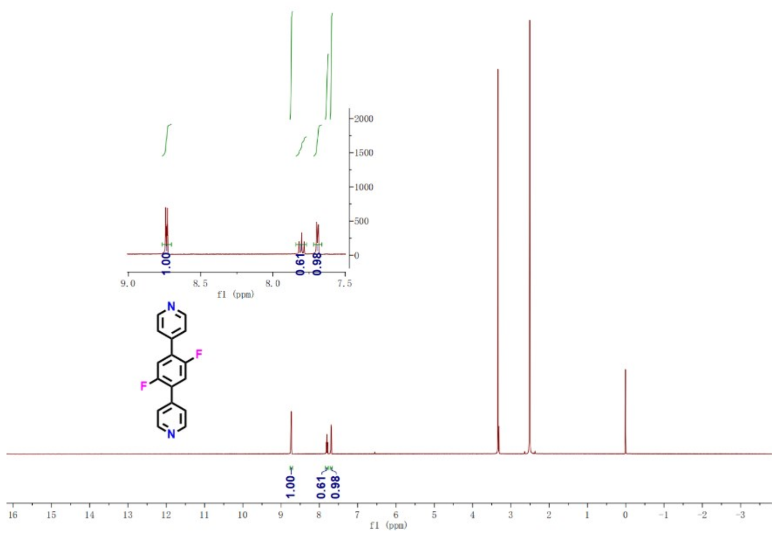


Fig. S3 NMR spectrum of dpd.

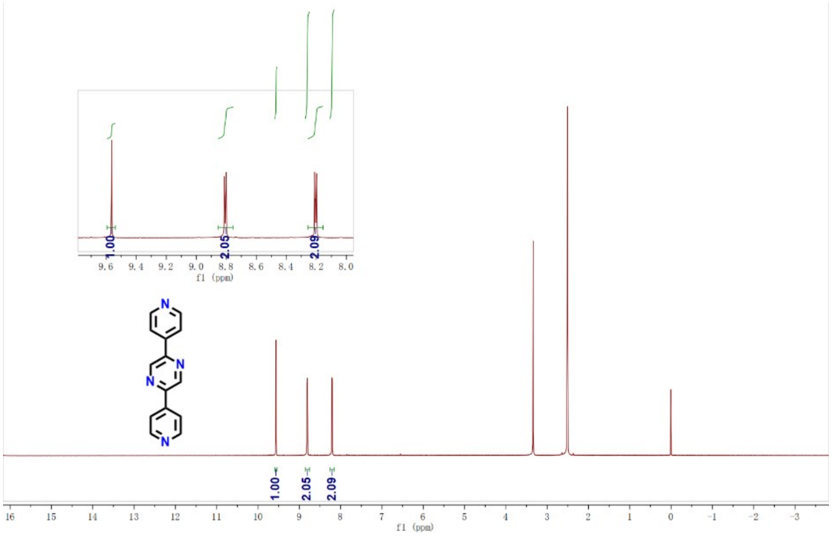


Fig. S4 NMR spectrum of dpp.

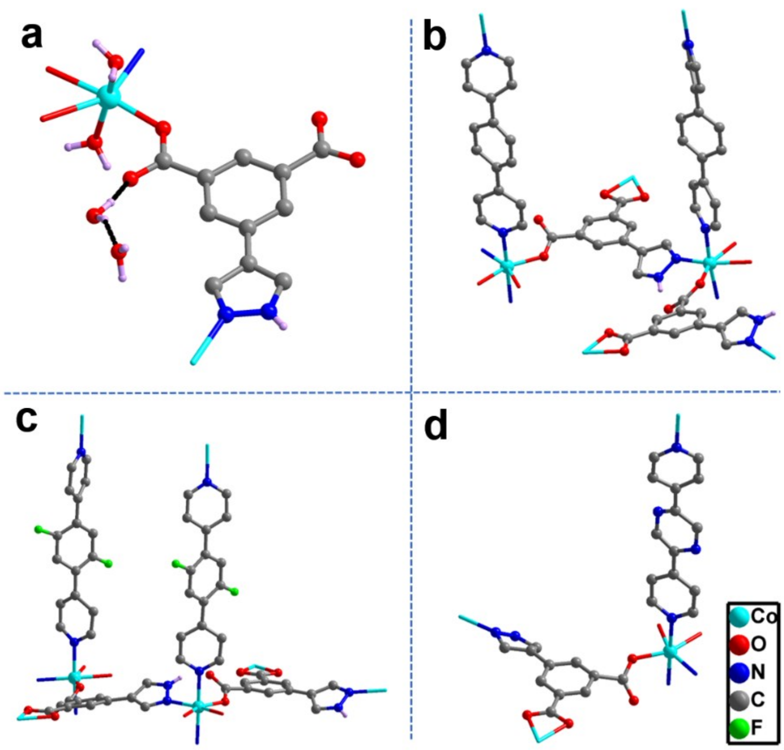


Fig. S5 The asymmetric units of **1** (**a**), **2-H** (**b**), **2-F** (**c**) and **2-N** (**d**), the disordered parts of ligands and hydrogen atoms are omitted for clarity.

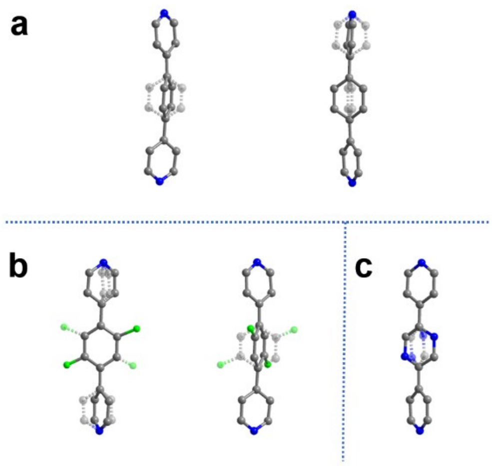


Fig. S6 The disordered configurations of N-containing ligands in compounds **2-H** (a), **2-F** (b) and **2-N** (c).

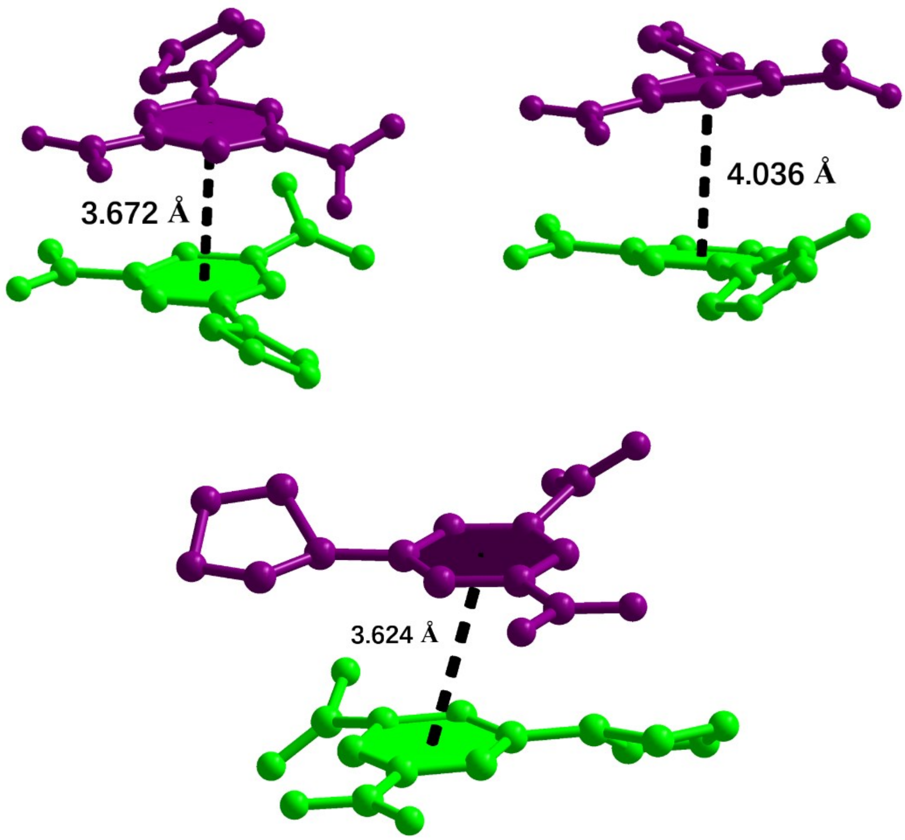


Fig. S7 The π···π interaction of ligand in **2-F** (top) and **2-N** (bottom).

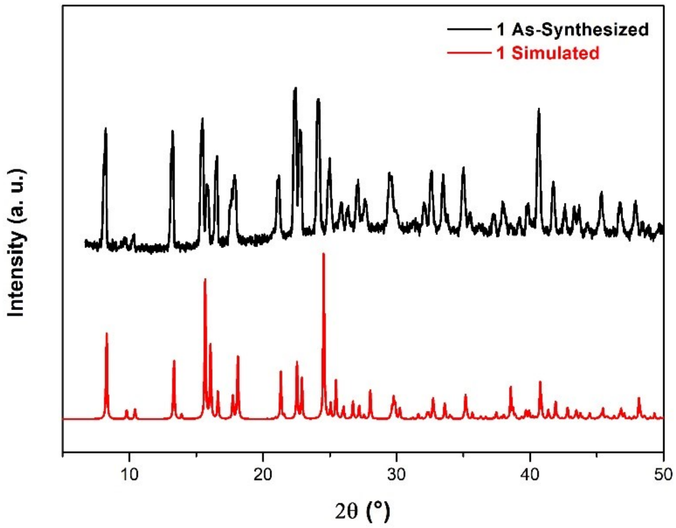


Fig. S8 PXRD patterns of compound **1**.

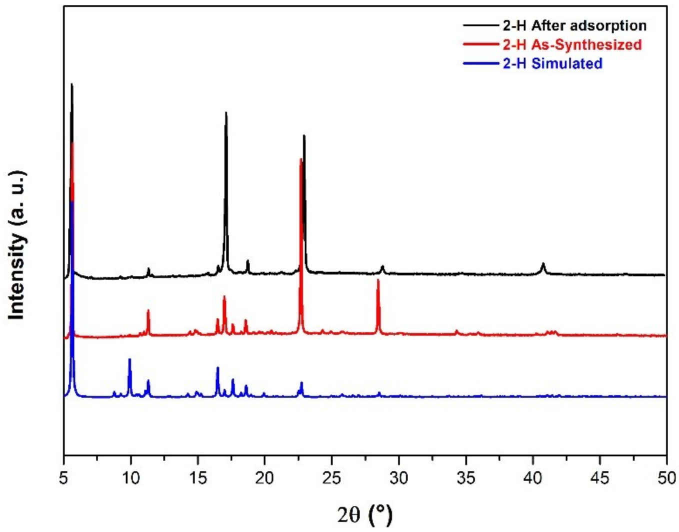


Fig. S9 PXRD patterns of **2-H** simulated, as-synthesized and after adsorption.

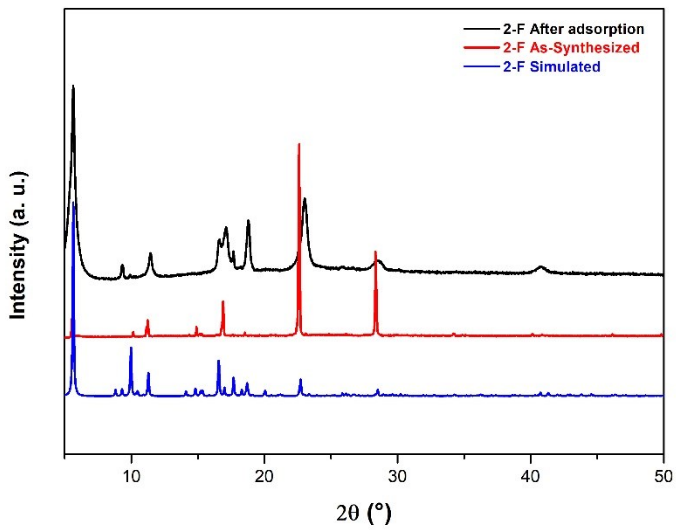


Fig. S10 PXRD patterns of **2-F** simulated, as-synthesized and after adsorption.

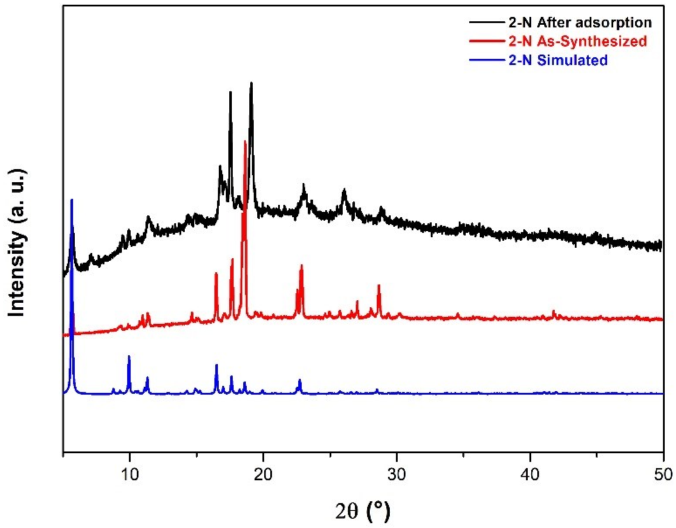


Fig. S11 PXRD patterns of **2-N** simulated, as-synthesized and after adsorption.

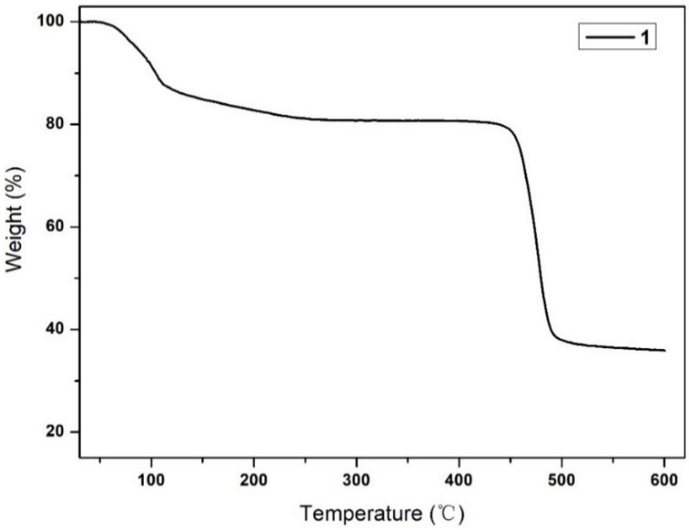


Fig S12. TGA curve of compound **1**.

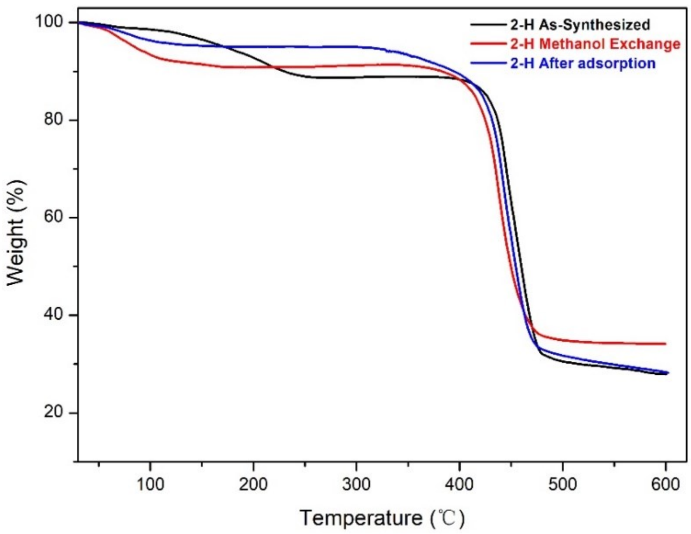


Fig. S13 TGA curves of **2-H** after as-synthesized, methanol exchange and adsorption.

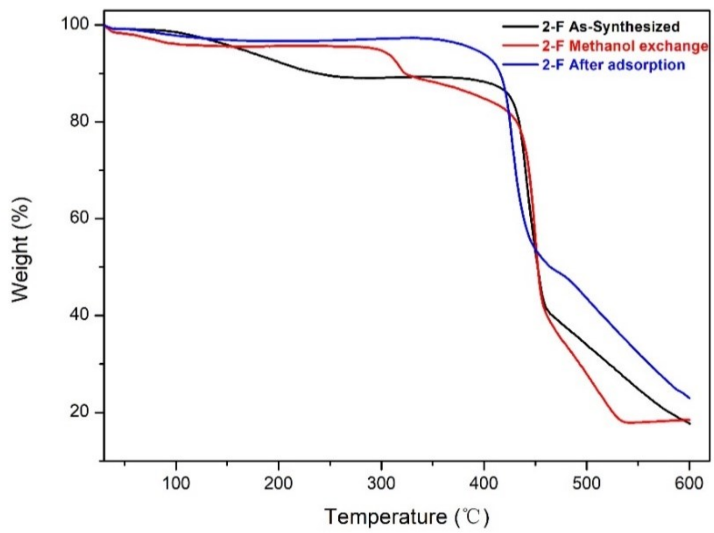


Fig. S14 TGA curves of **2-F** after as-synthesized, methanol exchange and adsorption.

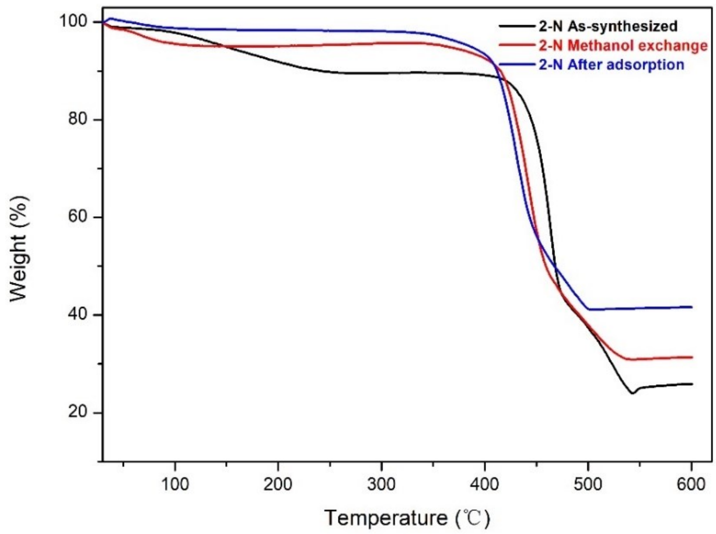


Fig. S15 TGA curves of **2-N** after as-synthesized, methanol exchange and adsorption.

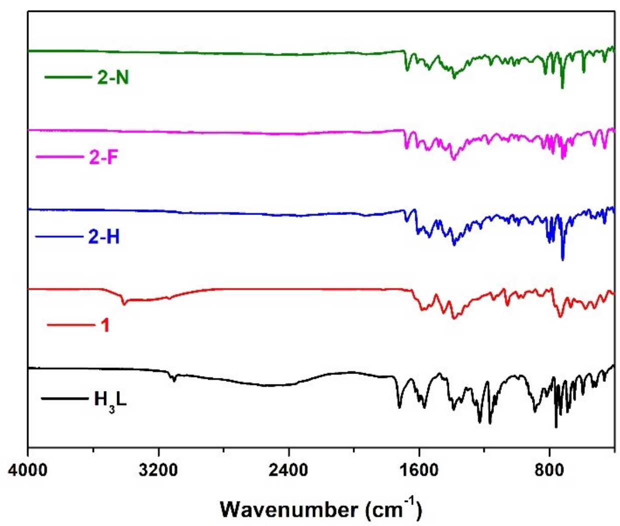


Fig S16. FT-IR spectra of H_3L,**1**, **2-H**, **2-F** and **2-N**.

Calculation of BET and Langmuir surface areas

The well-known BET isotherm model can be expressed by the following equation:

$$\frac{P}{Q(P_0 - P)} = \frac{1}{bQ_0} + \frac{b-1}{bQ_0}\left(\frac{P}{P_0}\right)$$

When the number of adsorption layers is 1, Langmuir isotherm model can be obtained by the following equation:

$$\frac{P}{Q} = \frac{1}{bQ_0} + \frac{1}{Q_0}P$$

Where Q/ (cm^{-3} g^{-1}) is the amount adsorbed; Q_0/ (cm^3 g^{-1}) is the saturated amount adsorbed; P/mmHg is the equilibrium pressure; and b/$mmHg^{-1}$ is the adsorption affinity.

A least-squares fit is performed on the ($\frac{P}{Q(P_0 - P)}$, $\frac{P}{P_0}$) designated pairs where $\frac{P}{Q(P_0 - P)}$ is the independent variable and $\frac{P}{P_0}$ is the dependent variable. Similarly, for Langmuir adsorption, a least-squares fit is performed on the ($\frac{P}{Q}$, P) designated pairs where $\frac{P}{Q}$ is the independent variable and P is the dependent variable. The following are calculated:

a) Slope ($\frac{b-1}{bQ_0}$, g/cm^3 STP) for BET, Slope ($\frac{1}{Q_0}$, g/cm^3 STP) for Langmuir

b) Y-intercept ($\frac{1}{bQ_0}$, g·mmHg/cm^3 STP)

c) Error of the slope (g/cm^3 STP)

d) Error of the y-intercept (g· mmHg/cm^3 STP)

Using the results of the above calculations, the BET or Langmuir surface area can be calculated as following:

$$S = A_m \times N_A \times \frac{Q_0}{22414} \times 10^{-18}$$

Where S is the BET or Langmuir surface area (m^2/g); A_m = molecular cross-sectional area (nm^2) of adsorbate i.e. 0.1700 nm^2 for CO_2,[1] and $N_A = 6.02 \times 10^{23}$.

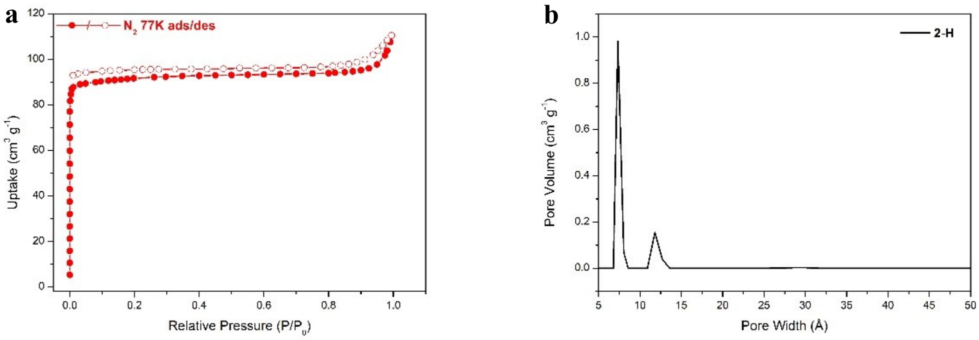


Fig. S17 (a) N_2 sorption isotherm at 77 K for **2-H**. (b) Pore size distribution for **2-H**.

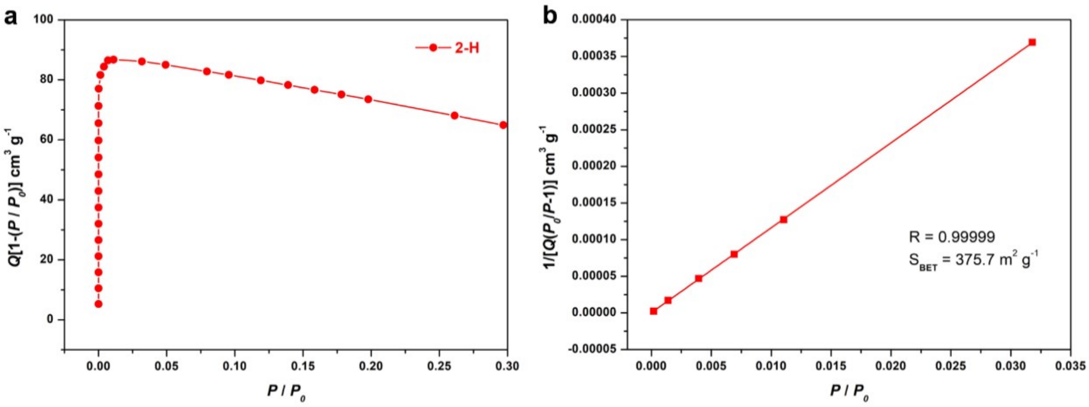


Fig. S18 (a) V[1-(P/P$_0$)] vs P/P$_0$ for **2-H**, only the range below P/P$_0$ = 0.03 satisfies the first consistency criterion for applying the BET theory. (b) Plot of the linear region for the BET equation.

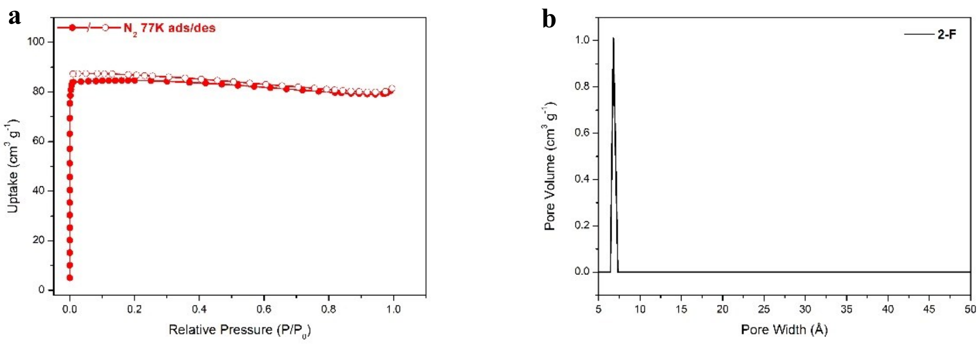


Fig. S19 (a) N_2 sorption isotherm at 77 K for **2-F.** (b) Pore size distribution for **2-F**.

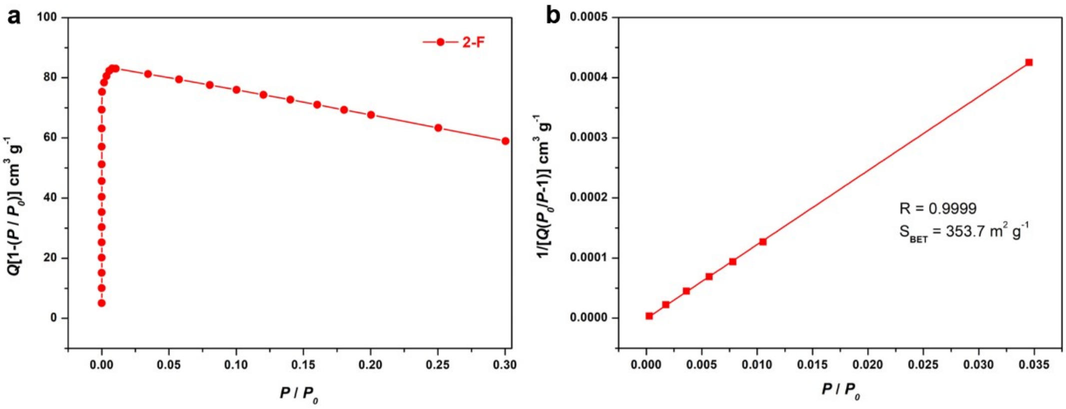


Fig. S20 (a) $V[1-(P/P_0)]$ vs P/P_0 for **2-F**, only the range below $P/P_0 = 0.03$ satisfies the first consistency criterion for applying the BET theory. (b) Plot of the linear region for the BET equation.

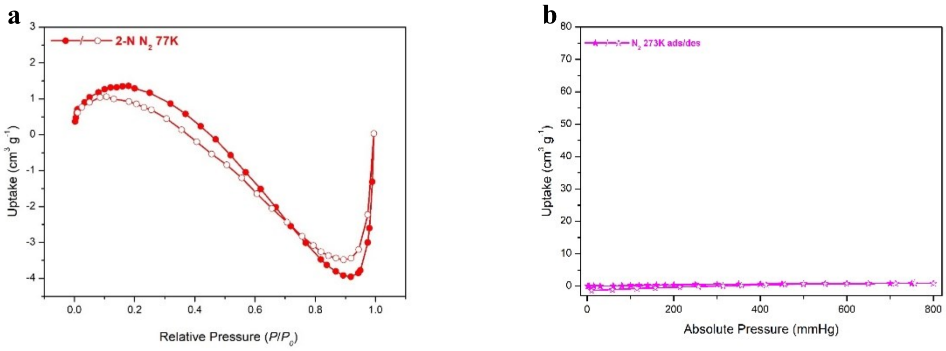
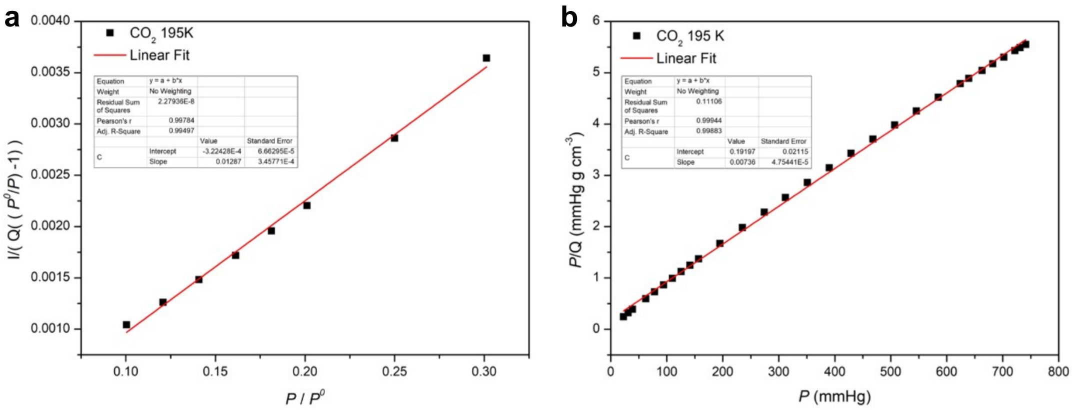


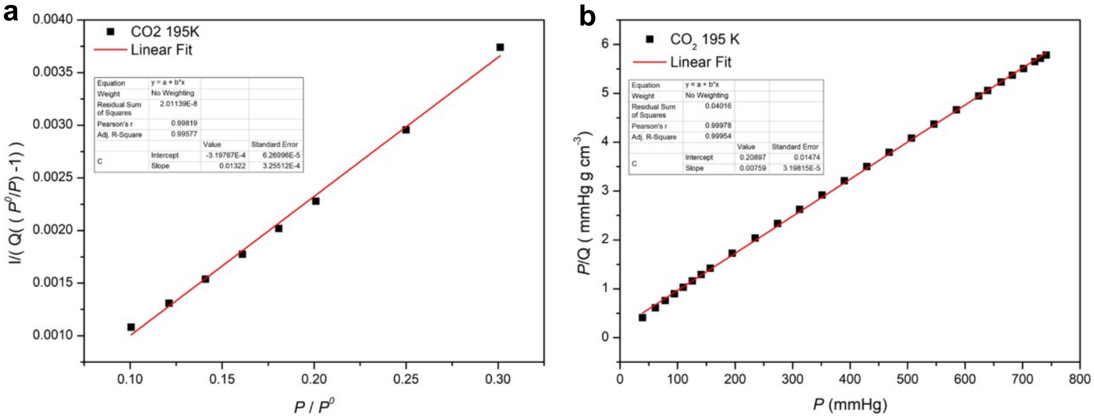
Fig S21. N_2 isotherms of **2-N** at 77 K (a) and 273K (b).



$$S_{\mathrm{BET}} = (1/\ (0.01287\text{-}0.000322428))/22414 \times 6.02 \times 10^{23} \times 0.170 \times 10^{-18} = 363.9\ \mathrm{m^2\ g^{-1}}.$$

$$S_{\mathrm{Langmuir}} = ((1/0.00736)/22414) \times 6.02 \times 10^{23} \times 0.170 \times 10^{-18} = 620.4\ \mathrm{m^2\ g^{-1}}.$$

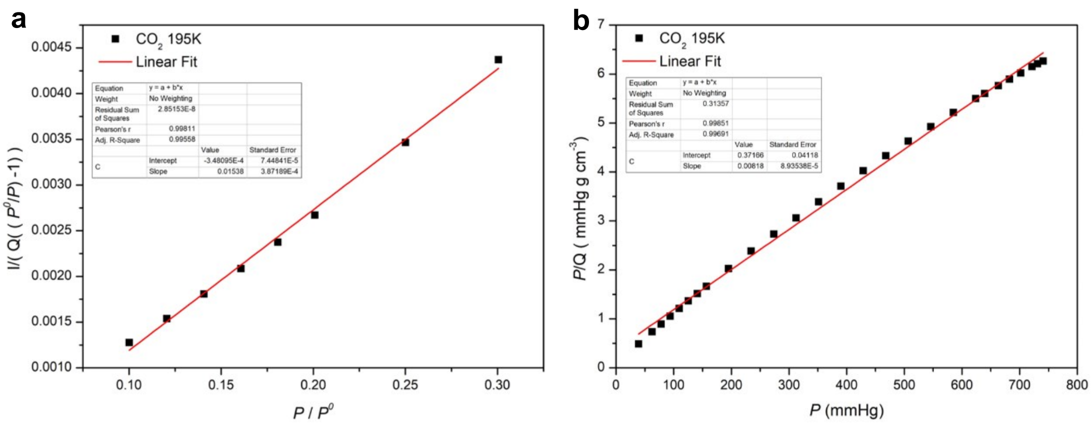
Fig. S22 The BET (a) and Langmuir (b) surface areas of **2-H** obtained from the CO_2 adsorption isotherm at 195 K.



S_{BET} = (1/ (0.01322-0.000319767))/22414 × 6.02 × 10^{23} × 0.170 × 10^{-18} = 353.9 $m^2\ g^{-1}$.

$S_{Langmuir}$ = ((1/0.00759)/22414) × 6.02 × 10^{23} × 0.170 × 10^{-18} = 601.6 $m^2\ g^{-1}$.

Fig. S23 The BET (a) and Langmuir (b) surface areas of **2-F** obtained from the CO_2 adsorption isotherm at 195 K.



S_{BET} = (1/ (0.01538-0.000348095))/22414 × 6.02 × 10^{23} × 0.170 × 10^{-18} = 303.7 $m^2\ g^{-1}$.

$S_{Langmuir}$ = ((1/0.00818)/22414) × 6.02 × 10^{23} × 0.170 × 10^{-18} = 558.2 $m^2\ g^{-1}$.

Fig. S24 The BET (a) and Langmuir (b) surface areas of **2-N** obtained from the CO_2 adsorption isotherm at 195 K.

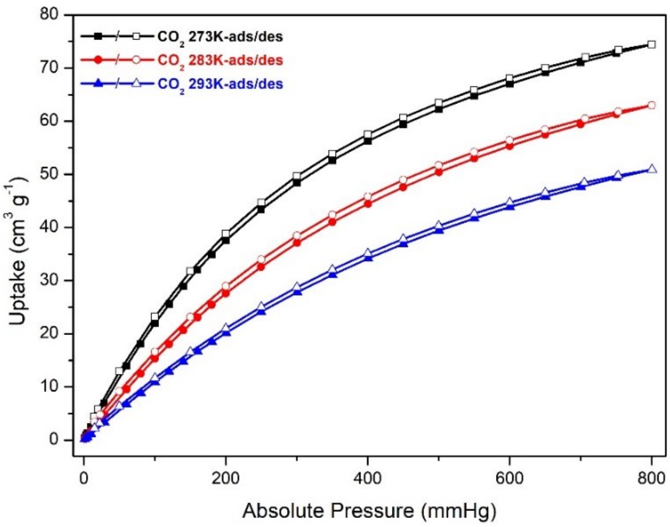


Fig. S25 CO_2 isotherms of **2-H** at 273, 283 and 293 K.

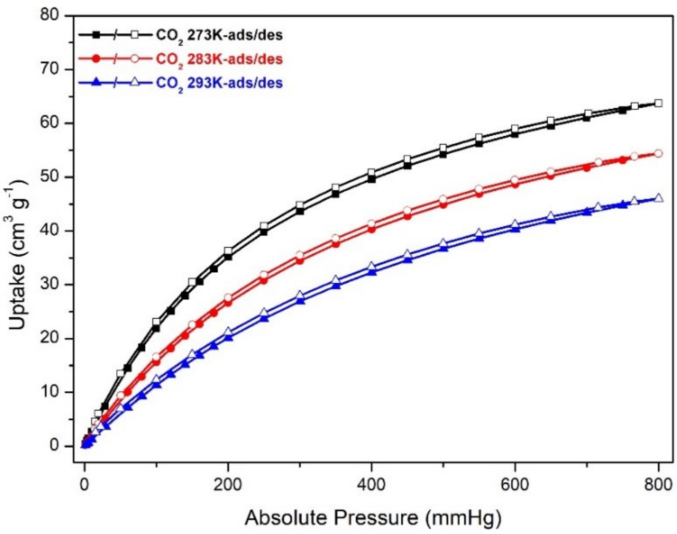


Fig. S26 CO_2 isotherms of **2-F** at 273, 283 and 293 K.

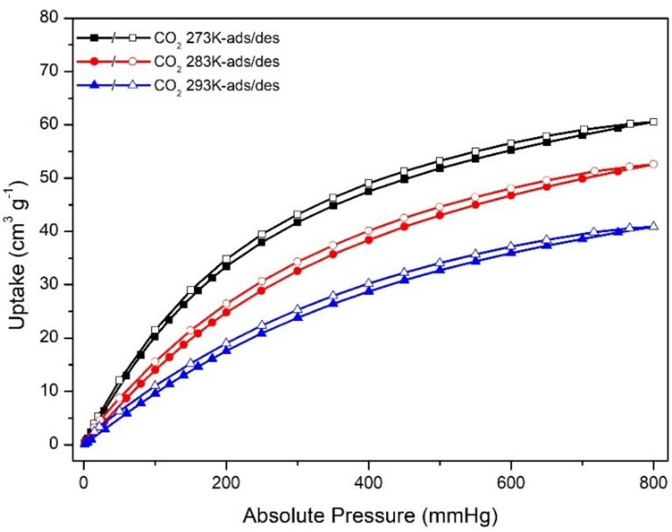


Fig. S27 CO_2 isotherms of **2-N** at 273, 283 and 293 K.

IAST Analysis of the selectivity data in 2-H, 2-F and 2-N.

Ideal adsorbed solution theory (IAST)[2] was used to determine the selectivity factor, *S*, for binary mixtures using pure component isotherm data. The selectivity factor, *S*, is defined according to Equation 1 where *xi* is the amount of each component adsorbed as determined from IAST and *yi* is the mole fraction of each component in the gas phase at equilibrium. The IAST adsorption selectivities were calculated for CO_2/N_2 and CO_2/CH_4 binary mixtures of compositions (15:85) and (50:50) at 273 K and a total pressure of 1.0 bar.

$$S = \frac{x_1/y_1}{x_2/y_2} \quad (1)$$

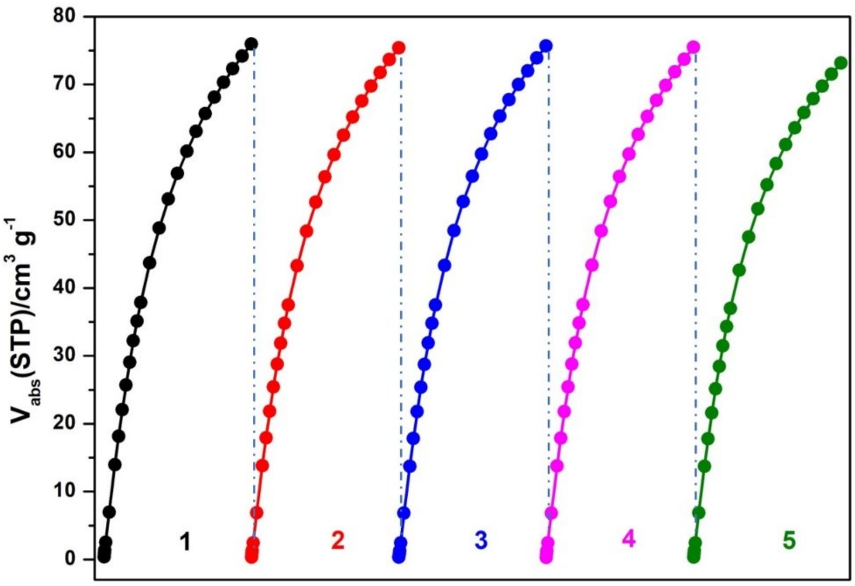


Fig. S28 5 cycles of CO_2 uptake of **2-H** at 273 K.

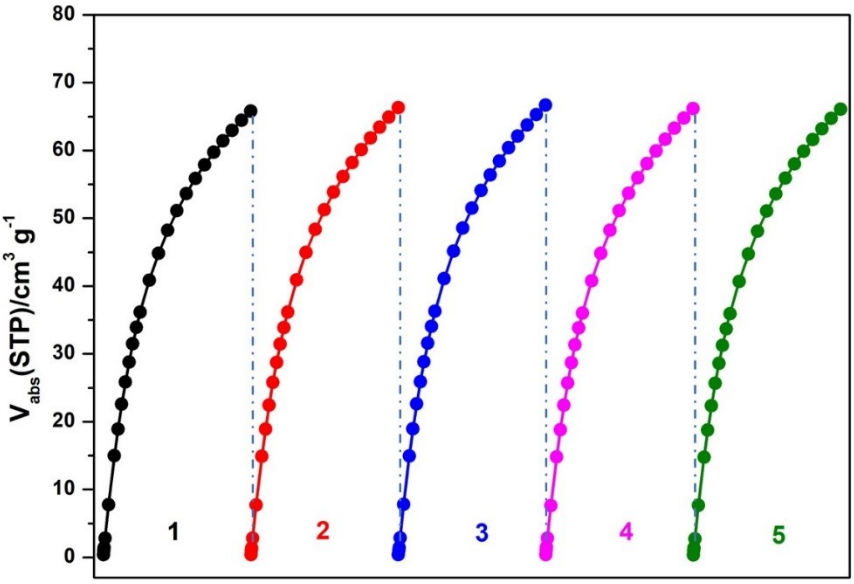


Fig. S29 5 cycles of CO_2 uptake of **2-F** at 273 K.

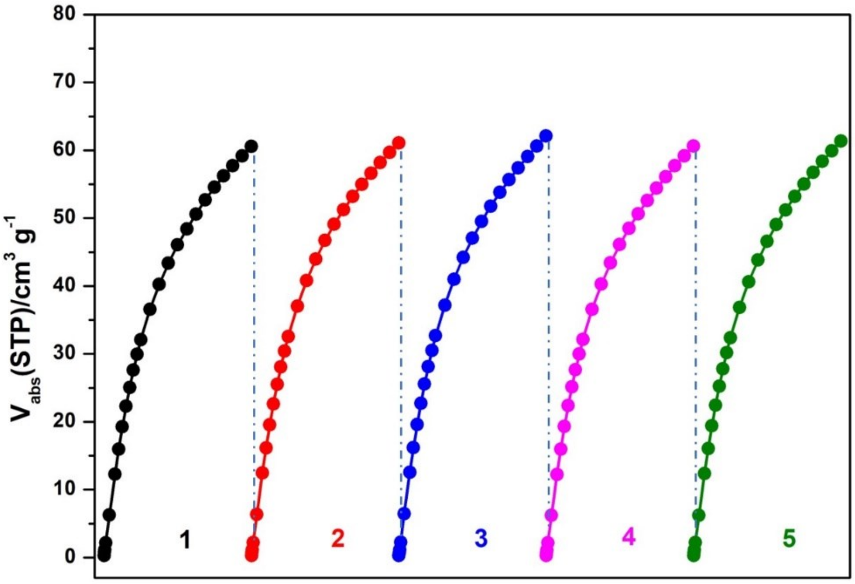


Fig. S30 5 cycles of CO_2 uptake of **2-N** at 273 K.

Table S1. Crystal and Structure Refinement Data for compounds **1**, **2-H**, **2-F** and **2-N**.

Identification code	**1**	**2-H**	**2-F**	**2-N**
Empirical formula	$C_{11}H_{14}CoN_2O_8$	$C_{60}H_{50}Co_2N_{10}O_{10}$	$C_{60}H_{56}Co_2F_4N_{10}O_{10}$	$C_{28}H_{23}CoN_7O_5$
Formula weight	361.17	1188.95	1260.91	596.46
Temperature (K)	296(2)	190.07	296(2)	296(2)
Wavelength (Å)	0.71073	1.34139	0.71073	0.71073
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	*P*bca	*P*2/n	*C*2/c	*P*2/c
a (Å)	17.0748(9)	19.079(4)	31.3666(10)	15.5398(13)
b (Å)	7.2456(4)	10.058(2)	20.0379(7)	10.0374(9)
c (Å)	21.3863(10)	31.296(6)	19.0191(6)	19.0268(19)
α (°)	90	90	90	90
β (°)	90	92.92(3)	94.3920(10)	90.593(3)
γ (°)	90	90	90	90
V (Å^3)	2645.9(10)	5998(2)	11918.8(7)	2967.6(5)
Z	8	4	8	4
ρ_{calc} (g/cm^3)	1.813	1.155	1.242	1.171
μ (mm^{-1})	1.344	3.272	0.623	0.614
F (000)	1480	2136	4528	1068
Reflections collected	22252	36906	50157	24348
Independent reflections	3050	10693	12668	6795
R (int)	0.0599	0.0589	0.0572	0.0860
Data / restraints / parameters	3050 / 13 / 226	10693 / 330 / 760	12668 / 824 / 869	6795 / 170 / 400
GOF on F^2	1.036	1.044	1.035	1.039
Final R indices [I>2sigma(I)]	R_1 = 0.0305, wR_2 = 0.0640	R_1 = 0.0679, wR_2 = 0.1870	R_1 = 0.0805, wR_2 = 0.2255	R_1 = 0.0617, wR_2 = 0.1540
R indices (all data)	R_1 = 0.0484, wR_2 = 0.0701	R_1 = 0.0882, wR_2 = 0.2024	R_1 = 0.1233, wR_2 = 0.2723	R_1 = 0.0877, wR_2 = 0.1699

Table S2. Selected Bond Lengths (Å) and bond angles (°) for Compounds **1**, **2-H**, **2-F** and **2-N**.

Compound **1**			
Co(1)-O(2)	2.0517(14)	Co(1)-O(1W)	2.0589(15)
Co(1)-N(2)$^{\#1}$	2.0720(17)	Co(1)-O(2W)	2.1123(15)
Co(1)-O(4)$^{\#2}$	2.1186(14)	Co(1)-O(3)$^{\#2}$	2.3493(14)
O(2)-Co(1)-O(1W)	88.10(6)	O(2)-Co(1)-N(2)$^{\#1}$	88.45(6)
O(1W)-Co(1)-N(2)$^{\#1}$	102.25(6)	O(2)-Co(1)-O(2W)	88.63(6)
O(1W)-Co(1)-O(2W)	166.83(6)	N(2)$^{\#1}$-Co(1)-O(2W)	90.40(6)
O(2)-Co(1)-O(4)$^{\#2}$	175.39(6)	O(1W)-Co(1)-O(4)$^{\#2}$	87.31(6)
N(2)$^{\#1}$-Co(1)-O(4)$^{\#2}$	92.82(6)	O(2W)-Co(1)-O(4)$^{\#2}$	95.79(5)
O(2)-Co(1)-O(3)$^{\#2}$	121.09(5)	O(1W)-Co(1)-O(3)$^{\#2}$	86.85(5)
N(2)$^{\#1}$-Co(1)-O(3)$^{\#2}$	149.62(6)	O(2W)-Co(1)-O(3)$^{\#2}$	83.94(5)
O(4)$^{\#2}$-Co(1)-O(3)$^{\#2}$	58.34(5)		

Compound **2-H**			
Co(1)-O(6)	2.057(3)	Co(2)-O(1)$^{\#3}$	2.139(3)
Co(1)-O(7)$^{\#1}$	2.151(3)	Co(2)-O(2)$^{\#3}$	2.184(3)
Co(1)-O(8)$^{\#1}$	2.176(3)	Co(2)-O(4)	2.065(3)
Co(1)-N(1)	2.127(3)	Co(2)-N(4)$^{\#4}$	2.132(3)
Co(1)-N(6)$^{\#2}$	2.163(4)	Co(2)-N(5)	2.142(3)
Co(1)-N(7)	2.137(4)	Co(2)-N(8)$^{\#5}$	2.157(4)
O(6)-Co(1)-O(7)$^{\#1}$	156.26(10)	O(4)-Co(2)-O(1)$^{\#3}$	153.95(10)
O(6)-Co(1)-O(8)$^{\#1}$	95.13(10)	O(4)-Co(2)-O(2)$^{\#3}$	93.24(11)
O(6)-Co(1)-N(1)	106.50(12)	O(4)-Co(2)-N(4)$^{\#4}$	107.53(12)
O(6)-Co(1)-N(6)$^{\#2}$	91.80(12)	O(4)-Co(2)-N(5)	91.03(12)

O(6)-Co(1)-N(7)	90.16(12)	O(4)-Co(2)-N(8)$^{\#5}$	90.54(12)
O(7)$^{\#1}$-Co(1)-O(8)$^{\#1}$	61.13(10)	N(4)$^{\#4}$-Co(2)-O(1)$^{\#3}$	98.48(11)
O(7)$^{\#1}$-Co(1)-N(6)$^{\#2}$	87.76(12)	N(4)$^{\#4}$-Co(2)-O(2)$^{\#3}$	159.14(12)
N(1)-Co(1)-O(7)$^{\#1}$	97.20(11)	N(4)$^{\#4}$-Co(2)-N(5)	89.23(13)
N(1)-Co(1)-O(8)$^{\#1}$	158.04(12)	N(4)$^{\#4}$-Co(2)-N(8)$^{\#5}$	92.17(14)
N(1)-Co(1)-N(6)$^{\#2}$	87.99(14)	N(5)-Co(2)-O(2)$^{\#3}$	88.51(12)
N(1)-Co(1)-N(7)	95.21(14)	N(5)-Co(2)-N(8)$^{\#5}$	177.49(13)
N(6)$^{\#2}$-Co(1)-O(8)$^{\#1}$	87.62(12)	N(8)$^{\#5}$-Co(2)-O(2)$^{\#3}$	89.44(12)
N(7)-Co(1)-O(7)$^{\#1}$	88.86(11)	O(1)$^{\#3}$-Co(2)-N(5)	87.83(12)
N(7)-Co(1)-O(8)$^{\#1}$	88.31(12)	O(1)$^{\#3}$-Co(2)-N(8)$^{\#5}$	89.90(12)
N(7)-Co(1)-N(6)$^{\#2}$	175.62(13)	O(1)$^{\#3}$-Co(2)-O(2)$^{\#3}$	60.71(10)

Compound **2-F**			
Co(1)-O(5)	2.057(3)	Co(2)-O(4)	2.063(3)
Co(1)-N(1)	2.124(4)	Co(2)-N(3)$^{\#3}$	2.118(4)
Co(1)-N(5)	2.143(4)	Co(2)-N(7)	2.143(4)
Co(1)-O(2)$^{\#1}$	2.148(3)	Co(2)-O(7)$^{\#4}$	2.144(3)
Co(1)-N(8)$^{\#2}$	2.156(4)	Co(2)-N(6)$^{\#5}$	2.161(4)
Co(1)-O(1)$^{\#1}$	2.171(3)	Co(2)-O(8)$^{\#4}$	2.162(3)
O(5)-Co(1)-N(1)	107.25(14)	O(4)-Co(2)-N(3)$^{\#3}$	105.05(14)
O(5)-Co(1)-N(5)	91.57(13)	O(4)-Co(2)-N(7)	89.67(14)
N(1)-Co(1)-N(5)	89.70(15)	N(3)$^{\#3}$-Co(2)-N(7)	94.79(15)
O(5)-Co(1)-O(2)$^{\#1}$	153.74(12)	O(4)-Co(2)-O(7)$^{\#4}$	155.89(12)
N(1)-Co(1)-O(2)$^{\#1}$	99.01(13)	N(3)$^{\#3}$-Co(2)-O(7)$^{\#4}$	99.06(13)
N(5)-Co(1)-O(2)$^{\#1}$	89.20(13)	N(7)-Co(2)-O(7)$^{\#4}$	88.31(14)
O(5)-Co(1)-N(8)$^{\#2}$	90.32(15)	O(4)-Co(2)-N(6)$^{\#5}$	92.08(15)
N(1)-Co(1)-N(8)$^{\#2}$	90.26(17)	N(3)$^{\#3}$-Co(2)-N(6)$^{\#5}$	86.97(16)
N(5)-Co(1)-N(8)$^{\#2}$	178.03(16)	N(7)-Co(2)-N(6)$^{\#5}$	177.12(15)

O(2)$^{\#1}$-Co(1)-N(8)$^{\#2}$	88.87(15)	O(7)$^{\#4}$-Co(2)-N(6)$^{\#5}$	89.17(14)
O(5)-Co(1)-O(1)$^{\#1}$	92.96(12)	O(4)-Co(2)-O(8)$^{\#4}$	94.97(12)
N(1)-Co(1)-O(1)$^{\#1}$	159.68(14)	N(3)$^{\#3}$-Co(2)-O(8)$^{\#4}$	159.39(14)
N(5)-Co(1)-O(1)$^{\#1}$	87.58(14)	N(7)-Co(2)-O(8)$^{\#4}$	90.08(13)
O(2)$^{\#1}$-Co(1)-O(1)$^{\#1}$	60.84(11)	O(7)$^{\#4}$-Co(2)-O(8)$^{\#4}$	61.01(11)
N(8)$^{\#2}$-Co(1)-O(1)$^{\#1}$	91.78(15)	N(6)$^{\#5}$-Co(2)-O(8)$^{\#4}$	87.48(14)
Compound **2-N**			
Co(1)-O(1)	2.054(2)	Co(1)-N(3)	2.150(3)
Co(1)-N(1)$^{\#1}$	2.127(3)	Co(1)-N(6)$^{\#3}$	2.163(3)
Co(1)-O(3)$^{\#2}$	2.141(2)	Co(1)-O(4)$^{\#2}$	2.166(2)
O(1)-Co(1)-N(1)$^{\#1}$	108.10(10)	O(3)$^{\#2}$-Co(1)-N(6)$^{\#3}$	89.20(10)
O(1)-Co(1)-O(3)$^{\#2}$	155.52(10)	N(3)-Co(1)-N(6)$^{\#3}$	176.90(11)
N(1)$^{\#1}$-Co(1)-O(3)$^{\#2}$	96.38(10)	O(1)-Co(1)-O(4)$^{\#2}$	94.36(9)
O(1)-Co(1)-N(3)	90.69(10)	N(1)$^{\#1}$-Co(1)-O(4)$^{\#2}$	157.48(10)
N(1)$^{\#1}$-Co(1)-N(3)	92.44(12)	O(3)$^{\#2}$-Co(1)-O(4)$^{\#2}$	61.16(8)
O(3)$^{\#2}$-Co(1)-N(3)	88.64(9)	N(3)-Co(1)-O(4)$^{\#2}$	88.85(10)
O(1)-Co(1)-N(6)$^{\#3}$	90.35(10)	N(6)$^{\#3}$-Co(1)-O(4)$^{\#2}$	88.16(10)
N(1)$^{\#1}$-Co(1)-N(6)$^{\#3}$	90.01(12)		

Symmetry codes: For **1**, #1: *x*, -*y*+1/2, *z*+1/2; #2: *x*-1/2, -*y*+1/2, -*z*+1; #3: *x*+1/2, -*y*+1/2, -*z*+1; #4: *x*, -*y*+1/2, *z*-1/2. For **2-H**, #1: *x*, *y*-1, *z*; #2: *x*-1/2, -*y*+1, *z*-1/2; #3: *x*, *y*+1, *z*; #4: *x*+1, *y*, *z*; #5: *x*+1/2, -*y*+1, *z*-1/2. For **2-F**, #1: *x*, -*y*, *z*+1/2; #2: *x*+1/2, -*y*+1/2, *z*+1/2; #3: *x*, *y*, *z*-1; #4: *x*, -*y*+1, *z*-1/2; #5: *x*+1/2, -*y*+1/2, *z*-1/2. For **2-N**, #1: *x*, -*y*+1, *z*+1/2; #2: *x*, *y*-1, *z*; #3: *x*-1, *y*, *z*; #4: *x*, *y*+1, *z*; #5: *x*, -*y*+1, *z*-1/2.

Table S3. Hydrogen bonds for **1** [Å and °].

D-H…A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(1WA)...O(1)[#5]	0.848(9)	1.874(11)	2.713(2)	170(2)
O(1W)-H(1WB)...O(3)[#6]	0.851(9)	2.028(15)	2.763(2)	144.0(18)
O(2W)-H(2WA)...O(3)[#7]	0.844(9)	1.979(11)	2.809(2)	168(2)
O(2W)-H(2WB)...O(3W)[#8]	0.850(9)	1.906(10)	2.756(2)	179(2)
O(3W)-H(3WA)...O(4W)	0.839(9)	1.887(11)	2.686(2)	159(2)
O(3W)-H(3WB)...O(1)	0.844(9)	1.896(11)	2.695(2)	157(2)
O(4W)-H(4WA)...O(4)[#9]	0.849(9)	1.930(10)	2.776(2)	174(3)
O(4W)-H(4WB)...O(3W)[#10]	0.852(9)	1.959(11)	2.802(2)	170(2)
N(1)-H(1N)...O(2)[#4]	0.857(10)	2.40(2)	2.927(2)	120(2)

Symmetry codes: #1 *x*, -*y*+1/2, *z*+1/2; #2 *x*-1/2, -*y*+1/2, -*z*+1; #3 *x*+1/2, -*y*+1/2, -*z*+1; #4 *x*, -*y*+1/2, *z*-1/2; #5 -*x*+1, -*y*+1, -*z*+1; #6 -*x*+3/2, *y*+1/2, *z*; #7 -*x*+3/2, *y*-1/2, *z*; #8 -*x*+1, -*y*, -*z*+1; #9 *x*-1/2, *y*, -*z*+1/2; #10 -*x*+1, *y*-1/2, -*z*+1/2.

Table S4. Supplemental summary of the porosity parameters and adsorption roperties of **2-H**, **2-F** and **2-N**.

Compounds	$S_{Langmuir}$ [a] (m^2 g^{-1})	CO_2 Uptake (cm^3 g^{-1})			N_2 Uptake (cm^3 g^{-1}, 273 K)	CH_4 Uptake (cm^3 g^{-1}, 273 K)
		273 K	283 K	293 K		
2-H	620.4	74.4	63.0	50.9	4.0	24.4
2-F	601.6	63.7	54.4	46.0	6.5	22.5
2-N	558.2	60.6	52.6	40.9	-	22.9

[a] Calculated by the CO_2 uptake at 195 K.

Table S5. All data points for the CO_2 adsorption-desorption isotherms at 273K for **2-H** in 5 cycles.

Cycle 1		**Cycle 2**		**Cycle 3**		**Cycle 4**		**Cycle 5**	
Absolute Pressure (mmHg)	**Uptake ($cm^3 g^{-1}$)**	**Absolute Pressure (mmHg)**	**Uptake ($cm^3 g^{-1}$)**	**Absolute Pressure (mmHg)**	**Uptake ($cm^3 g^{-1}$)**	**Absolute Pressure (mmHg)**	**Uptake ($cm^3 g^{-1}$)**	**Absolute Pressure (mmHg)**	**Uptake ($cm^3 g^{-1}$)**
1.36809	0.369556	1.385177	0.335788	1.392947	0.321538	1.394853	0.318309	1.39019	0.330882
3.585912	0.923749	3.593106	0.875632	3.595346	0.856517	3.597366	0.850649	3.597901	0.868671
5.33361	1.373497	5.366741	1.30353	5.382579	1.258832	5.378239	1.27304	5.392526	1.30588
9.958709	2.53717	10.16754	2.456705	10.20648	2.433352	10.22264	2.44744	9.971226	2.429367
28.75061	6.986091	28.83953	6.863705	28.94398	6.84182	28.76014	6.818912	28.98223	6.892552
59.93111	13.95576	60.24474	13.82384	60.09139	13.73154	60.17804	13.79305	60.16314	13.73088
80.15031	18.16282	80.11514	17.93062	80.01728	17.83133	80.00745	17.89291	79.99683	17.76086
100.2819	22.08954	100.2425	21.81528	100.2365	21.77697	100.2686	21.80616	100.0981	21.60151
120.2533	25.71541	120.2746	25.43858	120.3487	25.37949	120.2306	25.40257	120.0839	25.12814
140.0383	29.05337	140.2979	28.77157	140.2739	28.7419	140.3646	28.79978	140.2887	28.44717
160.2049	32.23975	160.1494	31.86948	160.3944	31.88178	160.1455	31.89629	160.2981	31.496
180.0579	35.13071	180.4104	34.80452	180.3636	34.79768	180.3003	34.83211	180.3202	34.34031
200.2651	37.86642	200.3033	37.48481	200.2933	37.49359	200.3229	37.54904	200.3181	36.99162
249.3611	43.70158	249.3001	43.25611	249.5046	43.3332	249.6632	43.37594	249.6523	42.6474
300.3957	48.83307	300.2243	48.35611	300.2331	48.4318	300.3121	48.42476	300.1058	47.51547
349.9708	53.11813	350.1653	52.64295	350.1445	52.72206	350.304	52.72757	350.1956	51.67479
400.1248	56.87745	400.2668	56.37621	400.0444	56.44897	400.0992	56.44216	400.0036	55.22125
450.0631	60.14915	450.1322	59.64575	450.1308	59.75235	450.2896	59.74227	450.2433	58.35384
500.1962	63.08899	500.1954	62.55348	500.041	62.6949	500.1564	62.63758	500.1472	61.12828
550.1709	65.71827	550.0969	65.17866	550.2241	65.34997	550.0154	65.26715	550.1158	63.59511
600.2766	68.11637	600.1664	67.54572	600.1186	67.75195	600.1964	67.66674	600.0145	65.83257
650.0587	70.29608	650.0931	69.75887	650.2767	69.98189	650.106	69.84848	649.8946	67.87524
699.9361	72.31548	700.165	71.77217	700.1436	72.00248	700.1552	71.86117	700.0994	69.77271

750.0529	74.19301	750.1514	73.64892	749.9687	73.90199	750.1528	73.72997	749.8622	71.50705
800.031	75.9519	799.9911	75.38129	800.1117	75.66612	800.1411	75.49296	800.0151	73.15869
757.6609	75.12731	757.4623	74.54806	757.8994	74.81891	758.1835	74.60451	757.8325	72.28644
715.6391	74.05023	715.4587	73.42908	716.2026	73.70668	716.092	73.46962	716.0661	71.19279
650.0718	71.78753	650.0959	71.22684	649.9652	71.37652	649.8436	71.15026	649.8407	69.02861
599.6774	69.7453	599.8844	69.19746	599.7054	69.32073	599.7091	69.12522	599.7162	67.12291
549.9175	67.52044	549.8755	66.93252	549.9377	67.04403	549.9469	66.84823	549.8328	64.95092
500.0258	65.01711	499.959	64.37696	499.8534	64.48447	499.9285	64.32325	499.9236	62.5437
449.9962	62.18953	449.9969	61.53313	449.9444	61.61765	449.9754	61.4848	449.9665	59.7999
400.0059	58.96238	399.9697	58.30556	400.0618	58.38427	400.0356	58.25954	400.0107	56.68636
350.0353	55.24711	350.0515	54.61656	350.0087	54.6578	350.1025	54.55506	350.0865	53.12161
300.0862	50.96598	300.0789	50.33286	300.0866	50.35769	300.0615	50.26795	300.0799	48.95389
250.1356	45.92455	250.1198	45.28485	250.1611	45.30377	250.176	45.21878	250.1257	44.05741
200.1551	39.94126	200.1243	39.33673	200.1368	39.31036	200.1381	39.21587	200.1521	38.22946
150.1873	32.78074	150.2256	32.19231	150.2014	32.1575	150.1897	32.06097	150.2112	31.21178
100.2211	24.14729	100.1801	23.5951	100.2316	23.54082	100.2455	23.44063	100.1985	22.75768
50.20612	13.7704	50.21885	13.30601	50.19298	13.24552	50.20264	13.11306	50.22752	12.60927
19.75611	6.538559	19.80734	6.040974	19.74458	6.037193	19.77704	5.897957	19.60733	5.443108
14.77271	5.138161	14.73694	4.61967	14.76378	4.656737	14.76664	4.52593	14.74913	4.141254

Table S6. All data points for the CO_2 adsorption-desorption isotherms at 273K for **2-F** in 5 cycles.

Cycle 1		**Cycle 2**		**Cycle 3**		**Cycle 4**		**Cycle 5**	
Absolute Pressure (mmHg)	**Uptake (cm^3 g^{-1})**	**Absolute Pressure (mmHg)**	**Uptake (cm^3 g^{-1})**	**Absolute Pressure (mmHg)**	**Uptake (cm^3 g^{-1})**	**Absolute Pressure (mmHg)**	**Uptake (cm^3 g^{-1})**	**Absolute Pressure (mmHg)**	**Uptake (cm^3 g^{-1})**
1.39715	0.382487	1.40242	0.36980	1.40020	0.37466	1.40076	0.37252	1.40335	0.36641
3.608788	1.005916	3.61152	0.98497	3.61012	0.99402	3.61046	0.98826	3.61285	0.97613
5.1108	1.4191	5.12843	1.38718	5.11616	1.41071	5.41467	1.49202	5.13201	1.35392
10.1547	2.815649	10.21793	2.80272	10.16886	2.85693	10.23767	2.80027	10.13881	2.72004

29.0838	7.73391	29.12233	7.71159	29.20486	7.80035	28.89867	7.60632	29.16381	7.65891
60.44421	14.96248	60.43523	14.91183	60.24186	14.92231	60.24627	14.79735	60.21592	14.76242
79.92251	18.89761	80.26034	18.89335	80.15296	18.95450	80.28777	18.81501	80.03481	18.73809
100.1732	22.5673	100.01592	22.44911	100.32057	22.62894	100.28188	22.44164	100.21181	22.36862
120.1932	25.82526	120.26713	25.78432	120.34297	25.87686	120.30067	25.72207	120.29441	25.63496
140.1973	28.77759	140.38194	28.75488	140.14937	28.82900	140.37268	28.67764	140.36942	28.58924
160.2346	31.46419	160.28595	31.41993	160.18436	31.55700	160.24529	31.34941	160.27502	31.24175
180.2828	33.91528	180.17014	33.86868	180.27896	34.03062	180.29605	33.80026	180.35280	33.68733
200.3199	36.14662	200.29073	36.12826	200.14288	36.27696	200.15468	36.02013	200.23340	35.91743
249.9618	40.86258	249.75774	40.90981	249.88338	41.09713	249.54697	40.76849	249.92102	40.68197
300.2664	44.83945	300.31296	44.95651	300.29480	45.14533	300.29816	44.83289	300.33554	44.71367
350.2136	48.19692	350.11298	48.34429	350.16666	48.53359	350.35312	48.21834	349.97723	48.07315
400.1848	51.08785	400.35419	51.27233	400.24161	51.48382	400.13065	51.11446	400.26636	51.04623
450.0875	53.61602	450.15659	53.85141	450.28696	54.08296	450.23969	53.68862	450.18741	53.59551
500.213	55.86916	500.35785	56.13975	500.11737	56.36233	500.14590	55.96879	500.09464	55.90997
550.1884	57.88785	550.26385	58.20360	549.99768	58.44771	550.02618	58.03492	550.05164	57.98714
600.2662	59.71464	600.01111	60.08959	600.20941	60.36478	600.17517	59.93951	600.13959	59.89087
650.0385	61.39627	650.27356	61.82228	650.15833	62.11933	650.00787	61.66795	650.10278	61.61118
700.0517	62.95214	700.17389	63.40571	700.16333	63.74887	700.09570	63.28087	700.13403	63.18584
750.0906	64.43349	750.08990	64.90870	750.04755	65.26180	750.03802	64.78343	750.12952	64.70604
800.0551	65.79123	800.14063	66.30100	800.11066	66.68632	800.13373	66.17432	799.95374	66.09399
764.8101	65.37269	765.03400	65.84480	765.09430	66.28898	765.02759	65.74404	764.79193	65.57450
707.318	64.37388	707.49402	64.67244	707.27539	65.17642	707.18073	64.67508	707.09900	64.44684
649.701	62.83198	649.92194	63.10098	649.80890	63.56586	650.04675	63.15428	649.82379	62.85719
599.7562	61.29388	599.88922	61.50682	599.76221	61.96242	599.84058	61.56307	599.80200	61.22564
549.9033	59.57033	549.91992	59.72332	549.99231	60.18039	549.93762	59.78054	549.90948	59.43536
499.9754	57.6922	500.02032	57.72471	499.90436	58.18626	499.95297	57.79795	499.85040	57.44262
449.9396	55.57045	449.94620	55.49452	449.99457	55.93532	449.95929	55.56612	449.92987	55.19909
399.9728	53.12272	400.06924	52.97858	400.00967	53.38443	400.05658	53.02665	400.02704	52.67701

350.0453	50.24271	350.04535	50.08022	350.03342	50.46005	350.03033	50.10070	350.04984	49.75602
300.022	46.8403	300.06097	46.68411	300.04739	47.06776	300.04108	46.72337	300.03625	46.37126
250.0744	42.76477	250.12363	42.65915	250.12236	43.03787	250.14487	42.70316	250.14401	42.33842
200.1324	37.85212	200.15422	37.77557	200.12625	38.15253	200.13579	37.84692	200.11752	37.46593
150.188	31.77564	150.19231	31.78239	150.18936	32.13523	150.21448	31.84187	150.20680	31.46255
100.2554	24.08658	100.31274	24.16246	100.27897	24.50750	100.27367	24.24380	100.28783	23.81527
50.52501	14.1084	50.61554	14.23701	50.50816	14.58860	50.53268	14.37012	50.58361	13.91735
19.7145	6.385713	19.82313	6.52021	19.64636	6.91117	19.71567	6.64243	19.74921	6.24998
14.5934	4.860333	14.59073	4.99958	14.60616	5.39331	14.55117	5.16987	14.60281	4.73946

Table S7. All data points for the CO_2 adsorption-desorption isotherms at 273K for **2-N** in 5 cycles.

Cycle 1		Cycle 2		Cycle 3		Cycle 4		Cycle 5	
Absolute Pressure (mmHg)	Uptake (cm^3 g^{-1})	Absolute Pressure (mmHg)	Uptake (cm^3 g^{-1})	Absolute Pressure (mmHg)	Uptake (cm^3 g^{-1})	Absolute Pressure (mmHg)	Uptake (cm^3 g^{-1})	Absolute Pressure (mmHg)	Uptake (cm^3 g^{-1})
1.484025	0.294564	1.48733	0.282043	1.486998	0.282754	1.486313	0.285806	1.484508	0.292761
3.74583	0.788184	3.74762	0.769433	3.748361	0.767676	3.746827	0.776781	3.74685	0.783802
5.372681	1.158907	5.383819	1.118188	5.370049	1.149665	5.373077	1.095944	5.361691	1.133007
10.10408	2.168318	10.31142	2.211791	10.28415	2.239922	10.23458	2.183624	10.28249	2.194794
29.68908	6.242215	29.68992	6.353627	29.76445	6.429312	29.64569	6.235673	29.59769	6.233303
60.17448	12.28245	60.29833	12.48109	60.32716	12.55871	60.06069	12.24341	60.29719	12.36463
80.33768	15.94563	80.25193	16.1535	80.06315	16.19796	80.28209	15.94943	80.19849	16.03202
100.2633	19.24953	100.3093	19.55114	100.2493	19.59952	100.2475	19.31966	100.4002	19.40915
120.3417	22.30632	120.0659	22.61063	120.3146	22.70844	120.3897	22.37559	120.2321	22.43157
140.253	25.0713	140.3484	25.50774	140.3317	25.54651	140.1266	25.13011	140.2204	25.24277
160.1048	27.62553	160.2674	28.0595	160.3383	28.14932	160.0635	27.64179	160.2241	27.81383
180.3971	29.96613	180.1137	30.39166	180.3259	30.51362	180.1929	29.98923	180.2078	30.17639
200.2812	32.09277	200.3645	32.56967	200.2937	32.67925	200.3262	32.12449	200.3741	32.38034
250.1456	36.55122	249.9879	37.04857	250.1354	37.19464	250.0265	36.56607	249.9761	36.86552

300.2969	40.26943	300.3056	40.79375	300.2919	40.99763	300.2619	40.27436	300.3001	40.63239
349.8885	43.37118	350.1744	43.98913	350.1793	44.2194	350.2742	43.39847	350.1861	43.82751
400.1191	46.0589	400.2319	46.72318	400.248	47.05179	400.2391	46.10515	400.2041	46.58911
450.0667	48.40452	450.1652	49.11111	450.1426	49.53495	450.0405	48.50047	450.1034	49.07173
500.1095	50.61574	500.0046	51.2438	500.2045	51.77548	500.1709	50.65473	500.1142	51.21224
550.1467	52.67725	550.2274	53.18872	550.2269	53.79656	550.0616	52.59463	550.1102	53.19884
600.2922	54.56289	600.078	54.95754	600.2708	55.69441	600.2031	54.40211	600.0616	55.04124
650.1097	56.2176	650.1075	56.6271	650.0718	57.42175	650.1094	56.09838	650.2587	56.74509
700.0023	57.73705	700.1356	58.19916	699.992	59.09297	700.1831	57.71357	700.0417	58.37339
750.0646	59.1929	750.2457	59.6975	750.0818	60.63373	750.0267	59.17909	750.2457	59.92613
800.0736	60.5668	800.1425	61.07301	800.0121	62.11206	799.9852	60.60926	800.1603	61.37449
762.5773	61.05072	762.383	61.74094	761.9779	62.75054	761.6421	61.30946	762.5302	61.89196
713.6211	60.96544	712.897	61.73825	712.9297	62.6351	712.3303	61.12243	713.108	61.76857
650.1796	59.5911	650.1299	60.24682	650.1593	61.06785	650.0646	59.62709	650.2941	60.24374
599.691	58.20139	599.6826	58.76767	599.7137	59.55279	599.6102	58.13147	599.705	58.74274
549.8683	56.61918	549.8303	57.12053	549.9076	57.88323	549.8607	56.46472	549.8317	57.12391
499.9427	54.8095	499.956	55.30911	499.9346	56.00607	499.8855	54.5873	499.9393	55.30913
449.9445	52.73555	449.9277	53.25976	449.9506	53.91173	449.9317	52.47784	449.9726	53.23327
399.9571	50.40983	400.0224	50.93043	400.0137	51.51466	399.9988	50.09645	399.9531	50.85825
350.0722	47.70611	349.997	48.24378	350.0406	48.73379	350.0175	47.37234	349.9903	48.13286
300.0386	44.544	300.0266	45.09796	300.0394	45.50398	300.0667	44.17102	300.0661	44.90931
250.0713	40.83056	250.0585	41.39497	250.1007	41.6937	250.0845	40.3827	250.0327	41.0923
200.1399	36.21573	200.1413	36.81807	200.1357	37.03622	200.1215	35.68391	200.1321	36.49291
150.1467	30.46915	150.1449	31.01806	150.1516	31.24463	150.1127	29.86393	150.1702	30.73046
100.1701	23.29644	100.1459	23.72237	100.1711	24.01846	100.1661	22.573	100.1573	23.51345
50.24008	14.11539	50.24202	14.34176	50.27125	14.7056	50.21708	13.34218	50.24609	14.26699
22.59218	8.053312	22.60472	8.176694	22.54865	8.657723	22.63168	7.375786	22.55849	8.243338
14.93068	6.101818	14.93632	6.156329	14.97805	6.664535	14.96908	5.400606	14.95579	6.269755

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