

Electronic Supplementary Information (ESI)

Synthesis of covalent triazine-based frameworks with high CO₂ adsorption and selectivity

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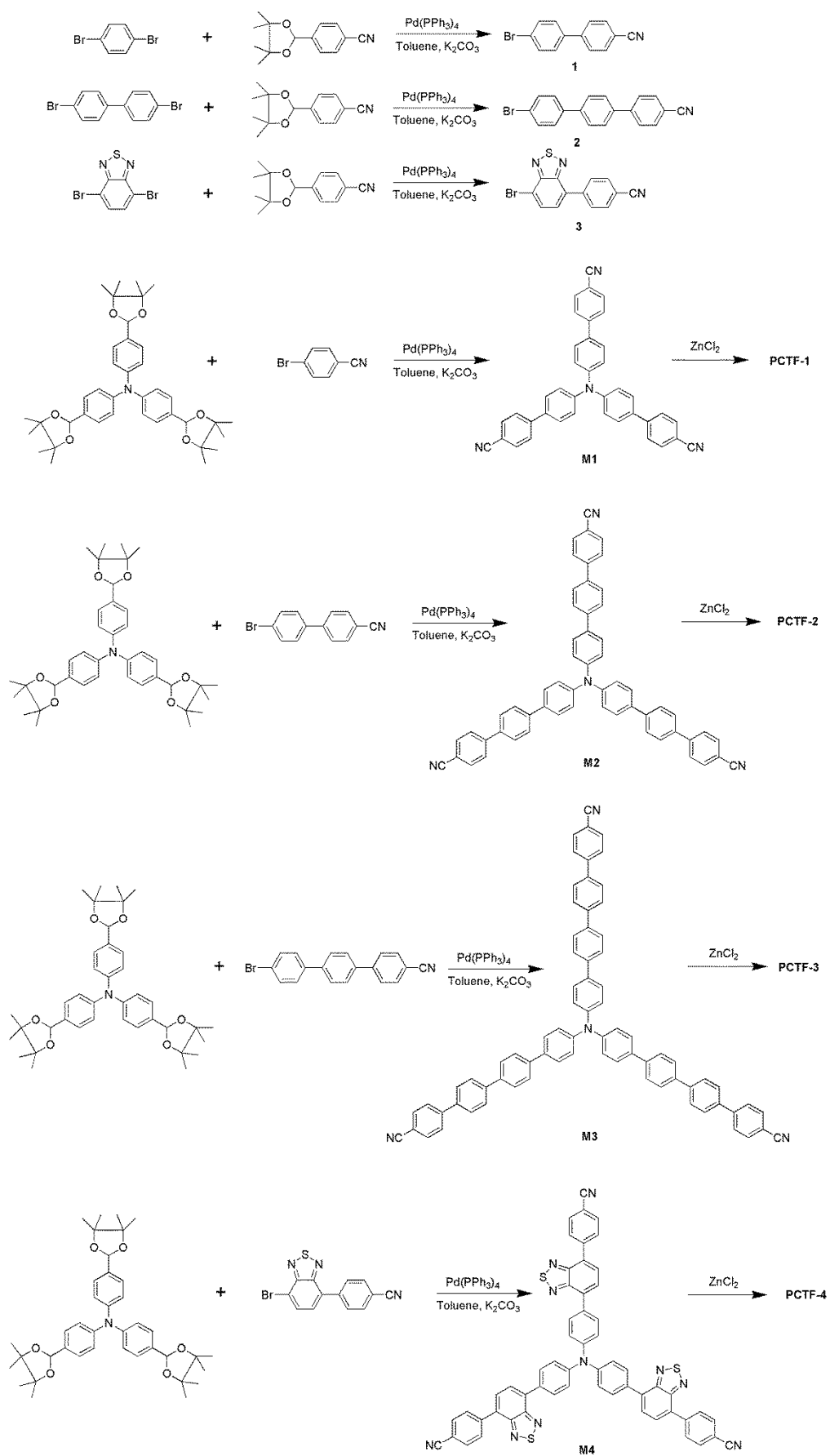
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1. Experimental Section

All reagents and solvents, unless otherwise specified, were obtained from J&K, Aldrich and Aladdin and were used as received. Anhydrous tetrahydrofuran (THF) and toluene were distilled over sodium/benzophenone and calcium hydride under N₂ prior to use.



Scheme S1 Synthetic routes for the preparation of monomers and polymers.

4'-Bromo-4-cyano-biphenyl (1): A mixture of 4-cyanophenylboronic acid (2.29 g, 10 mmol), 1,4-dibromobenzene (3.54 g, 15 mmol), Pd(PPh₃)₄ (289 mg, 0.25 mmol) and 3 drops of aliquat 336 was heated in toluene (40 mL) and 2 M K₂CO₃ (20 mL) at 90 °C for 10 h under nitrogen atmosphere. Then the mixture was extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate, after concentrating the crude product, column chromatography on silica gel with petroleum ether and ethyl acetate (3:1/v:v) gave **1** as off white solid (1.44 g, 5.6 mmol) in 56% yield. ¹H NMR (600 MHz, CDCl₃): δ(ppm) 7.76 (d, *J* = 8.4 Hz, 2H), 7.68 (d, *J* = 8.4 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H).

4'-Bromo-4-cyano-terphenyl (2): A mixture of 4-cyanophenylboronic acid (2.29 g, 10 mmol), 4,4'-dibromobiphenyl (4.68 g, 15 mmol), Pd(PPh₃)₄ (289 mg, 0.25 mmol) and 3 drops of aliquat 336 was heated in toluene (40 mL) and 2 M K₂CO₃ (20 mL) at 90 °C for 10 h under nitrogen atmosphere. Then the mixture was extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate, after concentrating the crude product, column chromatography on silica gel with petroleum ether and ethyl acetate (2:1/v:v) gave **2** as off white solid (2.04 g, 6.1 mmol) in 61% yield. ¹H NMR (600 MHz, CDCl₃): δ(ppm) 7.79-7.75 (m, 4H), 7.70 (s, 4H), 7.63 (d, *J* = 8.4 Hz, 2H), 7.53 (d, *J* = 8.5 Hz, 2H).

4-(7-Bromo-2,1,3-benzothiadiazol-4-yl)-benzonitrile (3): A mixture of 4-cyanophenylboronic acid (2.29 g, 10 mmol), 4,7-dibromobenzothiadiazole (4.41 g, 15 mmol), Pd(PPh₃)₄ (289 mg, 0.25 mmol) and 3 drops of aliquat 336 was heated in toluene (40 mL) and 2 M K₂CO₃ (20 mL) at 90 °C for 10 h under nitrogen atmosphere.

Then the mixture was extracted with dichloromethane. The organic layer was dried over anhydrous sodium sulfate, after concentrating the crude product, column chromatography on silica gel with dichloromethane and petroleum ether (2:1/v:v) gave **3** as yellow solid (1.64 g, 5.2 mmol) in 52% yield. ^1H NMR (600 MHz, CDCl_3): $\delta(\text{ppm})$ 8.07 (d, $J = 8.3$ Hz, 2H), 8.00 (d, $J = 7.5$ Hz, 1H), 7.85 (d, $J = 8.4$ Hz, 2H), 7.66 (d, $J = 7.5$ Hz, 1H).

M1: A mixture of tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine (748 mg, 1.2 mmol), 4-bromobenzonitrile (983 mg, 5.4 mmol), $\text{Pd}(\text{PPh}_3)_4$ (21 mg, 0.018 mmol) and 3 drops of aliquat 336 was heated in toluene (15 mL) and 2 M K_2CO_3 (8 mL) at 90 °C for 16 h under nitrogen atmosphere. Then the mixture was extracted with chloroform (100 mL) and washed with water (30 mL). The organic layer was dried over anhydrous sodium sulfate, after concentrating the crude product, column chromatography on silica gel with dichloromethane and petroleum ether (2:1) gave **M1** (400 mg, 0.73 mmol) in 61% yield. ^1H NMR (600 MHz, CDCl_3): $\delta(\text{ppm})$ 7.75 (d, $J = 8.3$ Hz, 6H), 7.71 (d, $J = 8.3$ Hz, 6H), 7.58 (d, $J = 8.6$ Hz, 6H), 7.30 (d, $J = 8.4$ Hz, 6H). ^{13}C NMR (150 MHz, CDCl_3): $\delta(\text{ppm})$ 147.52, 144.74, 134.00, 132.70, 128.30, 127.17, 124.72, 118.98, 110.61.

M2: A mixture of tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine (623 mg, 1.0 mmol), 4'-bromo-4-cyano-biphenyl (1.16 g, 4.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (18 mg, 0.015 mmol) and 3 drops of aliquat 336 was heated in toluene (14 mL) and 2 M K_2CO_3 (7 mL) at 90 °C for 16 h under nitrogen atmosphere. Then the mixture was extracted with chloroform (100 mL) and washed with water (30 mL). The organic

layer was dried over anhydrous sodium sulfate, after concentrating the crude product, column chromatography on silica gel with chloroform gave **M2** (389 mg, 0.5 mmol) in 50% yield. ^1H NMR (600 MHz, CDCl_3): δ (ppm) 7.76-7.70 (m, 18H), 7.68 (d, J = 8.3 Hz, 6H), 7.60 (d, J = 8.6 Hz, 6H), 7.29 (d, J = 8.5 Hz, 6H). ^{13}C NMR (150 MHz, CDCl_3) δ 147.06, 145.09, 140.82, 137.60, 134.75, 132.65, 127.94, 127.65, 127.49, 127.28, 124.57, 118.96, 110.89.

M3: A mixture of tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine (623 mg, 1.0 mmol), 4'-bromo-4-cyano-terphenyl (1.50 g, 4.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (18 mg, 0.015 mmol) and 3 drops of aliquat 336 was heated in toluene (16 mL) and 2 M K_2CO_3 (8 mL) at 90 °C for 16 h under nitrogen atmosphere. Then the mixture was extracted with chloroform (100 mL) and washed with water (30 mL). The organic layer was dried over anhydrous sodium sulfate, after concentrating the crude product, column chromatography on silica gel with chloroform gave **M3** (250 mg, 0.25 mmol) in 25% yield. ^1H NMR (600 MHz, CDCl_3): δ (ppm) 7.81-7.72 (m, 36H), 7.64 (d, J = 8.6 Hz, 6H), 7.32 (d, J = 8.5 Hz, 6H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm) 146.96, 145.12, 141.01, 139.95, 138.67, 138.00, 135.03, 132.70, 127.88, 127.70, 127.63, 127.57, 127.46, 127.18, 124.56, 118.97, 110.98.

M4: A mixture of tris(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)amine (623 mg, 1.0 mmol), 4-(7-bromo-2,1,3-benzothiadiazol-4-yl)-benzonitrile (1.42 g, 4.5 mmol), $\text{Pd}(\text{PPh}_3)_4$ (18 mg, 0.015 mmol) and 3 drops of aliquat 336 was heated in toluene (16 mL) and 2 M K_2CO_3 (8 mL) at 90 °C for 16 h under nitrogen atmosphere. Then the mixture was extracted with chloroform (100 mL) and washed with water (30

mL). The organic layer was dried over anhydrous sodium sulfate, after concentrating the crude product, column chromatography on silica gel with dichloromethane and petroleum ether (10:1/v:v) gave **M4** (390mg, 0.41 mmol) in 41% yield. ^1H NMR (600 MHz, CDCl_3): δ (ppm) 8.17 (d, J = 8.3 Hz, 6H), 8.04 (d, J = 8.6 Hz, 6H), 7.92-7.85 (m, 12H), 7.49 (d, J = 8.6 Hz, 6H). ^{13}C NMR (150 MHz, CDCl_3): δ (ppm) 154.01, 153.73, 147.59, 141.81, 134.13, 132.41, 131.92, 130.69, 130.42, 129.81, 128.98, 127.32, 124.53, 118.85, 111.83.

PCTF-1: **M1** (329 mg, 0.6 mmol) and the melt salt ZnCl_2 (818 mg, 6 mmol) were transferred into a pyrex ampoule (3 x 12 cm) under an inert atmosphere. The ampoule was evacuated, sealed and heated to 400 °C for 40 h. Then the mixture was cooled to room temperature, and the black powder was stirred in diluted HCl (75 mL) for 5h. After the filtration, the crude products were washed with water, methanol, dichloromethane and acetone, respectively. Further purification of the polymers was carried out by Soxhlet extraction with tetrahydrofuran for 24 h. The target product was dried in vacuum to give black powder, yield 94%. Calcd: C 85.38%, N 10.21%, H 4.41%. Found: C 78.16%, N 3.74%, H 5.73%.

PCTF-2: The same procedure with PCTF-1 network gave black powder, yield 90%. Calcd: C 88.12%, N 7.21%, H 4.67%. Found: C 82.80%, N 2.65%, H 5.54%.

PCTF-3: The same procedure with PCTF-1 network gave black powder, yield 93%. Calcd: C 89.61%, N 5.57%, H 4.81%. Found: C 83.32%, N 1.44%, H 5.21%.

PCTF-4: The same procedure with PCTF-1 network gave black powder, yield 96%.

Calcd: C 71.98%, N 14.73%, H 3.18%, S 10.11%. Found: C 67.59%, N 4.86%, H 4.62%, S 8.63%.

2. Thermogravimetric Analysis (TGA) of PCTFs

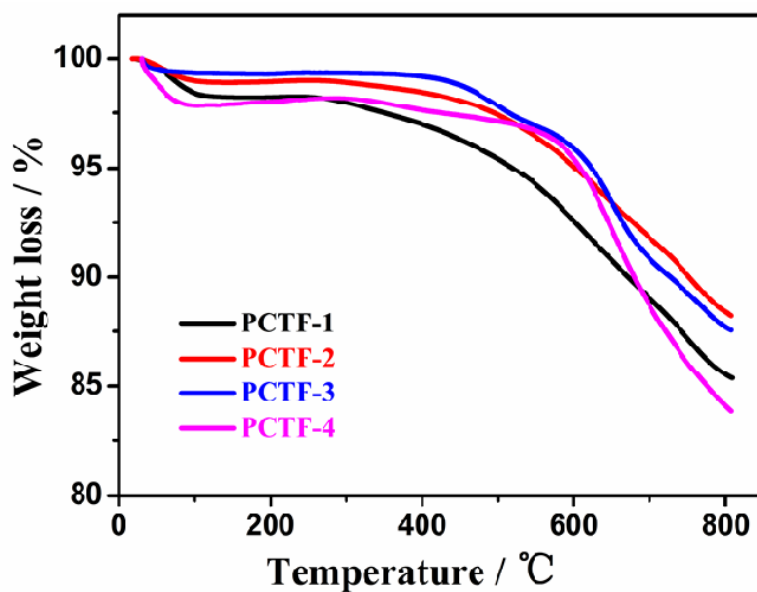


Figure S1. TGA plots of PCTFs under N₂ atmosphere.

3. Powder X-ray Diffraction Patterns (PXRD)

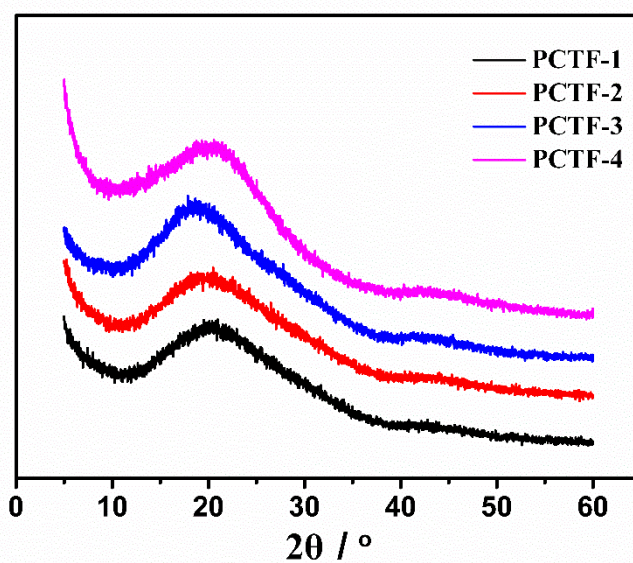


Figure S2. Powder X-ray patterns of PCTFs.

4. Solid-state ^{13}C NMR

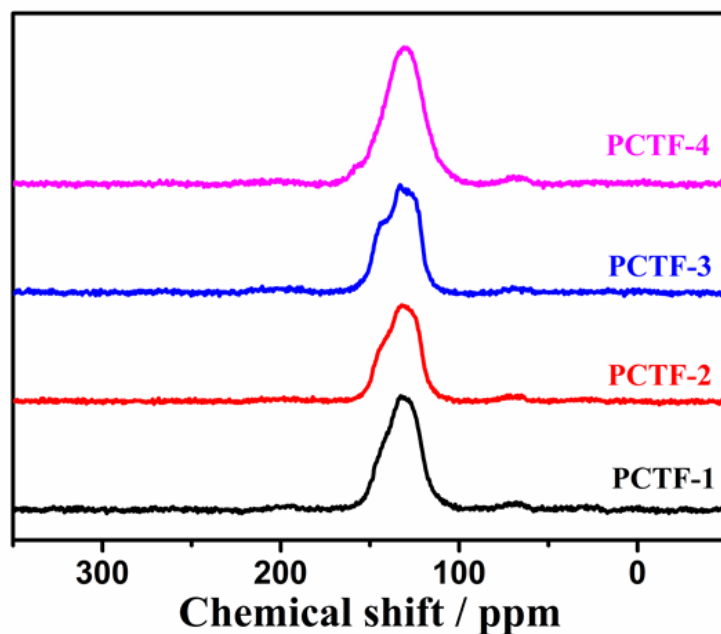


Figure S3. Solid state magic angle spinning ^{13}C CP/MAS NMR spectra of PCTFs.

5. Elemental Analysis of PCTFs

Table S1 Elemental analysis of PCTFs

Polymers	Calculated (%)						Found (%)					
	C	H	N	S	C/H	C/N	C	H	N	S	C/H	C/N
PCTF-1	85.38	4.41	10.21	—	19.36	8.36	78.16	5.73	3.74	—	13.64	20.90
PCTF-2	88.12	4.67	7.21	—	18.87	12.22	82.80	5.54	2.65	—	14.95	31.25
PCTF-3	89.61	4.81	5.57	—	18.63	16.09	83.32	5.21	1.44	—	15.99	57.86
PCTF-4	71.98	3.18	14.73	10.11	22.64	4.89	67.59	4.62	4.86	8.63	14.63	13.91

The elemental analyses of PCTF-1 to PCTF-4 give substantially low nitrogen contents and concomitantly higher C/N ratios than those of calculated, which were probably caused by the carbonization of the polymers.

6. Gas Uptake (CO_2 , CH_4) at 298 K and 1 bar

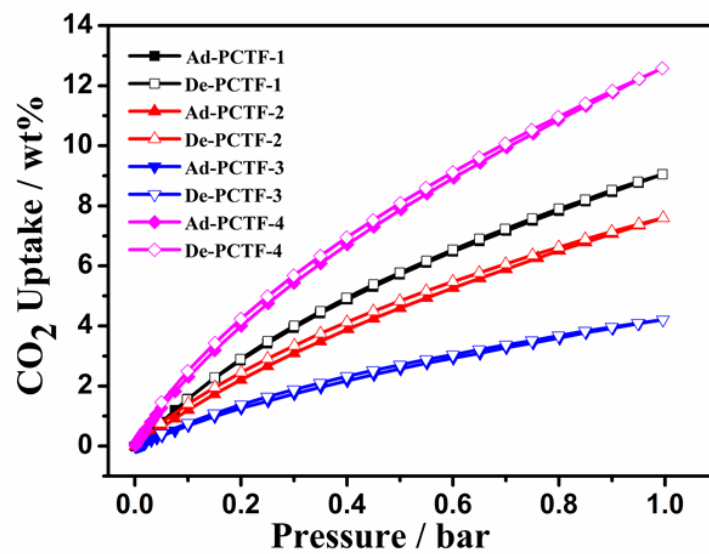


Figure S4. CO₂ uptake isotherms at 298 K.

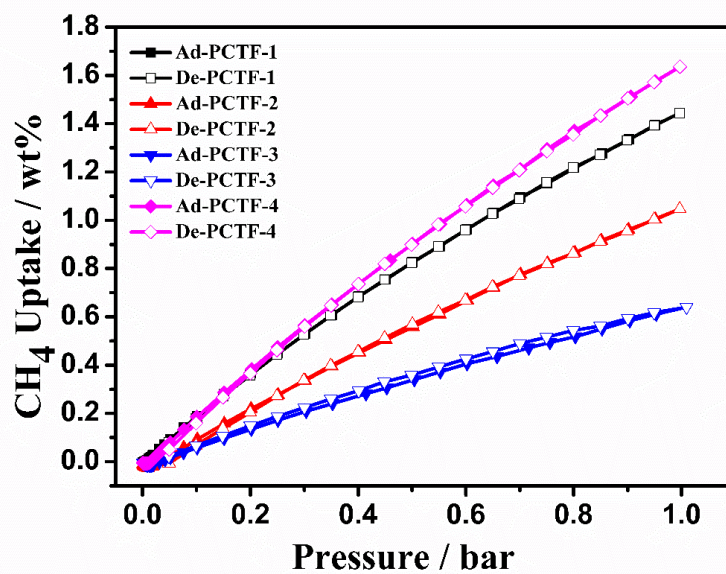


Figure S5. CH₄ uptake isotherms at 298 K.

7. CO₂ Uptake in the humidity condition

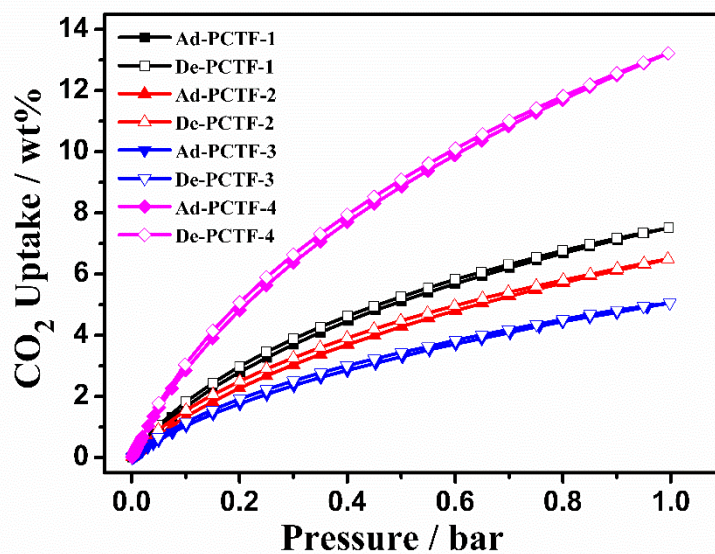


Figure S6. CO₂ uptake isotherms at 273 K under 70% humidity.

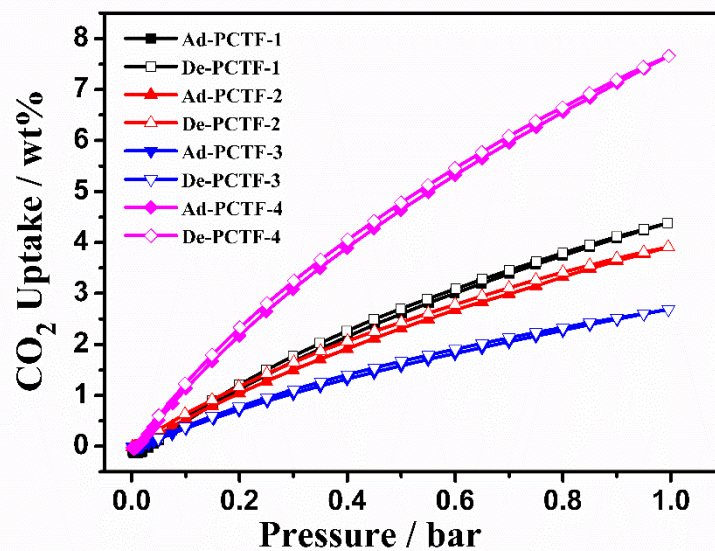


Figure S7. CO₂ uptake isotherms at 298 K under 70% humidity.