

Supporting Information

Remoulding MOFs pore by auxiliary ligand introduction for stability improvement and highly selective CO₂-capture

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Experimental section

Materials and instrumentation

All the reagents and solvents employed were commercially available and used as supplied without further purification. Tris (3-pyridyl)-1,3,5-benzene (TPB) was synthesized according to the literature.¹ ¹H NMR and ¹³C NMR spectra were recorded on a Bruker DRX spectrometer operating at 400 MHz in DMSO-*d*₆. Elemental analyses (EA) were conducted using a Perkin-Elmer 240 elemental analyzer. Thermogravimetry analyses (TGA) were performed using a TA Q50 instrument from room temperature to 800 °C at a rate of 10 °C / min under N₂ flow. Powder X-ray diffraction (PXRD) patterns of the samples were recorded on a Rigaku B/Max-RB diffractometer with Cu-K α radiation ($\lambda = 1.5418 \text{ \AA}$) at room temperature. Gas sorption isotherms were measured by a BEL-max physisorption analyzer with activated samples. X-ray photoelectron spectroscopy (XPS) was conducted by HP5950A XPS with an Mg-K α as source and the C 1s peak at 284.6 eV as an internal standard.

Synthesis of 2,4,6-tris(3,5-dimethylphenyl)pyridine (L₁)

The organic ligand L₁ was synthesized according to the literature methods with slight modification, as shown in **Fig. S1**. 3,5-dimethylbenzaldehyde (20.2 mmol), 1-(3,5-dimethylphenyl) ethanone (40.4 mmol), ammonium acetate (404 mmol) and acetic acid (40 mL) were introduced to a round-bottom flask. Then, the mixture was stirred at 140 °C for 8 hours. After cooling to room temperature, the solution was poured into water and stirred for another hour. Subsequently, the resulting brown oily substance was dissolved in 3 mL ethanol. Filtrating, washing with ethanol, and drying under high vacuum afforded the desired product as a white solid. ¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 8.07$ (s, 2 H), 7.90 (s, 4 H), 7.83 (s, 2 H), 7.15 (d, 3 H), 2.42 (s, 18 H) ppm. Elemental analyses calcd. (%) for C₁₅H₁₂N: C 87.38, H 5.83, N 6.79 %; found: C 87.43, H 5.77, N 6.80 %.

Synthesis of 5,5',5''-(pyridine-2,4,6-triyl)triisophthalic acid (H₆pydc)

A mixture of L₁ (1 g), H₂O (10 mL) and HNO₃ (3 mL) was sealed in a glass vial. The vial was tightly capped and placed in a 180 °C oven for 24 h. After being cooled to room temperature, the yellow reaction product was filtrated, washed with water and dried in air. ¹H NMR (400 MHz, DMSO-*d*₆): $\delta = 13.49$ (s, 6 H), 9.05 (s, 4 H), 8.75 (s, 2 H), 8.6 (s, 3 H), 8.5 (s, 2 H) ppm. Elemental analyses calcd. (%) for C₂₉H₁₇NO₁₂: C 60.95, H 3.00, N 2.45 %; found: C 58.09, H 3.34, N 3.12 %.

Synthesis of Co-pydc

A mixture of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (18 mg, 0.06 mmol), H_6pydc (11 mg, 0.02 mmol), *N,N*-dimethylformamide (DMF) (2 mL) and H_2O (0.5 mL) was stirred for 10 min in air, and then 150 μL fluoroboric acid (HBF_4) was added. Thereafter, the red suspension was transferred in a 23 mL teflon-lined stainless steel autoclave and kept at 120 °C for 3 d. After cooling to room temperature slowly, red fusiform-shaped crystals of **Co-pydc** were obtained. For further analysis, the crystalline samples were washed with fresh DMF and dried in air. Yield: 42% (based on Co). Elemental analyses calcd. (%) for $[\text{Co}_3(\mu_3\text{-OH})(\text{pydc})(\text{H}_2\text{O})_3] \cdot 3\text{DMF} \cdot 8\text{H}_2\text{O}$: C 38.79, H 4.71, N 4.76; found: C 38.71, H 4.66, N 4.87.

Synthesis of Co-pydc-TPB

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (18 mg, 0.06 mmol) and H_6pydc (11 mg, 0.02 mmol) were dissolved in *N,N*-dimethylformamide (DMF) (2 mL) and H_2O (0.5 mL). The solution was stirred for 10 min in air, followed by an addition of TPB (5 mg, 0.016 mmol). After another 10 min stirring, 150 μL fluoroboric acid (HBF_4) was added. The resulting mixture was transferred into a 23 ml Teflon-lined autoclave and heated at 120 °C for 3 days. After cooling to room temperature, red hexagonal crystals of **Co-pydc-TPB** were obtained. For further analysis, the crystalline samples were washed with fresh DMF and dried in air. Yield: 65% (based on Co). Elemental analyses calcd. (%) for $[\text{Co}_3(\mu_3\text{-OH})(\text{pydc})(\text{TPB})] \cdot 2\text{DMF} \cdot 2\text{H}_2\text{O}$: C 53.82, H 3.55, N 6.72; found: C 53.80, H 3.43, N 6.71.

Single-Crystal X-ray crystallography

Single-crystal X-ray diffraction data were collected on a Rigaku XtaLAB Pro diffractometer with $\text{Cu-K}\alpha$ radiation ($\lambda = 1.54184 \text{ \AA}$) at room temperature. All structures were solved by the direct method and refined with full-matrix least-squares on F^2 using the *SHELXTL-2014* program package. All host-framework non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed geometrically. The PLATON SQUEEZE treatment was applied to Co-pydc and Co-pydc-TPB because all of the guest solvent molecules are extremely disordered and cannot be modeled. Refinements were carried out with constraints on a few bond distances, fixed using the DFIX command. The quantities of solvent molecules were confirmed by elemental analyses and thermogravimetry analyses. Crystallographic data and refinement parameters are provided in **Table S1**. Distances and angles are on the whole well defined and summarized in **Table S2 and S3**.

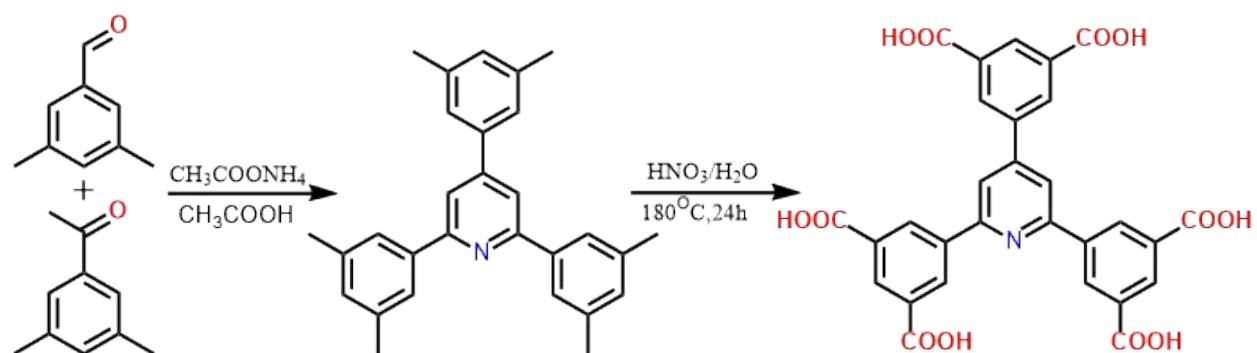


Fig. S1 Synthetic route of H₆pydc

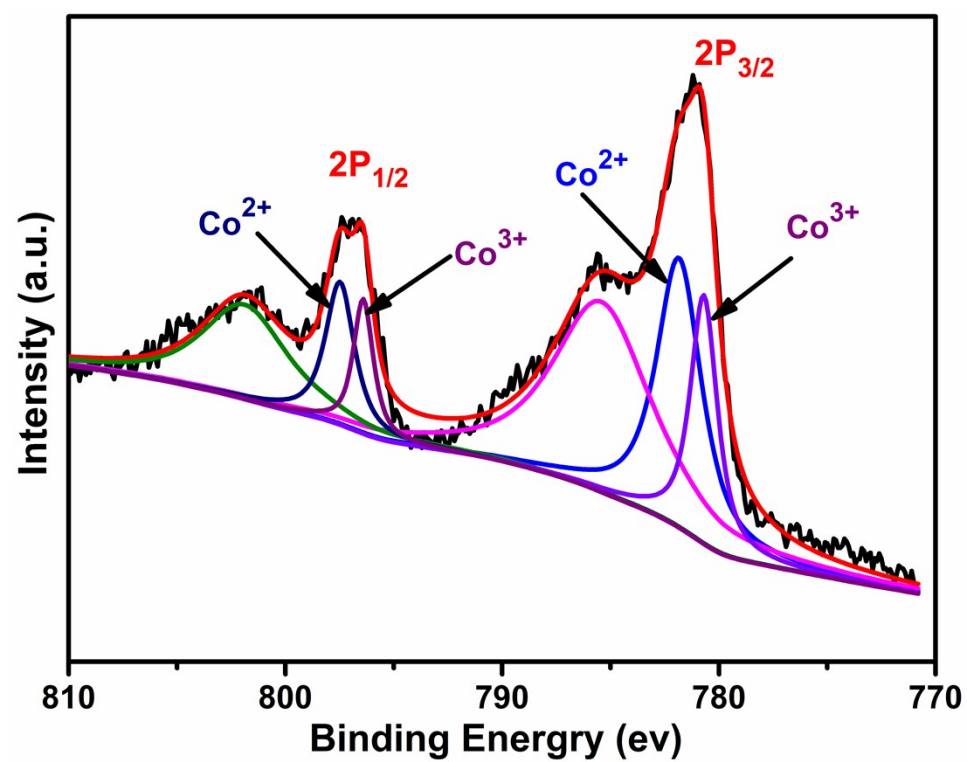


Fig. S2 X-ray photoelectron spectroscopy of Co-pydc

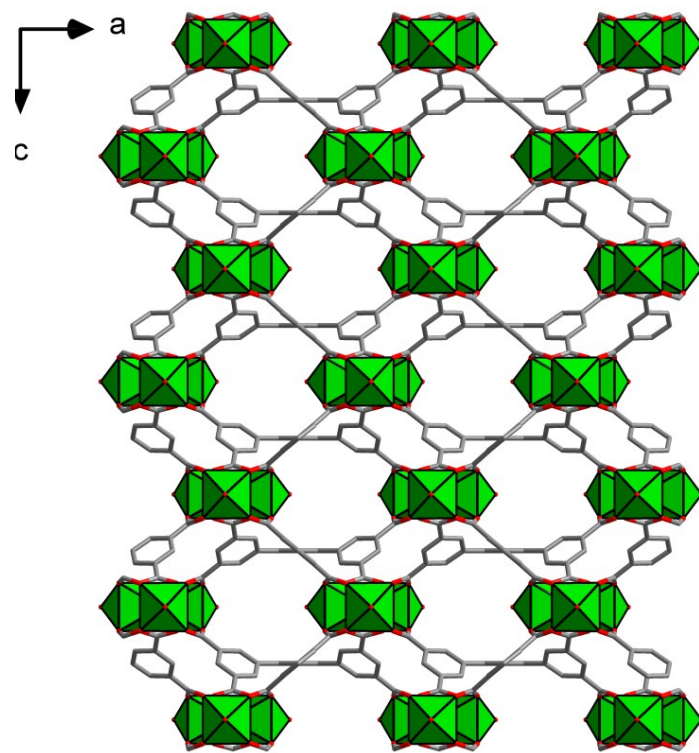


Fig. S3 Perspective view of Co-pydc along *b* axis

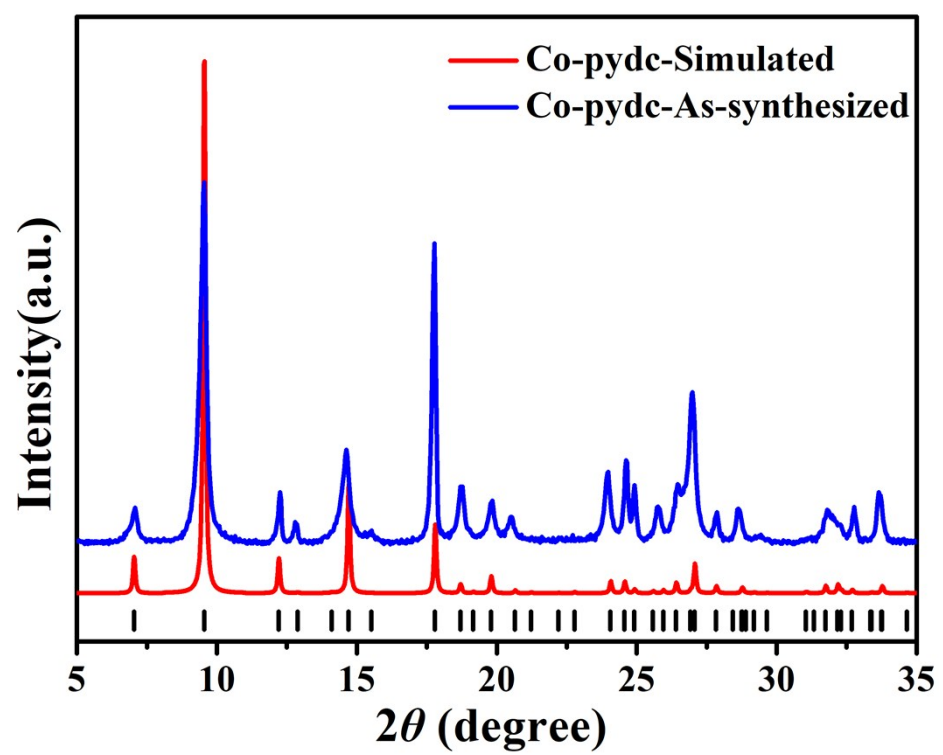


Fig. S4. PXRD patterns of Co-pydc

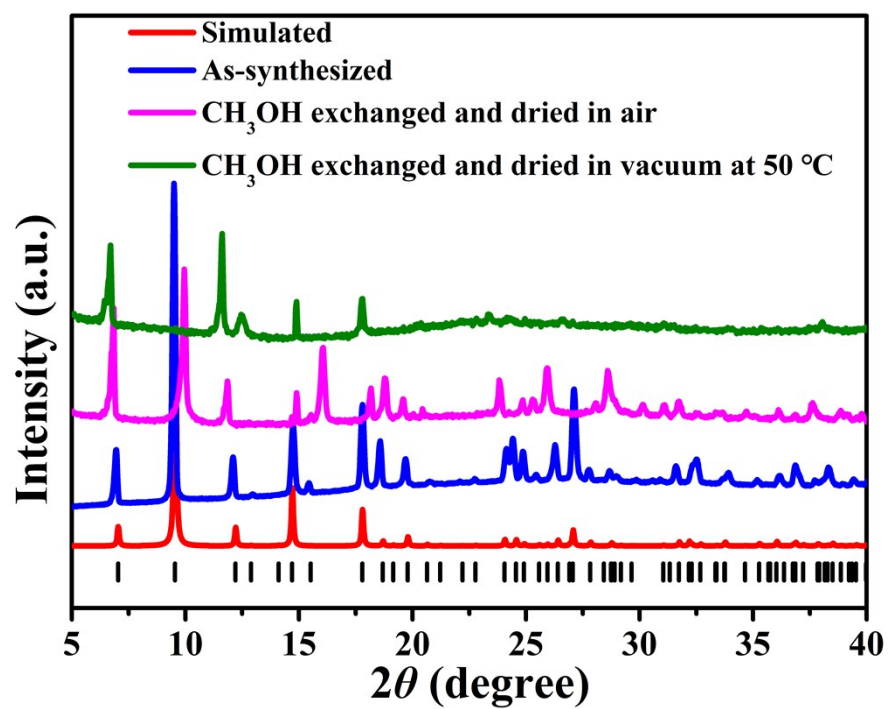


Fig. S5. PXR D patterns of Co-pydc under different conditions

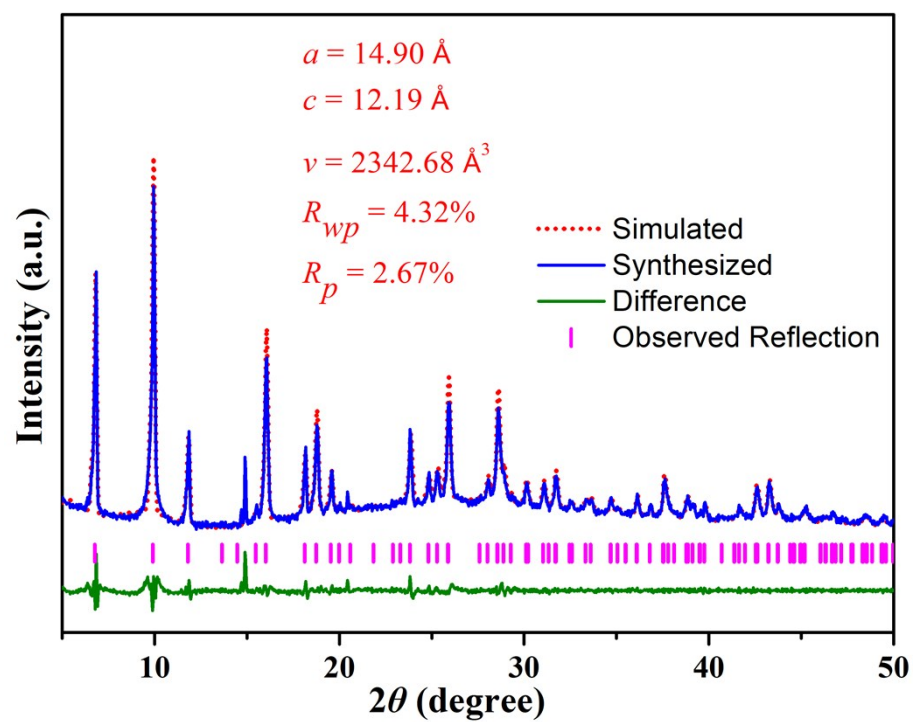


Fig. S6. Pawley refinements of the PXR D patterns of Co-pydc after CH₃OH exchanging and drying in air

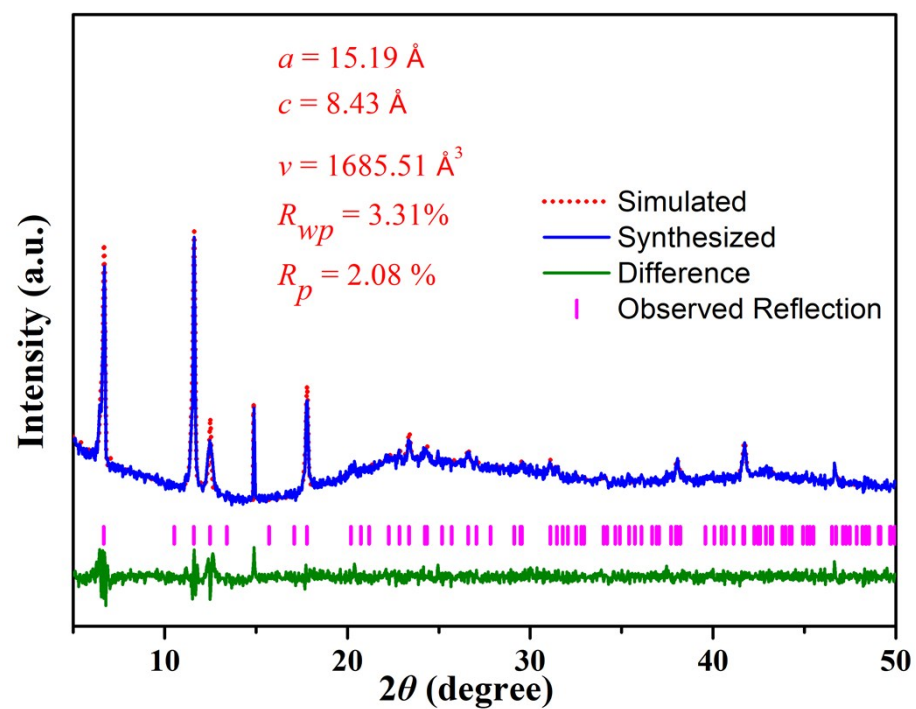


Fig. S7. Pawley refinements of the PXRD patterns of Co-pydc after CH₃OH exchanging and drying in vacuum at 50 °C

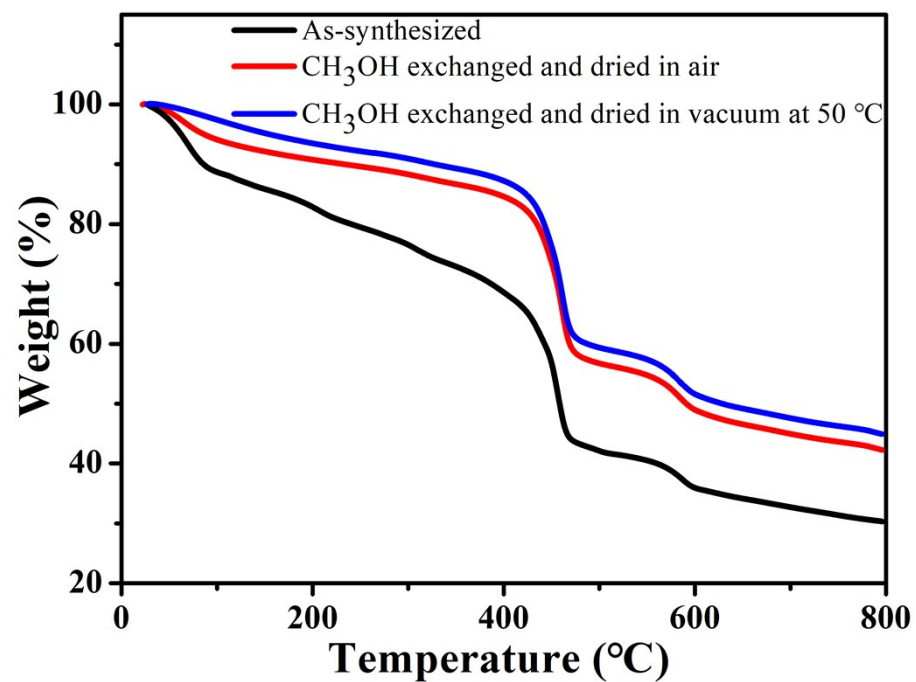


Fig. S8. Thermogravimetric analysis plots of Co-pydc under different conditions

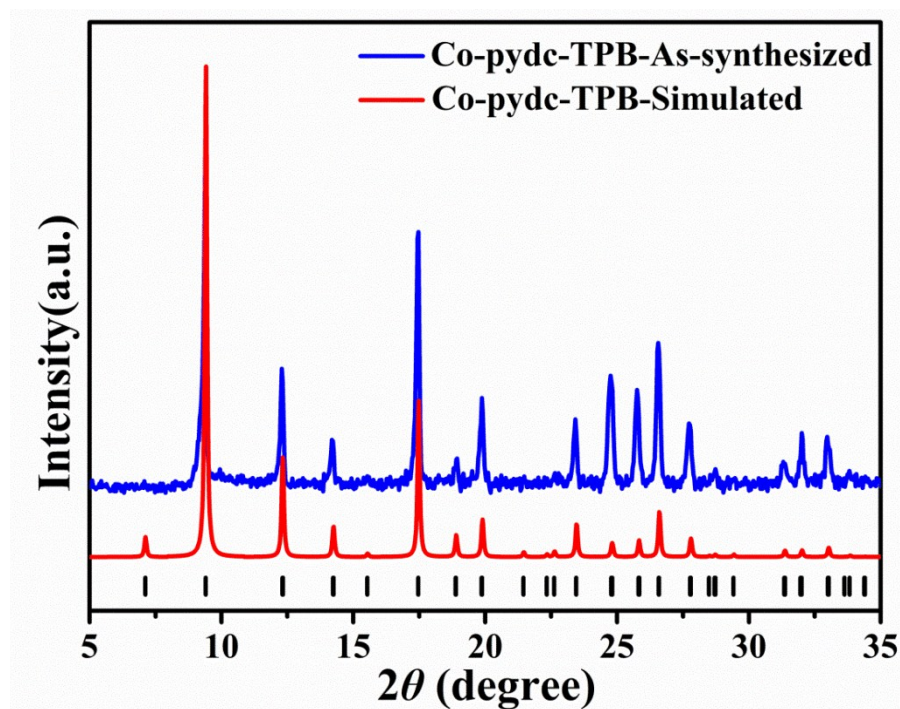


Fig. S9. PXRD patterns of Co-pydc-TPB

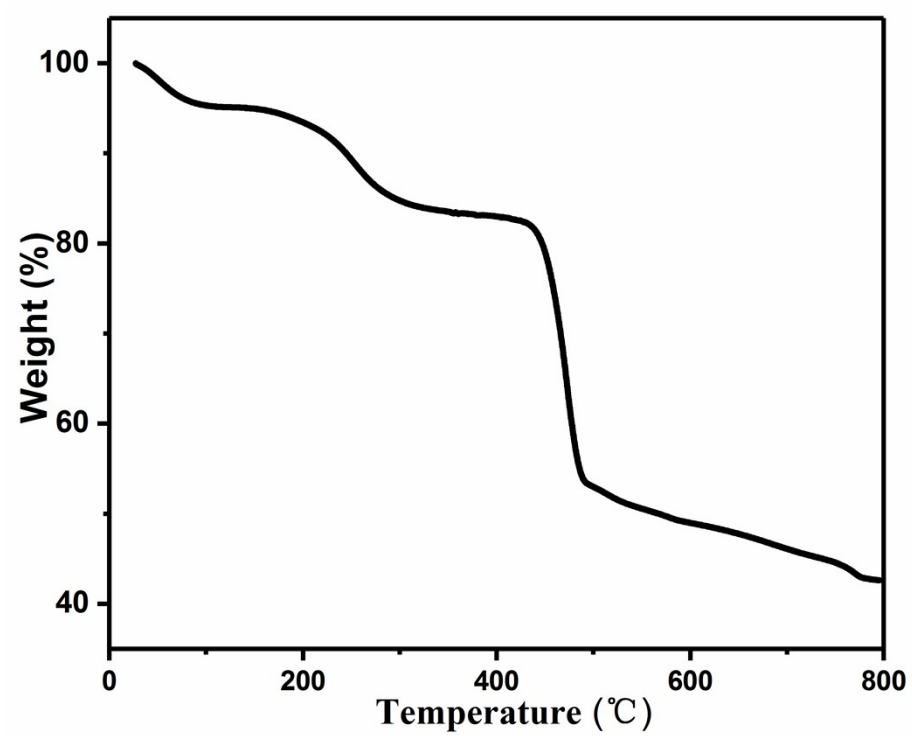


Fig. S10. Thermogravimetric analysis plot of Co-pydc-TPB.

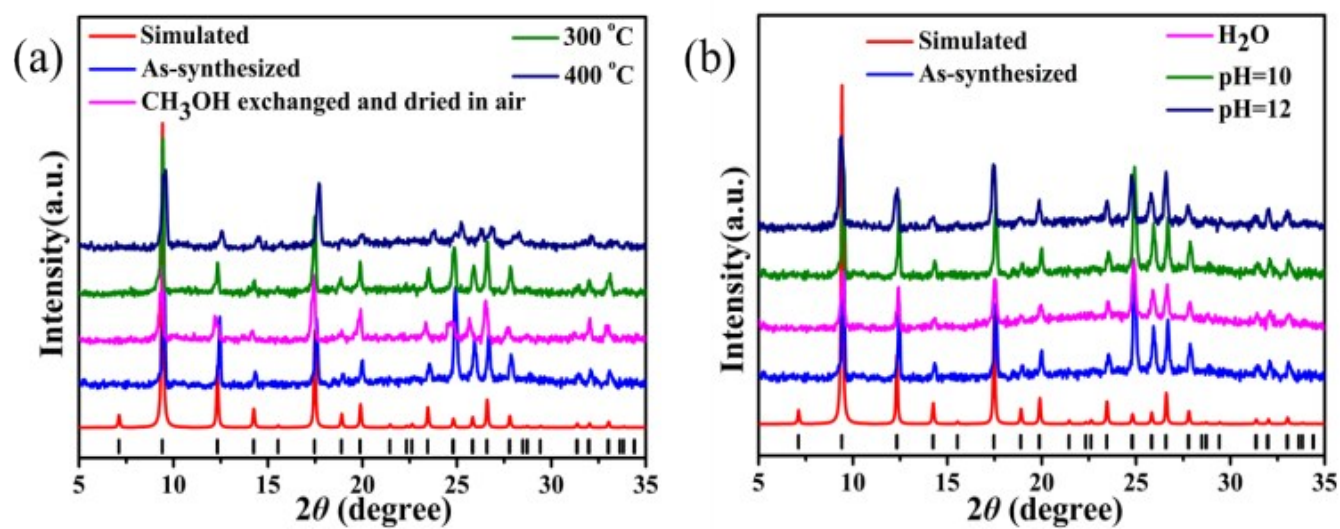


Fig. S11. PXR D patterns of Co-pydc collected during stability test.

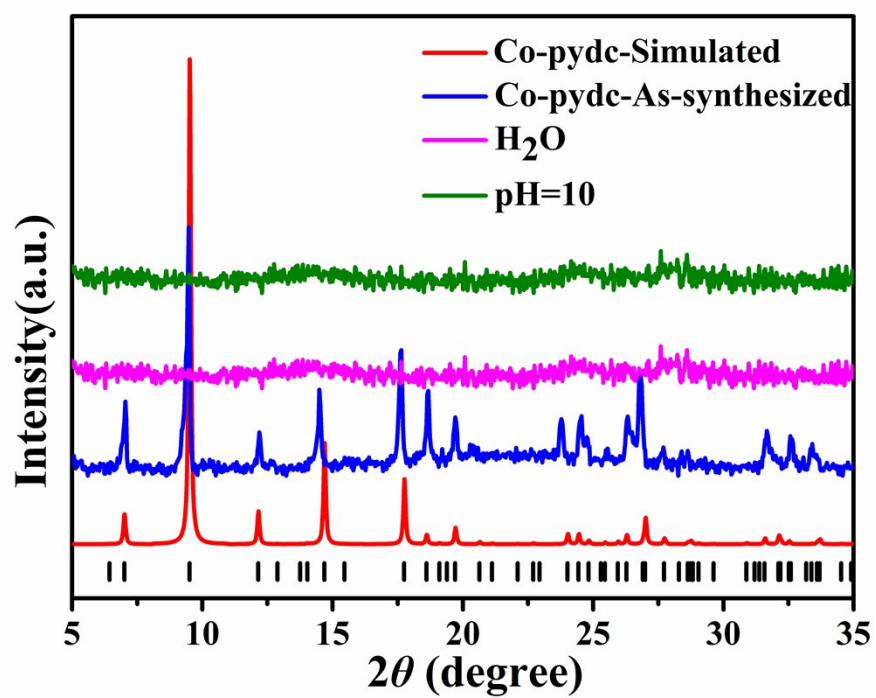


Fig. S12. PXR D patterns of Co-pydc collected during stability test.

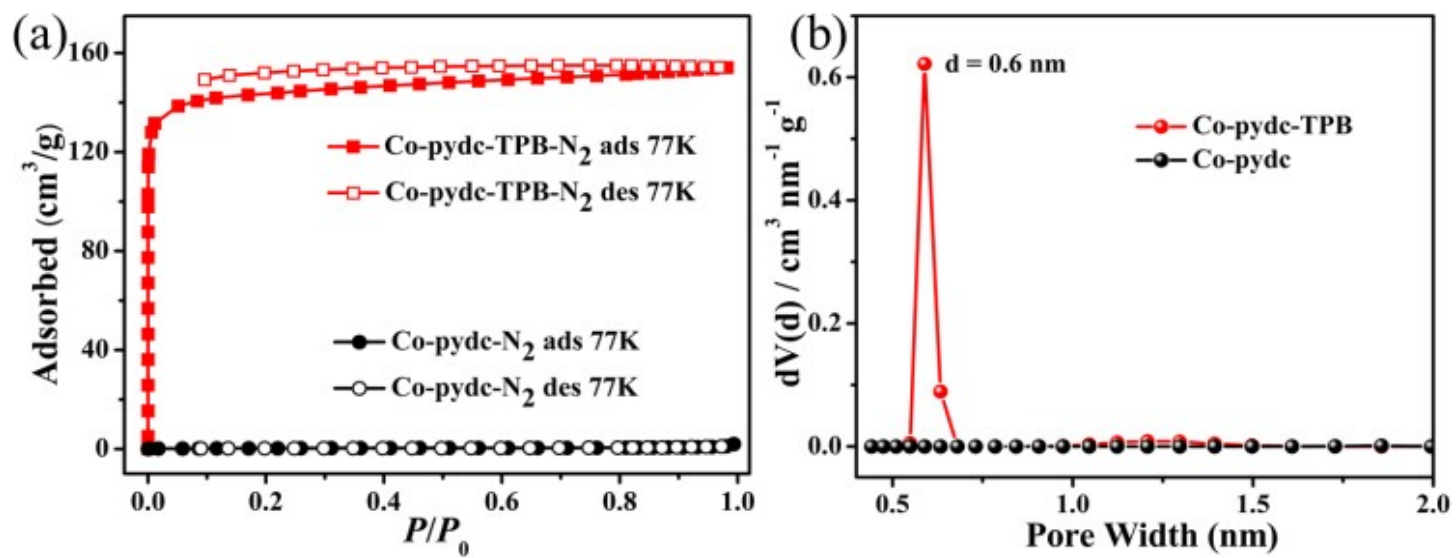


Fig. S13 (a) N₂ adsorption–desorption isotherms at 77 K and (b) pore size distribution of Co-pydc-TPB and Co-pydc.

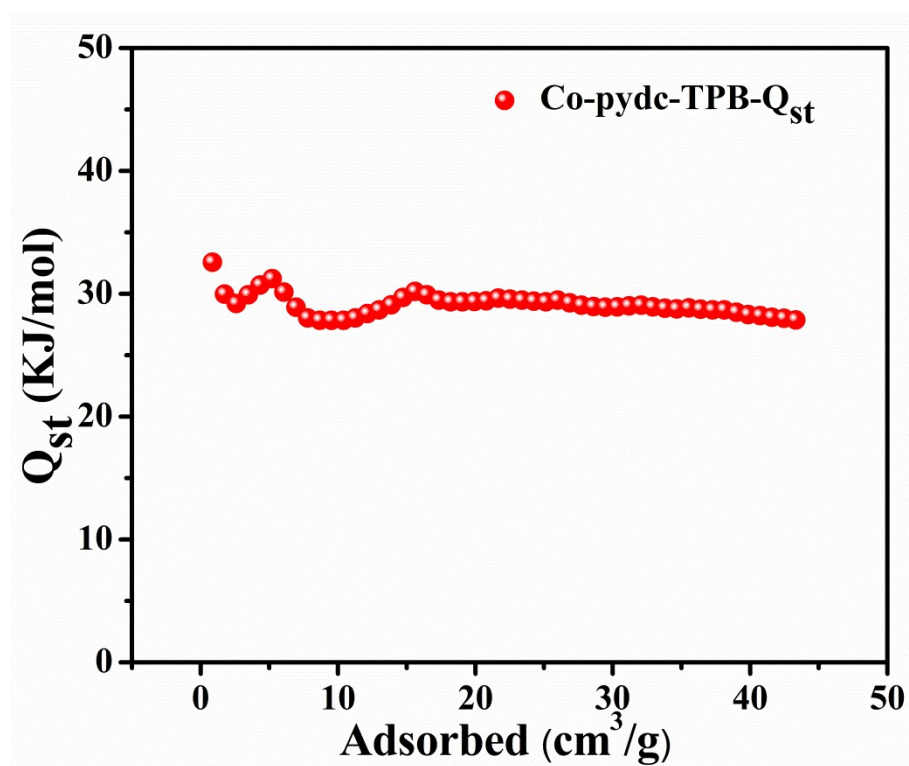


Fig. S14. Isothermic heat of adsorption for CO₂ in Co-pydc-TPB

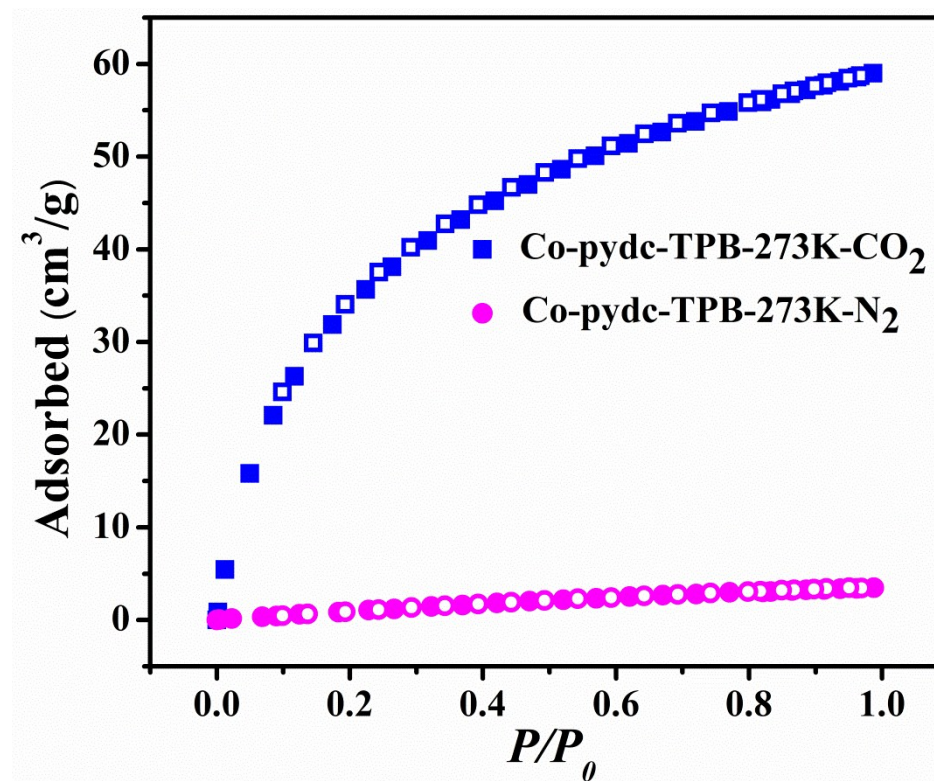


Fig. S15. Adsorption isotherms for the uptake of CO₂ and N₂ at 273 K in Co-pydc-TPB.

A nice fitting of CO₂, N₂ isotherms adsorption branch of Co-pydc-TPB at 298 K and 273 K have been calculated based on Toth's isotherm model².

$$\text{Toth Model: } M = M_{\max} \cdot B^{(1/n)} \cdot P / (1 + B \cdot P)^{(1/n)} \dots \dots \dots (1)$$

M , gas uptake (mmol g⁻¹); M_{\max} , maximum gas uptake (mmol g⁻¹); B and n , fitting constants;

$$\text{Henry's law constant } K = \lim_{P \rightarrow 0} \frac{dN}{dP} = B^{(1/n)} \cdot M_{\max} \dots \dots \dots (2)$$

Henry's law selectivity (upper limit selectivity), gas component i over j $S_{i,j}$

$$S_{i,j} = K_i / K_j \dots \dots \dots (3)$$

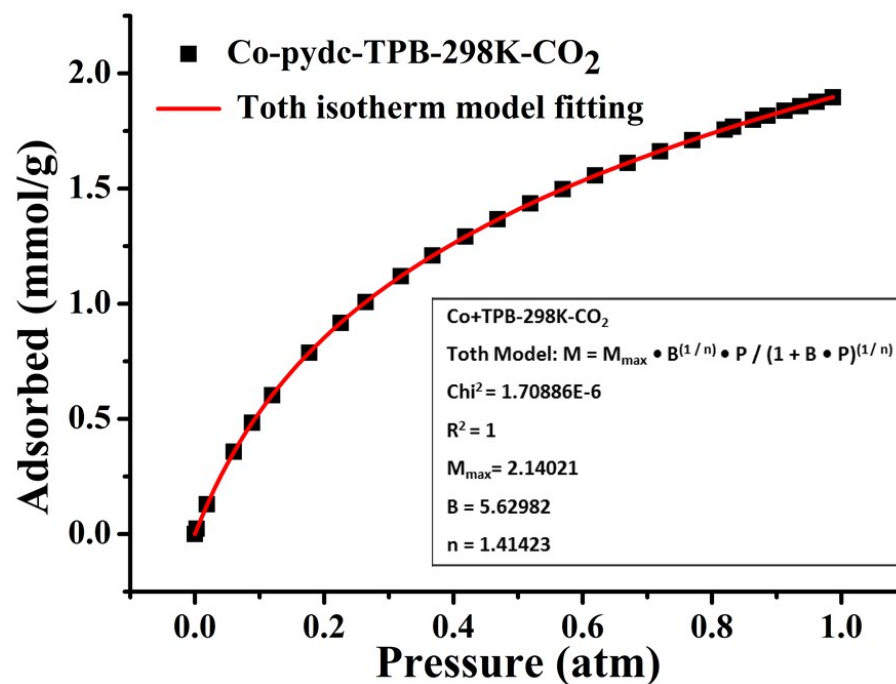


Fig. S16. CO₂ isotherm adsorption of activated Co-pydc-TPB and fitting based on Toth isotherm model; M_{\max} , maximum uptake; B and n, fitting constants; R^2 fitting error; K, Henry's law constant: 7.263 mmol g⁻¹ atm⁻¹.

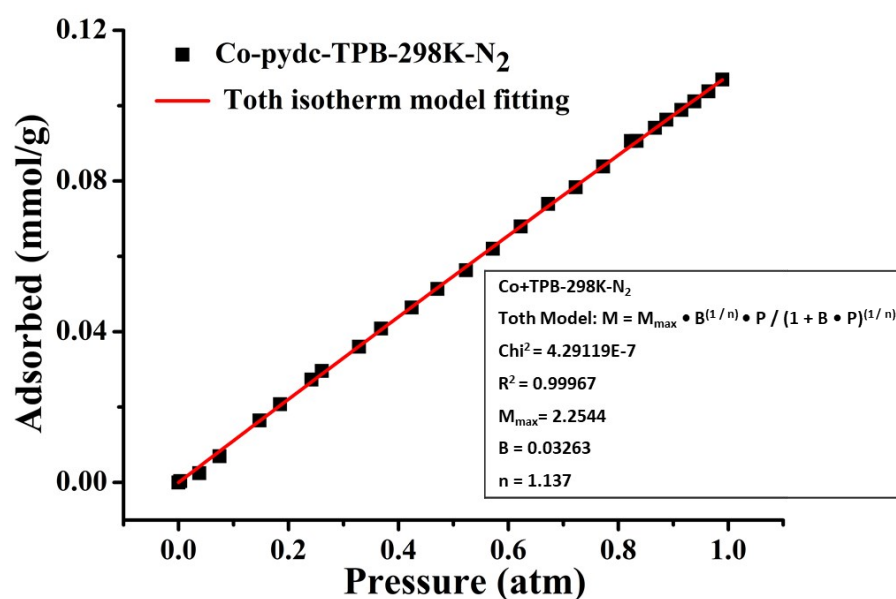


Fig. S17. N₂ isotherm adsorption of activated Co-pydc-TPB and fitting based on Toth isotherm model; M_{\max} , maximum uptake; B and n, fitting constants; R^2 fitting error; K, Henry's law constant: 0.111 mmol g⁻¹ atm⁻¹.

Henry's law selectivity (upper limit selectivity), gas component CO₂ over N₂:

$$S_{\text{CO}_2/\text{N}_2} = K_{\text{CO}_2}/K_{\text{N}_2} = 65$$

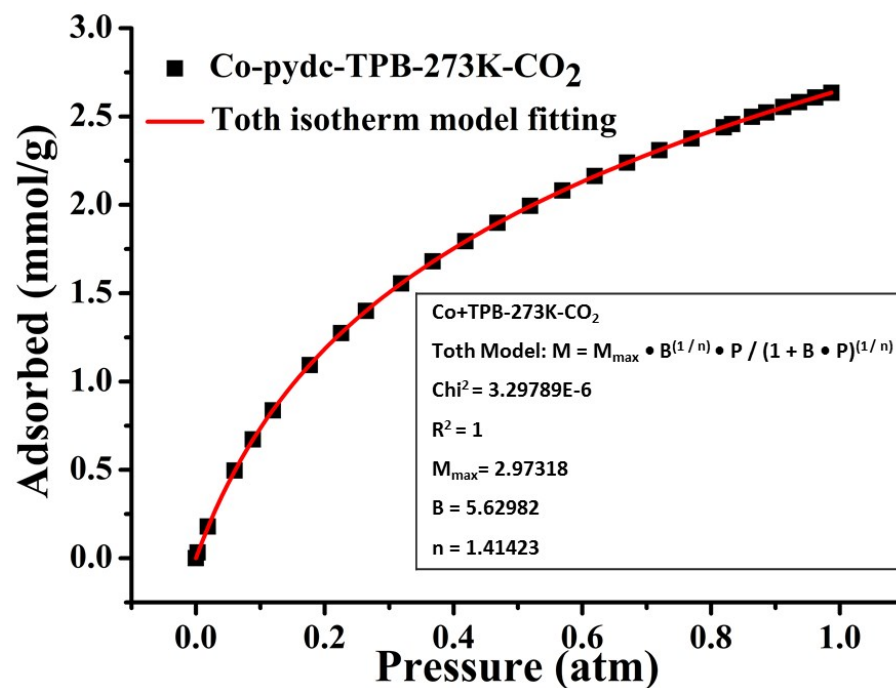


Fig. S18. CO₂ isotherm adsorption of activated Co-pydc-TPB and fitting based on Toth isotherm model; M_{\max} , maximum uptake; B and n, fitting constants; R^2 fitting error; K, Henry's law constant: 10.090 mmol g⁻¹ atm⁻¹.

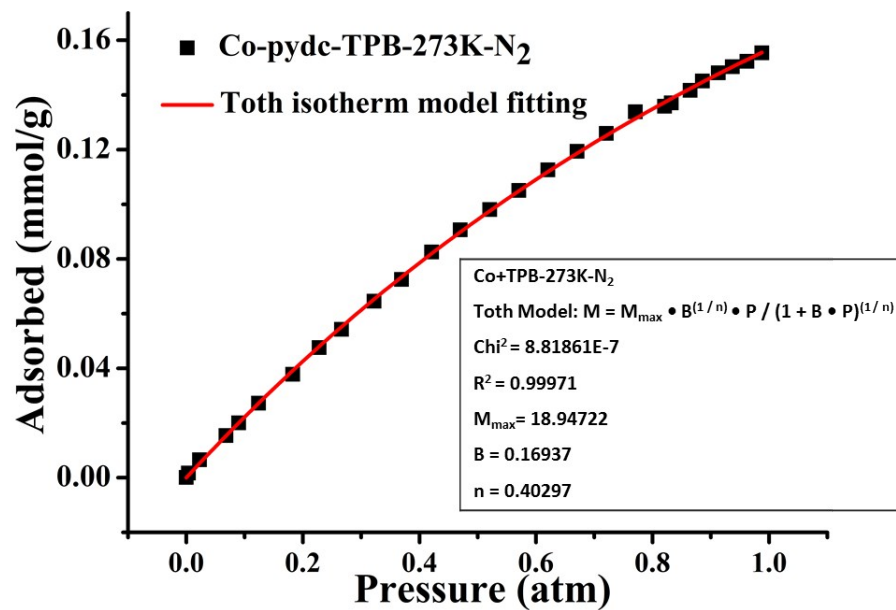


Fig. S19. N₂ isotherm adsorption of activated Co-pydc-TPB and fitting based on Toth isotherm model; M_{\max} , maximum uptake; B and n, fitting constants; R^2 fitting error; K, Henry's law constant: 0.231 mmol g⁻¹ atm⁻¹.

Henry's law selectivity (upper limit selectivity), gas component CO₂ over N₂:

$$S_{\text{CO}_2/\text{N}_2} = K_{\text{CO}_2}/K_{\text{N}_2} = 44$$

Table S1. Crystal data and structure refinement for Co-pydc, Co-pydc-TPB and Co-pydc-TPB-activated.

| Compound | Co-pydc | Co-pydc-TPB | Co-pydc-TPB-activated |
|--|--|--|--|
| Empirical formula | C ₂₉ H ₁₈ Co ₃ NO ₁₆ | C ₅₀ H ₂₈ Co ₃ N ₄ O ₁₃ | C ₅₀ H ₂₈ Co ₃ N ₄ O ₁₃ |
| Formula weight | 813.23 | 1069.67 | 1069.67 |
| Temperature/K | 100.01(10) | 150.00(10) | 150.00(10) |
| Crystal system | hexagonal | hexagonal | hexagonal |
| Space group | <i>P</i> -62 <i>c</i> | <i>P</i> -62 <i>c</i> | <i>P</i> -62 <i>c</i> |
| <i>a</i> /Å | 14.5594(5) | 14.3390(2) | 14.3406(2) |
| <i>b</i> /Å | 14.5594(5) | 14.3390(2) | 14.3406(2) |
| <i>c</i> /Å | 13.7247(7) | 14.3590(3) | 14.1626(4) |
| α /° | 90 | 90 | 90 |
| β /° | 90 | 90 | 90 |
| γ /° | 120 | 120 | 120 |
| Volume/Å ³ | 2519.5(2) | 2556.78(11) | 2522.37(10) |
| <i>Z</i> | 2 | 2 | 2 |
| ρ_{calc} /cm ³ | 1.071 | 1.389 | 1.407 |
| μ /mm ⁻¹ | 1.025 | 8.085 | 8.195 |
| F(000) | 814.0 | 1082.0 | 1080.0 |
| Crystal size/mm ³ | 0.15 × 0.1 × 0.1 | 0.1 × 0.1 × 0.1 | 0.1 × 0.1 × 0.1 |
| Radiation | MoK α (λ = 0.71073) | CuK α (λ = 1.54184) | CuK α (λ = 1.54184) |
| 2 θ range for data collection/° | 4.386 to 52.988 | 7.118 to 144.79 | 7.118 to 132.98 |
| Index ranges | -16 ≤ <i>h</i> ≤ 19, -19 ≤ <i>k</i> ≤ 15, -18 ≤ <i>l</i> ≤ 16 | -10 ≤ <i>h</i> ≤ 17, -14 ≤ <i>k</i> ≤ 13, -15 ≤ <i>l</i> ≤ 17 | -9 ≤ <i>h</i> ≤ 16, -17 ≤ <i>k</i> ≤ 14, -11 ≤ <i>l</i> ≤ 17 |
| Reflections collected | 12677 | 8196 | 9154 |
| Independent reflections | 1821 [R _{int} = 0.0462, R _{sigma} = 0.0382] | 1654 [R _{int} = 0.0407, R _{sigma} = 0.0383] | 1526 [R _{int} = 0.0632, R _{sigma} = 0.0406] |

| | | | |
|---|----------------------------------|----------------------------------|----------------------------------|
| Data/restraints/parameters | 1821/16/84 | 1654/6/128 | 1526/20/137 |
| Goodness-of-fit on F^2 | 1.077 | 1.114 | 1.053 |
| Final R indexes [$I \geq 2\sigma(I)$] | $R_1 = 0.0259$, $wR_2 = 0.0673$ | $R_1 = 0.0646$, $wR_2 = 0.1835$ | $R_1 = 0.0593$, $wR_2 = 0.1619$ |
| Final R indexes [all data] | $R_1 = 0.0282$, $wR_2 = 0.0680$ | $R_1 = 0.0695$, $wR_2 = 0.1914$ | $R_1 = 0.0630$, $wR_2 = 0.1650$ |
| Largest diff. peak/hole / $e \text{ \AA}^{-3}$ | 0.32/-0.21 | 0.61/-0.63 | 0.54/-0.41 |
| CCDC number | 1851529 | 1851530 | 1851531 |
| $^a R_1 = \frac{\sum F_o - F_c }{\sum F_o }$. $^b wR_2 = \left[\frac{\sum w(F_o^2 - F_c^2)^2}{\sum w(F_o^2)^2} \right]^{1/2}$ | | | |

Table S2. Selected bond lengths (Å) and bond angles (°) for Co-pydc

| bond lengths (Å) | | | |
|---|------------|--------------------------------------|------------|
| Co1–O4 ¹ | 2.084(2) | O4–Co1 ⁴ | 2.084(2) |
| Co1–O4 ² | 2.084(2) | Co1–O1 | 2.0237(5) |
| Co1–O3 ³ | 2.063(2) | O1–Co1 ² | 2.0237(5) |
| Co1–O3 | 2.063(2) | O1–Co1 ⁴ | 2.0237(5) |
| Co1–O2 | 2.111(3) | | |
| bond angles (°) | | | |
| O4 ¹ –Co1–O4 ² | 89.73(14) | O3 ³ –Co1–O4 ² | 173.98(10) |
| O4 ¹ –Co1–O2 | 88.02(10) | O3–Co1–O4 ² | 90.63(11) |
| O4 ² –Co1–O2 | 88.02(10) | O3–Co1–O4 ¹ | 173.98(10) |
| O3 ³ –Co1–O4 ¹ | 90.63(11) | O3–Co1–O3 ³ | 88.39(16) |
| O3–Co1–O2 | 85.98(10) | O3 ³ –Co1–O2 | 85.98(10) |
| O1–Co1–O4 ² | 93.55(7) | O1–Co1–O4 ¹ | 93.55(7) |
| O1–Co1–O3 ³ | 92.43(7) | O1–Co1–O3 | 92.43(7) |
| O1–Co1–O2 | 177.78(11) | C1–O4–Co1 ⁴ | 132.9(2) |
| Co1–O1–Co1 ⁴ | 120.0 | C1–O3–Co1 | 135.9(2) |
| Co1 ² –O1–Co1 ⁴ | 120.0 | Co1 ² –O1–Co1 | 120.0 |
| Symmetry codes: ¹ +Y-X,1-X,3/2-Z; ² +Y-X,1-X,+Z; ³ +X,+Y,3/2-Z; ⁴ 1-Y,1+X-Y,+Z. | | | |

Table S3. Selected bond lengths (Å) and bond angles (°) for Co-pydc-TPB

| bond lengths (Å) | | | |
|---|------------|---------------------------------------|------------|
| Co1–O1 | 2.0385(13) | Co1–N1 | 2.158(6) |
| Co1–O2 | 2.085(5) | O1–Co1 ⁴ | 2.0385(14) |
| Co1–O2 ¹ | 2.085(5) | O1–Co1 ³ | 2.0385(13) |
| Co1–O3 ² | 2.063(5) | O3–Co1 ⁴ | 2.063(5) |
| Co1–O3 ³ | 2.063(5) | | |
| bond angles (°) | | | |
| O1–Co1–O2 | 95.06(18) | O3 ³ –Co1–O2 | 89.4(3) |
| O1–Co1–O2 ¹ | 95.06(18) | O3 ² –Co1–O2 | 174.3(2) |
| O1–Co1–O3 ² | 90.63(16) | O3 ³ –Co1–O3 ² | 90.2(4) |
| O1–Co1–O3 ³ | 90.63(16) | O3 ² –Co1–N1 | 87.6(5) |
| O1–Co1–N1 | 172.6(5) | O3 ³ –Co1–N1 | 82.2(6) |
| O2–Co1–O2 ¹ | 90.5(4) | Co1 ² –O1–Co1 ⁴ | 120.0 |
| O2–Co1–N1 | 86.7(5) | Co1 ² –O1–Co1 | 120.000(1) |
| O2 ¹ –Co1–N1 | 92.1(6) | Co1 ⁴ –O1–Co1 | 120.000(1) |
| O3 ² –Co1–O2 ¹ | 89.4(3) | C1–O2–Co1 | 129.7(5) |
| O3 ³ –Co1–O2 ¹ | 174.3(2) | C1–O3–Co1 ⁴ | 137.0(5) |
| Symmetry codes: ¹ +X,+Y,3/2-Z; ² +Y-X,1-X,3/2-Z; ³ +Y-X,1-X,+Z; ⁴ 1-Y,1+X-Y,+Z. | | | |

Table S4. Selected bond lengths (Å) and bond angles (°) for Co-pydc-TPB-activated

| bond lengths (Å) | | | |
|---|------------|---------------------------------------|------------|
| Co1–O1 | 2.038(2) | O1–Co1 ⁴ | 2.038(2) |
| Co1–O3 ¹ | 2.096(10) | O1–Co1 ² | 2.038(2) |
| Co1–O3 ² | 2.096(10) | O3–Co1 ⁴ | 2.096(10) |
| Co1–O2 | 2.049(10) | Co1–N1 | 2.179(19) |
| Co1–O2 ³ | 2.049(10) | | |
| bond angles (°) | | | |
| O1–Co1–O3 ¹ | 94.1(3) | O2 ³ –Co1–O3 ¹ | 176.1(5) |
| O1–Co1–O3 ² | 94.1(3) | O2 ³ –Co1–O3 ² | 88.2(7) |
| O1–Co1–O2 ³ | 89.8(3) | O2–Co1–O2 ³ | 91.0(9) |
| O1–Co1–O2 | 89.8(3) | O2 ³ –Co1–N1 | 86.4(4) |
| O1–Co1–N1 | 174.5(4) | C2–N1–Co1 | 116.3(13) |
| O3 ¹ –Co1–O3 ² | 92.3(8) | C3–N1–Co1 | 122.3(18) |
| O3 ¹ –Co1–N1 | 89.7(4) | O2–Co1–O3 ¹ | 88.2(7) |
| O3 ² –Co1–N1 | 89.7(4) | O2–Co1–O3 ² | 176.1(5) |
| Co1–O1–Co1 ⁴ | 120.001(1) | O2–Co1–N1 | 86.4(4) |
| C1–O3–Co1 ⁴ | 130.5(10) | C1–O2–Co1 | 139.0(10) |
| Co1 ¹ –O1–Co1 | 119.999(1) | Co1 ¹ –O1–Co1 ⁴ | 120.000(1) |
| Symmetry codes: ¹ +Y-X,1-X,+Z; ² +Y-X,1-X,3/2-Z; ³ +X,+Y,3/2-Z; ⁴ 1-Y,1+X-Y,+Z. | | | |

References:

1. G. Marin, M. Andruh, A. M. Madalan, A. J. Blake, C. Wilson, N. R. Champness and M. Schroder, *Crystal Growth & Design*, 2008, **8**, 964-975.
2. L. L. Tan, H. Li, Y. Tao, S. X. Zhang, B. Wang and Y. W. Yang, *Adv Mater*, 2014, **26**, 7027-7031.