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Electronic Supplementary Information

Highly selective room temperature acetylene sorption by an unusual triacetylenic phosphine MOF

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Experimental

General Comments

All syntheses were carried out under a N_2 atmosphere using standard Schleck line techniques. All glassware was oven dried before use (90 °C) for at least 18 hours or flame dried. Hydrochloric acid and potassium hydroxide were purchased through Fischer Scientific. CuI was purchased from Strem Chemicals. $PdCl_2(PPh_3)_2$, TMS acetylene, and methyl-4-iodobenzoate were all purchased from Combi-Blocks. Phosphorous trichloride (PCl_3) was purchased from Sigma Aldrich and was then purified through distillation. All organic solvents were purchased from Fischer Scientific. Tetrahydrofuran (THF) was prepared by distillation (Na/benzophenone) and dried over molecular sieves (4 Å). Triethylamine (TEA) was prepared by distillation (CaH_2) and dried over molecular sieves (4 Å). All other solvents were deoxygenated *via* bubbling N_2 gas for no less than fifteen minutes and dried over sieves.

General Instrumentation

All analyses were performed in house. All nuclear magnetic resonance (NMR) shifts were software standardized and are expressed as δ in parts per million (ppm). Coupling constants (J) are reported in Hz and apparent peak multiplicities are noted. ^{1}H, ^{13}C, and ^{31}P NMR analysis were performed on a Varian Unity 300 MHz NMR spectrometer and a Bruker Prodigy 500 MHz NMR spectrometer. High resolution mass spectrometry was performed on an Agilent Technologies 6530 Accurate Mass QTofLC/MS (ESI). Infrared spectroscopy (IR) was performed on a Thermo Scientific iS50 FT-IR spectrometer. Single Crystal X-Ray Crystallography (SCXRD) was performed on a Bruker Nonius Kappa CCD with Apex II detector using MoKα (0.709 Å) instrument is equipped with an Oxford 600 series Cryostream. Powder X-ray Diffraction (PXRD) was performed on a Rigaku R-Axis Spider diffractometer using CuKα (1.5405 Å) radiation operating at 40 kV and 40 mA. X-ray spectra were collected using a sample rotation speed of 15°/s with data collected in the range 5–40° 2θ. Simulated PXRD was generated using single crystal reflection data *via* SimPowPatt facility in PLATON. Thermogravimetric analyses (TGA) were collected

using a TA Instruments Q50 system using high purity N_2 carrier gas. in the range of 25–800 °C. A ramp rate of 3.50 °C s^{-1} was applied between 25–500 °C and 5.00 °C s^{-1} between 500–800 °C. Inductively coupled plasma optical emission spectrometry (ICP-OES) was conducted on a Varian 710 using pre-dried NaCl and KCl as standards. The standards were dissolved in nano pure 2 % HNO_3 and further diluted for calibration points at 0 ppm, 0.25 ppm, 0.625 ppm, 1.25 ppm, 2.50 ppm, 5.00 ppm, and 10.00 ppm. ICP-OES samples were prepared by digesting Mn-PCM-48 in a CEM-MARS-5 microwave reactor at 120 °C for 2 h in a 1:1 mixture (v:v) of 2 % HNO_3 and trace metal grade aqua regia. Elemental microanalyses were performed by Midwest Microlab LLC (Indianapolis).

Gas sorption measurements

A Micromeritics ASAP 2020 surface area analyzer was used to measure gas adsorption isotherms. To remove all the guest solvents in the framework, the fresh samples were first solvent-exchanged with dry acetone at least 10 times within two days, and degassed at 273 K for one day, and then at room temperature for additional 24 hours until the outgas rate was 5 mmHg min^{-1} prior to measurements. The sorption measurement was maintained at 196 K under dry ice-acetone bath. An ice-water bath (slush) and water bath were used for adsorption isotherms at 273 and 296 K, respectively.

Fitting of pure component isotherms

Experimental data on pure component isotherms for C_2H_2, CO_2, CH_4, and N_2 in Mn-PCM-48 were measured at 296 and 273 K. The pure component isotherm data for C_2H_2, CO_2, CH_4, and N_2 were fitted with the Dual site Langmuir-Freundlich (DSLF) model:

$$N = N_1^{\max} \frac{b_1 p^{1/n1}}{1 + b_1 p^{1/n1}} + N_2^{\max} \frac{b_2 p^{1/n2}}{1 + b_2 p^{1/n2}} \quad \text{(S1)}$$

where p (unit: Kpa) is the pressure of the bulk gas at equilibrium with the adsorbed phase, N (unit: mol/Kg) is the adsorbed amount per mass of adsorbent, N_1^{max} and N_2^{max} (unit: mol/Kg) are the saturation capacities of sites 1 and 2, b_1 and b_2 (unit: 1/kPa) are the affinity coefficients of sites 1 and 2, and n_1 and

n_2 represent the deviations from an ideal homogeneous surface. Here, the single-component C_2H_2, CO_2, CH_4, and N_2 adsorption isotherms have been fit to enable the application of IAST in simulating the performance of Mn-PCM-48 under a mixed component gas. Adsorption isotherms and gas selectivity calculated by IAST for mixed C_2H_2/CH_4 (50/50, v/v), C_2H_2/CO_2 (50/50, v/v), CO_2/N_2 (15/85, v/v), and CO_2/CH_4 (50/50, v/v) in the Mn-PCM-48.

IAST calculations of adsorption selectivities

The selectivity of preferential adsorption of component *1* over component *2* in a mixture containing *1* and *2*, can be formally defined as:

$$S_{ads} = \frac{q_1/q_2}{p_1/p_2} \tag{S2}$$

In equation (2), q_1 and q_2 are the absolute component loadings of the adsorbed phase in the mixture. These component loadings are also termed the uptake capacities. We calculate the values of q_1 and q_2 using the Ideal Adsorbed Solution Theory (IAST) of Myers and Prausnitz.

Q_{st} calculation information

Adsorption isotherms of PCM-48 at 273 K and 296 K and their corresponding Q_{st} *versus* loading plots are shown below. The virial-type equation (eq. S3) was used to fit the adsorption data at 273 K and 296 K. P is the pressure, n is the amount adsorbed and A_0, A_1, A_2, etc. are virial coefficients. Q_{st} is calculated as a function of surface coverage using the Clausius–Clapeyron equation (eq. S4).

$$\ln\left(\frac{n}{p}\right) = A_0 + A_1 n + A_2 n^2 + \cdots \tag{S3}$$

$$Q_{st} = R ln\left(\frac{P_1}{P_2}\right) \frac{T_1 T_2}{T_2 - T_1} \tag{S4}$$

Synthetic Details

Methyl 4-(trimethylsilylethynyl)benzoate synthesis (1).[1] Methyl 4-iodobenzoate (10.00 g, 38.2 mmol), CuI (145 mg, 0.76 mmol), and $PdCl_2(PPh_3)_2$ (268 mg, .38 mmol) were loaded into a 100 mL Schlenk flask under N_2. 50 mL of dry THF were added to the flask, followed by the addition of 12.5 mL of dry trimethylamine. After 5 minutes, 6.30 mL of (trimethylsilyl)acetylene (44.0 mmol) were then added. The resulting yellow/orange suspension was allowed to stir overnight. The reaction was then reduced and extracted with ethyl acetate and water. The organic layers were combined and dried over $MgSO_4$. The crude product was then purified using column chromatography (eluted with dichloromethane/hexanes (1:2) on silica gel) affording 8.28 g (94 %) of an orange/yellow solid. ^{1}H NMR ($CDCl_3$, 300.14 MHz) δ = 0.26 (s, 9H), 3.91 (s, 3H), 7.52 (d, 2H, J_{HH} = 9.0 Hz), 7.97 (d, 2H, J_{HH} = 9.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.48) δ = 0.01 (s), 52.39 (s), 97.84 (s), 104.19 (s), 127.90 (s), 129.51 (s), 129.82(s), 132.01 (s), 166.66 (s). FT-IR (ATR): ν_{max} (cm^{-1}) = 2952 w, 2899 w, 2159 w, 1716 m, 1602 m, 1442 m, 1405 w, 1274 s, 1244 m, 1108 m, 835 s, 758 s, 695 m, 666 m.

Parameters		
	Parameter	**Value**
1	Origin	Varian
2	Instrument	uplus
3	Solvent	CDCl3
4	Temperature	29.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	60
9	Relaxation Delay	1.0000
10	Pulse Width	3.0000
11	Acquisition Time	3.8128
12	Spectrometer Frequency	300.14
13	Spectral Width	4196.4
14	Lowest Frequency	-445.1
15	Nucleus	1H
16	Acquired Size	16000
17	Spectral Size	65536

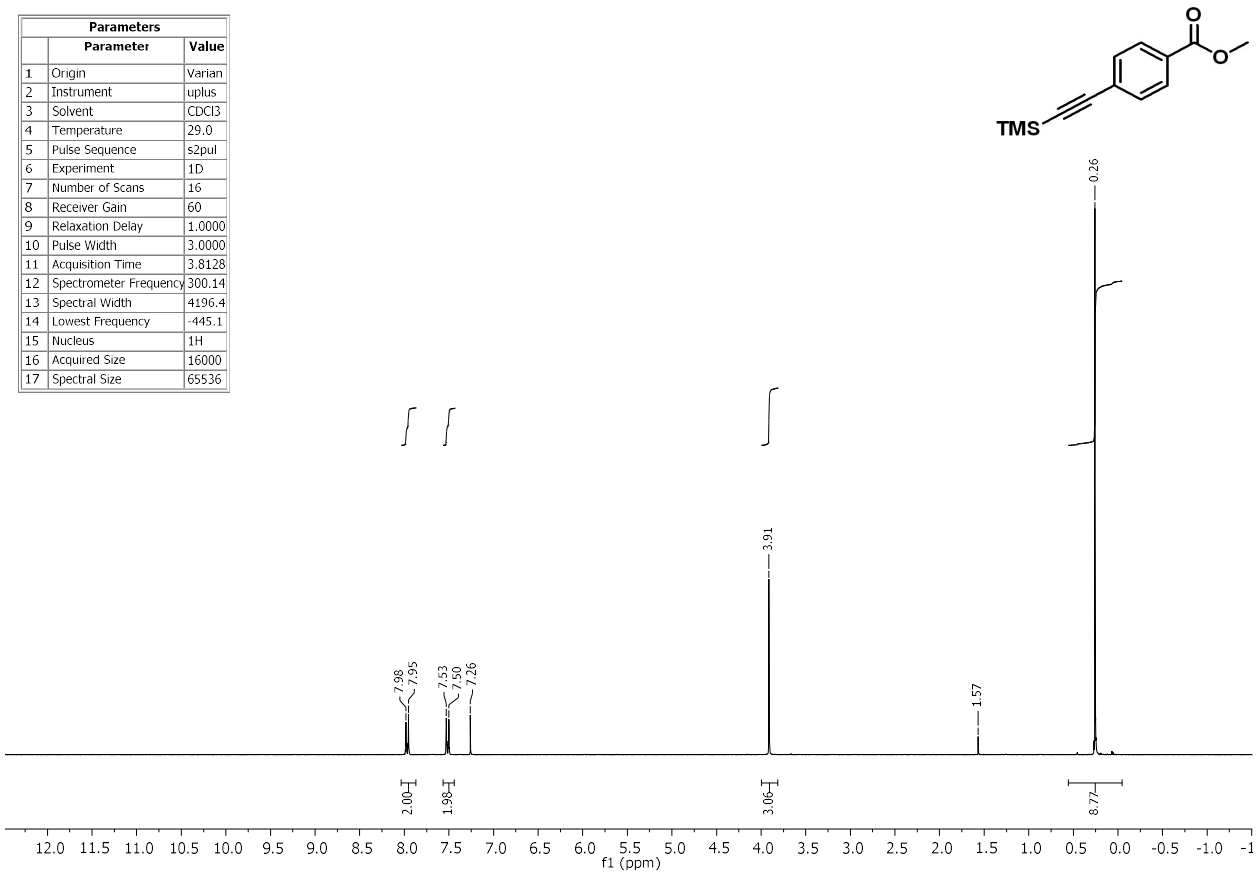

Figure S1. ^{1}H NMR spectrum of methyl 4-(trimethylsilylethynyl)benzoate

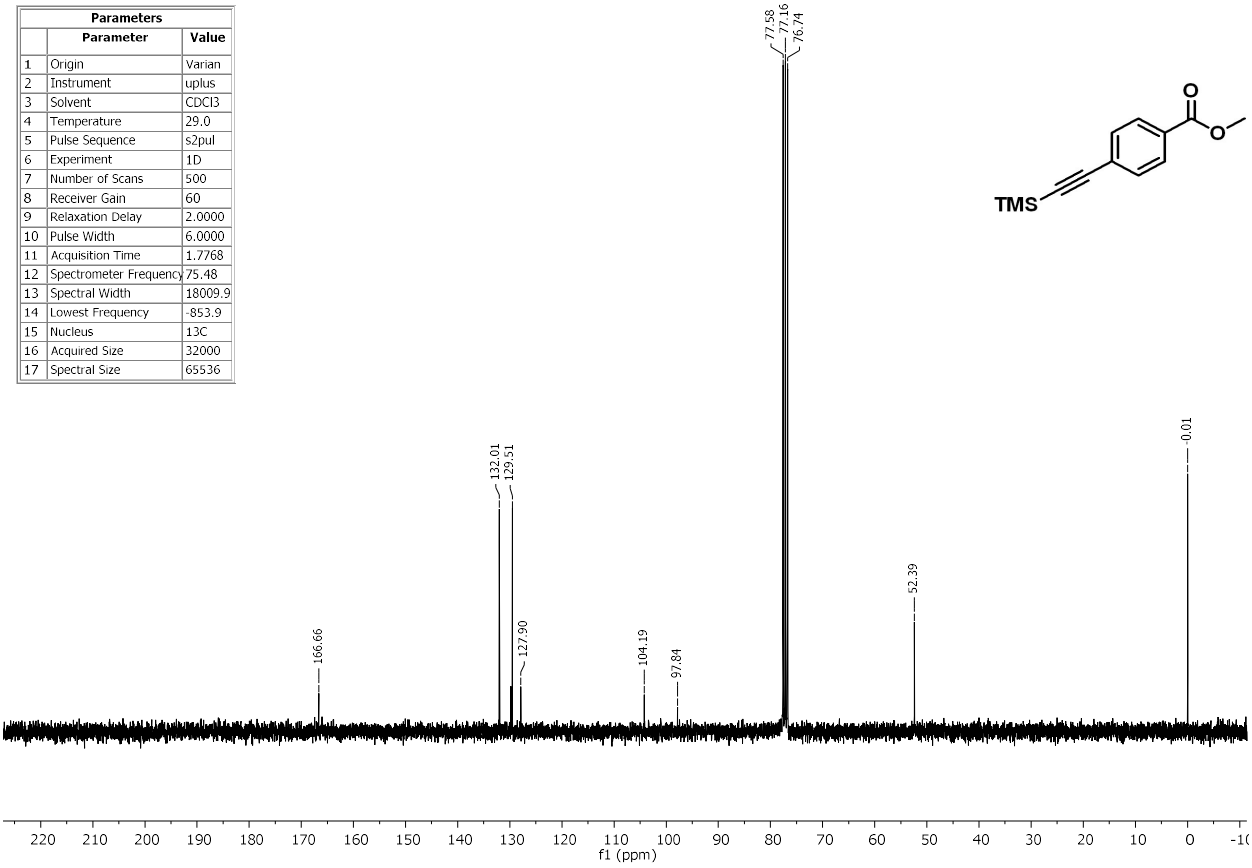

Figure S2. ^{13}C NMR spectrum of methyl 4-(trimethylsilylethynyl)benzoate

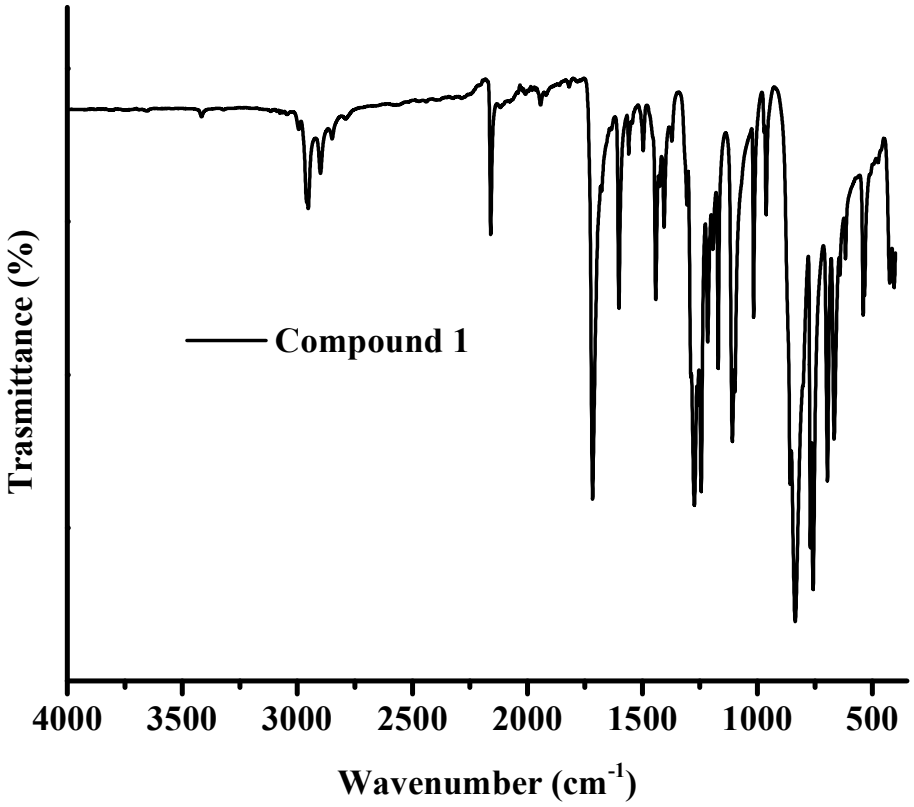

Figure S3. Infrared spectrum of methyl 4-(trimethylsilylethynyl)benzoate

Methyl 4-ethynylbenzoate synthesis (2).[1] In a 100 mL round bottom flask, **1** (4.00 g, 17.2 mmol) and K_2CO_3 (0.952 g, 6.9 mmol) were stirred together in 40 mL of methanol for 1.5 hours. The suspension was reduced to a solid, which was combined with 50 mL of 1 M HCl. The product was extracted with DCM. The organic layers were combined and dried over Na_2SO_4. The solvent was removed under reduced pressure to give 2.69 g (98%) of a burnt orange solid. ^{1}H NMR ($CDCl_3$, 300.14 MHz) δ = 3.91 (s, 3H), 7.54 (d, 2H, J_{HH} = 9.0 Hz), 7.99 (d, 2H, J_{HH} = 9.0 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 75.48) δ = 52.42 (s), 80.19 (s), 82.91 (s), 126.86 (s), 129.58 (s), 130.24 (s), 132.20 (s), 166.53 (s). FT-IR (solid): ν_{max} (cm^{-1}) = 3241 m, 2951 w, 2103 w, 1699 s, 1606 m, 1433 m, 1349 m, 1277 s, 1192 m, 1174 m, 1108 s, 1016 m, 957 m, 859 m, 770 s, 719 s, 676 s, 528 m, 460 w.

Parameters		
	Parameter	**Value**
1	Origin	Varian
2	Instrument	uplus
3	Solvent	CDCl3
4	Temperature	29.0
5	Pulse Sequence	s2pul
6	Experiment	1D
7	Number of Scans	16
8	Receiver Gain	59
9	Relaxation Delay	1.0000
10	Pulse Width	3.0000
11	Acquisition Time	3.8128
12	Spectrometer Frequency	300.14
13	Spectral Width	4196.4
14	Lowest Frequency	-445.1
15	Nucleus	1H
16	Acquired Size	16000
17	Spectral Size	65536

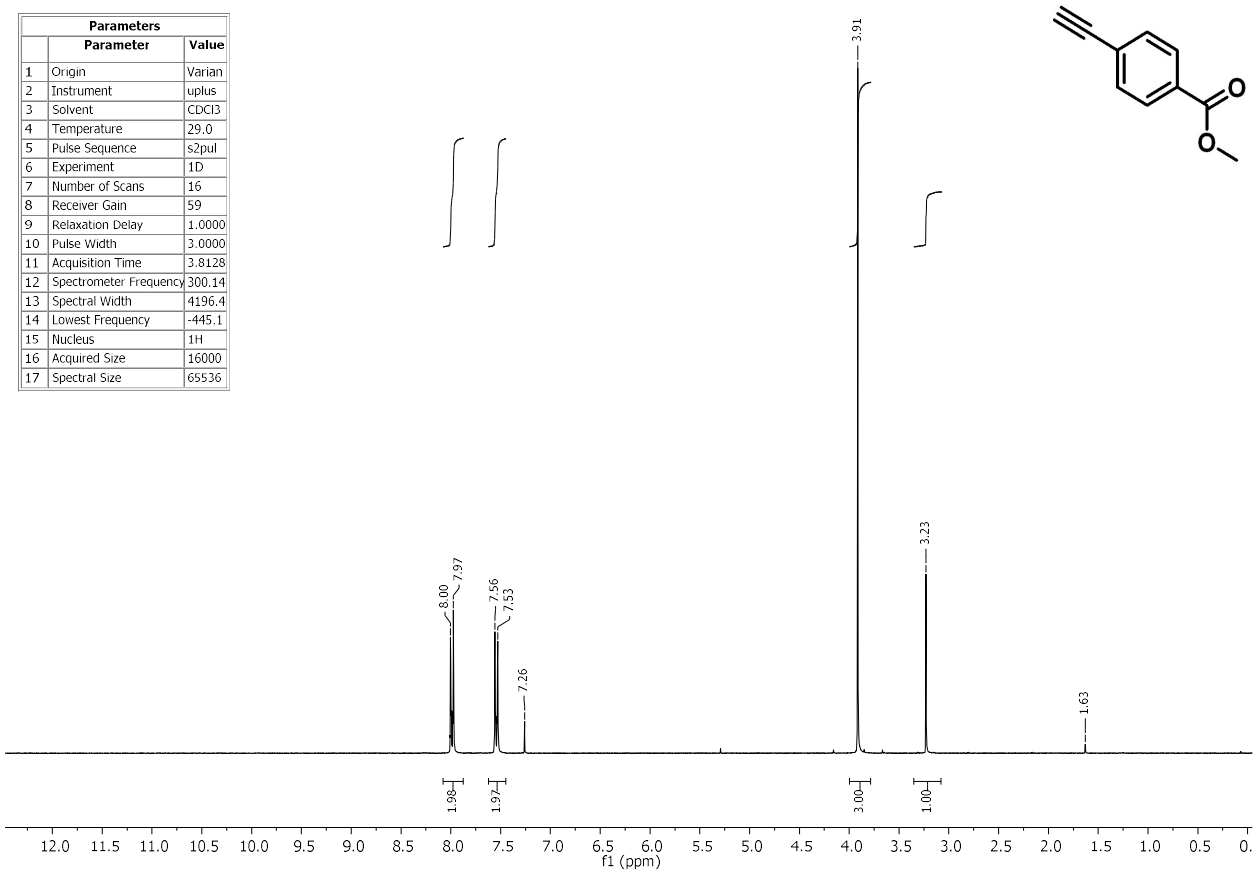

Figure S4. ^{1}H NMR spectrum of methyl 4-ethynylbenzoate

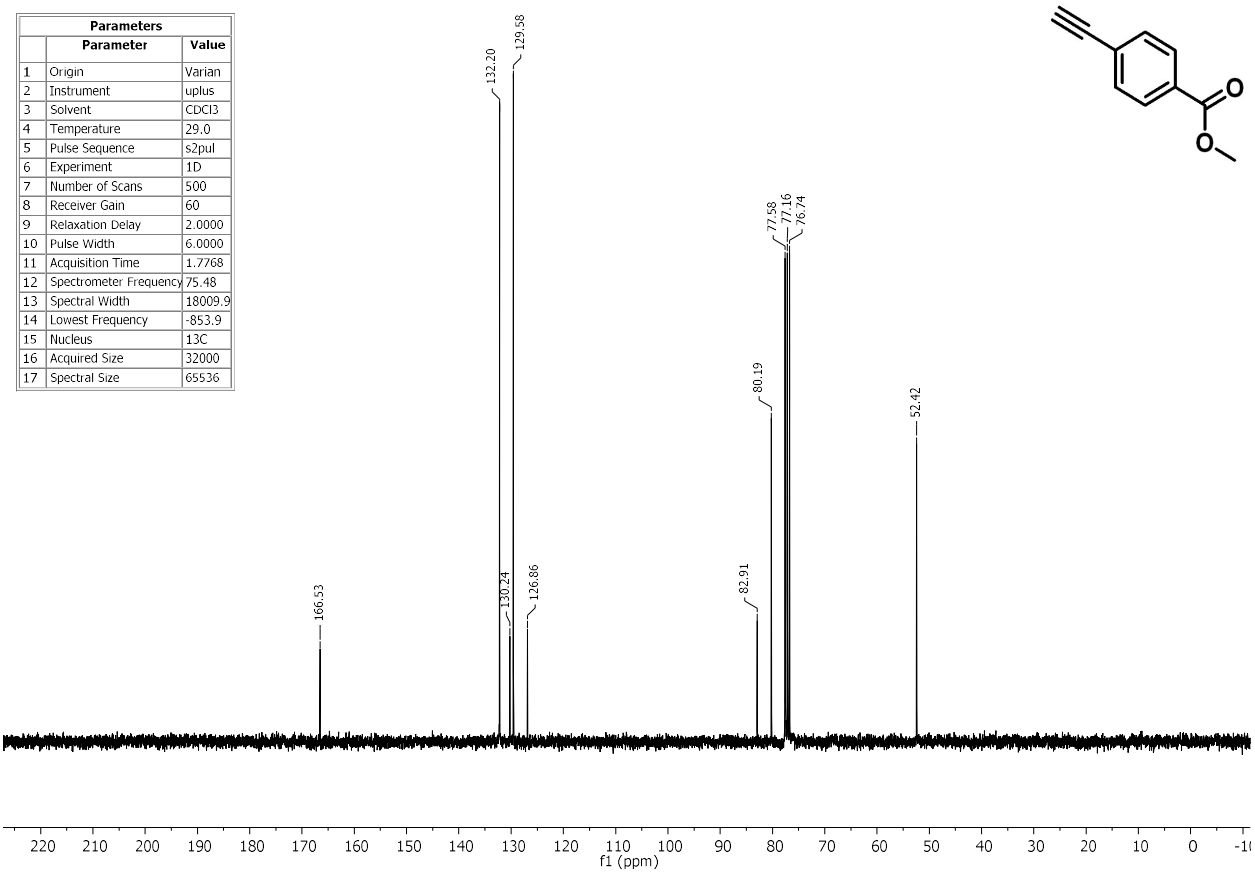

Figure S5. ^{13}C NMR spectrum of methyl 4-ethynylbenzoate

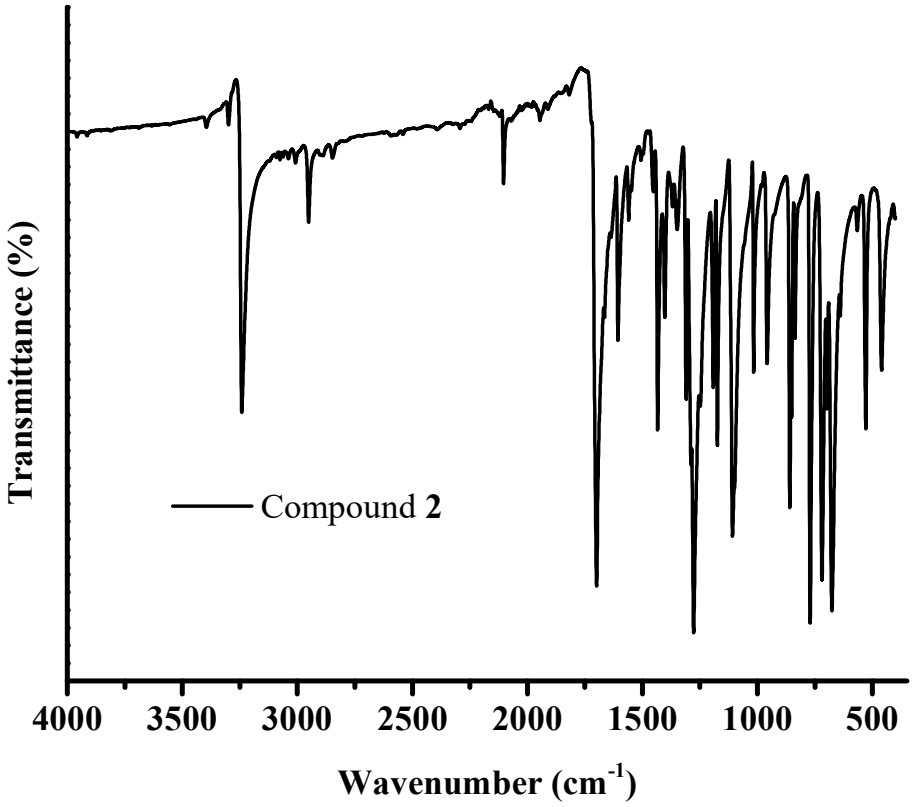

Figure S6. Infrared spectrum of methyl 4-ethynylbenzoate

Tris(4-methylcarboxyphenylethynyl)phosphine synthesis (3).[2] Methyl 4-ethynylbenzoate (3.00 g, 18.7 mmol) and CuI (0.18 g, 0.95 mmol) were loaded into a dry 25 mL Schlenk flask under N_2. The solids were then dissolved in 15 mL of dry toluene. PCl_3 (0.54 mL, 6.2 mmol) and triethylamine 7.8 mL, 55.6 mmol) were then added subsequently to the reaction. The flask was then stirred at room temperature for 1 hour. The reaction was then reduced to a beige solid. The crude product was then purified using column chromatography (eluted with dichloromethane/hexanes (4:1) on silica gel) affording 2.66 g (84 %) of an off-white solid. ^{1}H NMR ($CDCl_3$, 499.39 MHz) δ = 3.93 (s, 9H), 7.62 (d, 6H, J_{HH} = 9.9 Hz), 8.02 (d, 6H, J_{HH} = 9.9 Hz); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.58) δ =52.51 (s), 81.82 (d, J_{PC} = 5.0 Hz), 105.18 (d, J_{PC} = 11.3 Hz), 126.43 (s), 129.66 (s), 130.87(s), 132.17 (s), 166.42 (s); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.15 MHz) δ = -88.52. FT-IR (ATR): ν_{max} (cm^{-1}) = 2953 w, 2167 m, 1715 s, 1602 m, 1560 w, 1431 m, 1268 s, 1191 m, 1170 m, 1103 s, 1013 m, 962 w, 851 s, 814 m, 766 s, 677 s, 533 m, 445 m. HRMS (ESI+) *m/z*: $[M + Na]^+$ Exact mass calculated for $[C_{30}H_{21}O_6PNa]^+$: 531.0973; Found: 531.0968. Elem. Anal. Calculated for $C_{30}H_{21}O_6P$ requires: C 70.87, H 4.16. Found: C 70.88, H 4.29.

Parameters		
	Parameter	Value
1	Solvent	CDCl3
2	Temperature	298.0
3	Pulse Sequence	zg30
4	Experiment	1D
5	Probe	Z150364_0001 (CPP BBO 500S2 BB-H&F-05 Z)
6	Number of Scans	8
7	Receiver Gain	62.4
8	Relaxation Delay	2.0000
9	Pulse Width	12.0000
10	Spectrometer Frequency	499.39
11	Spectral Width	10000.0
12	Lowest Frequency	-1962.9
13	Nucleus	1H
14	Acquired Size	32768
15	Spectral Size	65536

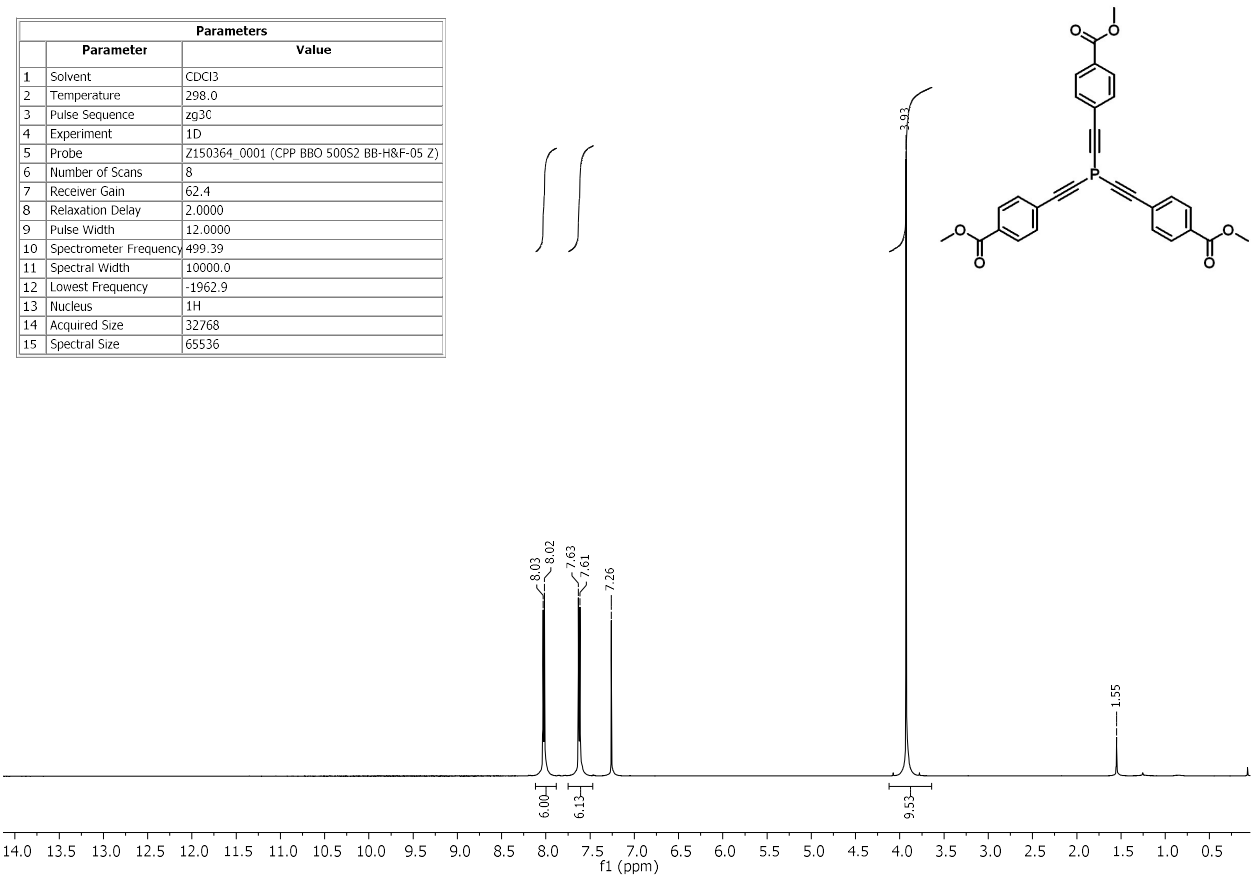

Figure S7. ^{1}H NMR spectrum of *tris*(4-methylcarboxyphenylethynyl)phosphine

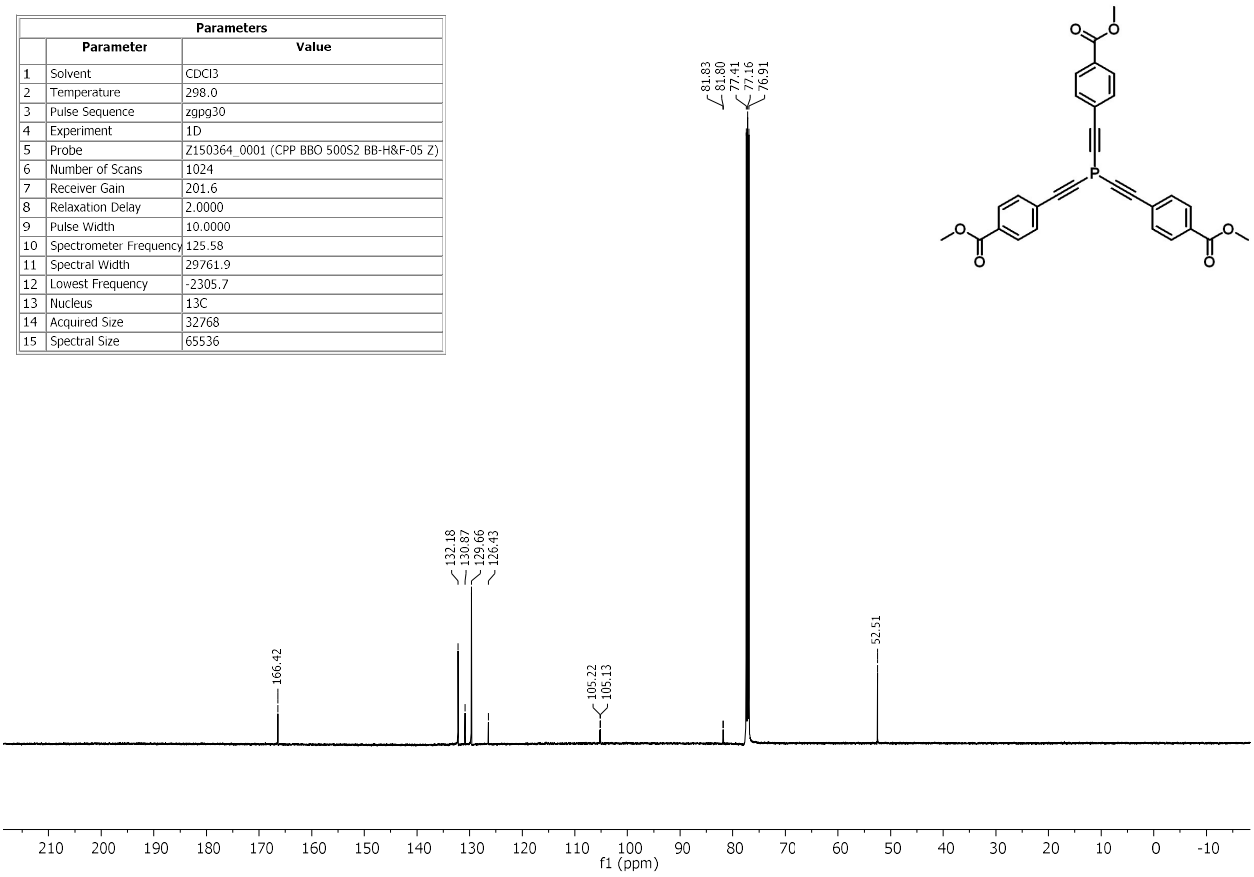

Figure S8. ^{13}C NMR spectrum of *tris*(4-methylcarboxyphenylethynyl)phosphine

Parameters		
	Parameter	Value
1	Solvent	CDCl3
2	Temperature	298.0
3	Pulse Sequence	zgpg30
4	Experiment	1D
5	Probe	Z150364_0001 (CPP BBO 500S2 BB-H&F-05 Z)
6	Number of Scans	64
7	Receiver Gain	201.6
8	Relaxation Delay	2.0000
9	Pulse Width	12.0000
10	Spectrometer Frequency	202.15
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13	Nucleus	31P
14	Acquired Size	32768
15	Spectral Size	65536

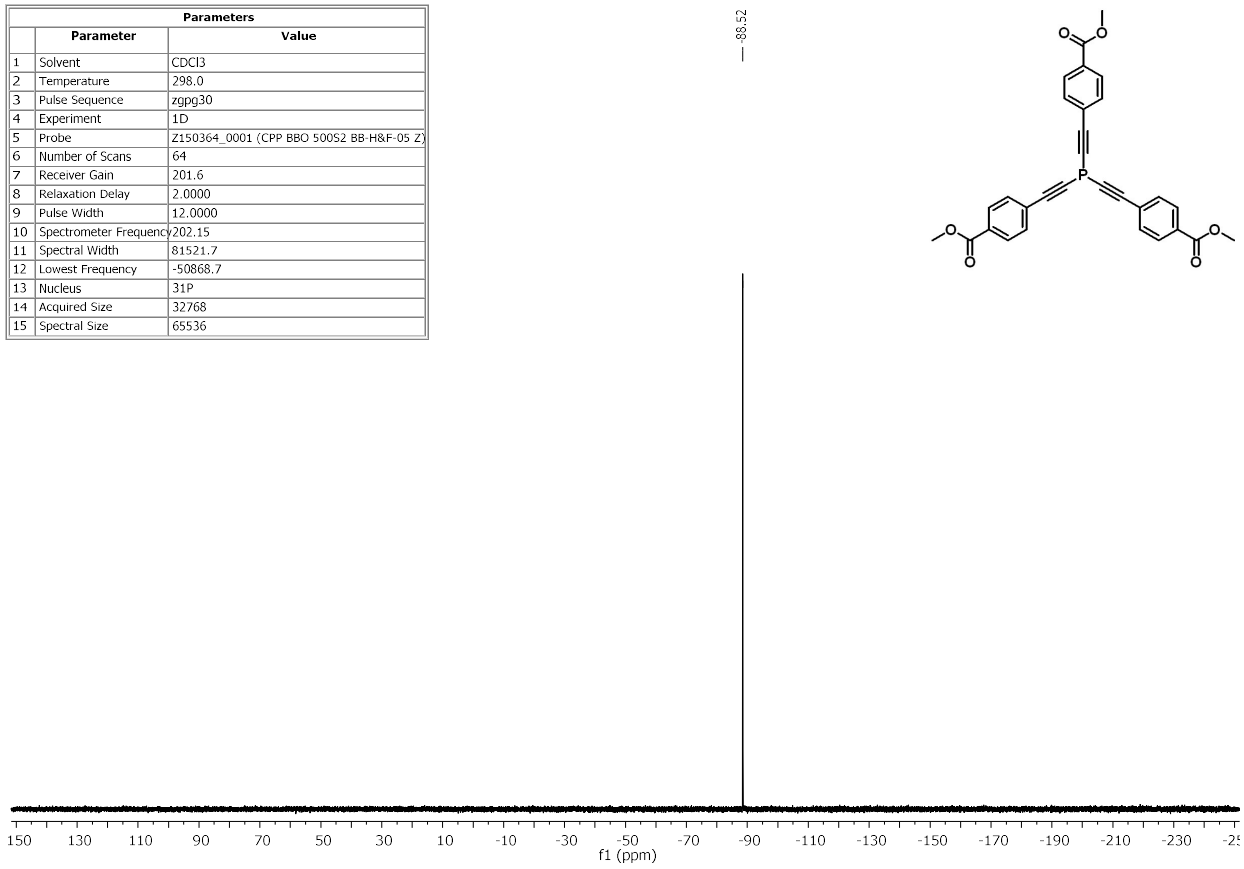

Figure S9. 31P NMR spectrum of *tris*(4-methylcarboxyphenylethynyl)phosphine

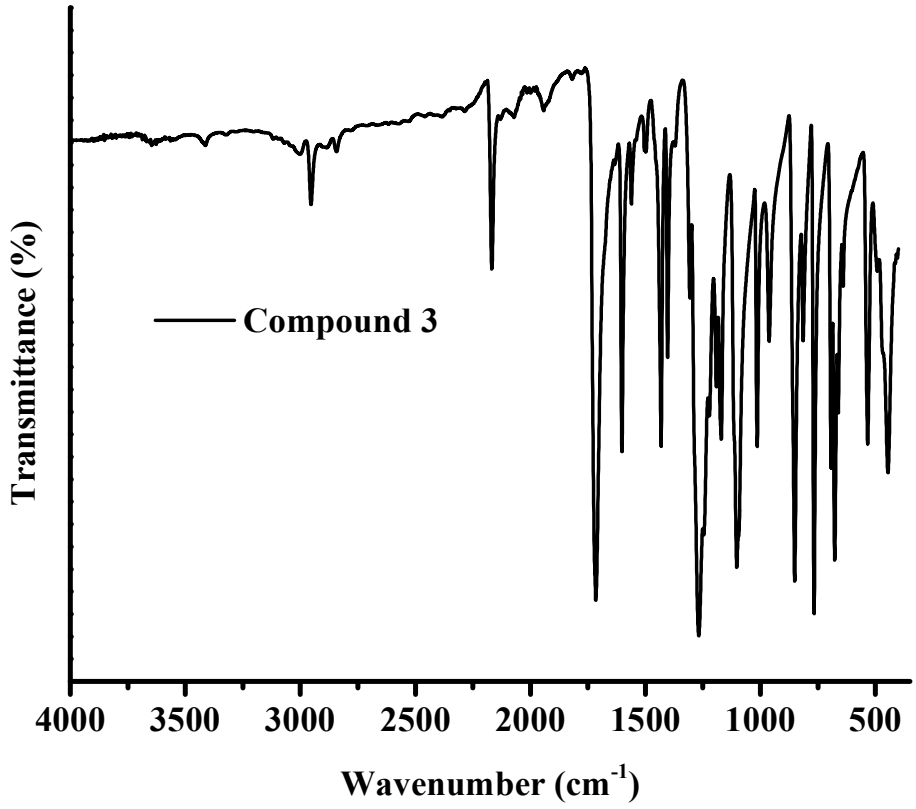

Figure S10. Infrared spectrum of *tris*(4-methylcarboxyphenylethynyl)phosphine

Tris(4-carboxyphenylethynyl)phosphine synthesis (tcpepH$_3$). In a 25 mL schlenk tube under N_2, **3** (200 mg, 0.4 mmol) was dissolved in dry THF and degassed 0.5 M $KOH_{(aq)}$ (2.8 mL, 1.4 mmol) was then added. The resulting orange emulsion was then allowed to stir at room temperature for 24 hours. Diethyl ether was then added to extract the organic layer. The remaining aqueous layer was then acidified to pH = 2 using 2 M HCl. The resulting crude white precipitate was collected *via* centrifugation. The product was purified by recrystallization in methanol affording 170 mg (93 %) of the title compound. ^{1}H NMR (DMSO-d$_6$, 499.39 MHz) δ = 7.75 (d, 6H, J_{HH} = 9.9 Hz), 7.98 (d, 6H, J_{HH} = 9.9 Hz); ^{13}C{^{1}H} NMR (DMSO-d$_6$, 125.58) δ = 80.73 (d, J_{PC} = 5.0 Hz), 105.28 (d, J_{PC} = 11.3 Hz), 124.58 (s), 129.60 (s), 131.96 (s), 132.23 (s), 166.47 (s); ^{31}P{^{1}H} NMR (DMSO-*d$_6$*, 202.15 MHz) δ = -88.84. FT-IR (ATR): ν_{max} (cm^{-1}) = 3330 w (br), 2839 w (br), 2666 w (br), 2543 w (br), 2169 w, 1726 s, 1674 s, 1603 s, 1560 w, 1419 m, 1372 w, 1304 m, 1284 m, 1211 m, 1100 w, 1015 w, 934 w (br), 853 s, 767 s, 730 w, 691 w, 665 m, 641 m, 555 w, 527 m, 482 m. HRMS (ESI-) *m/z*: [M - H]$^-$ Exact mass calculated for [$C_{27}H_{14}O_6P$]$^-$: 465.0528; Found: 465.0533. Elem. Anal. Calculated for $C_{27}H_{15}O_6P$ requires: C 69.53, H 3.24. Found: C 69.03, H 3.43.

Parameters		
	Parameter	Value
1	Solvent	DMSO
2	Temperature	298.0
3	Pulse Sequence	zg30
4	Experiment	1D
5	Probe	Z150364_0001 (CPP BBO 500S2 BB-H&F-05 Z)
6	Number of Scans	16
7	Receiver Gain	55.5
8	Relaxation Delay	2.0000
9	Pulse Width	12.0000
10	Spectrometer Frequency	499.39
11	Spectral Width	10000.0
12	Lowest Frequency	-1916.3
13	Nucleus	1H
14	Acquired Size	32768
15	Spectral Size	65536

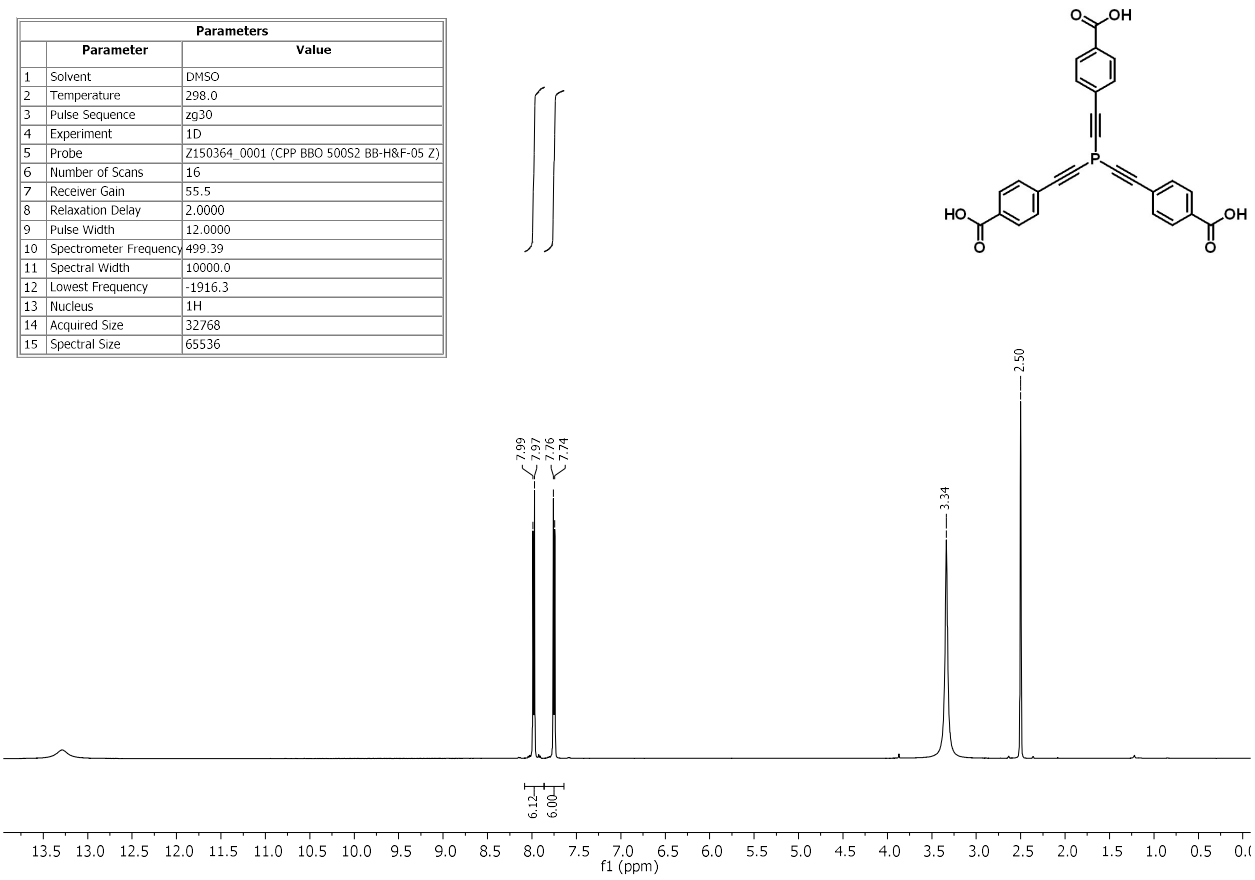

Figure S11. 1H NMR spectrum of tris(4-carboxyphenylethynyl)phosphine

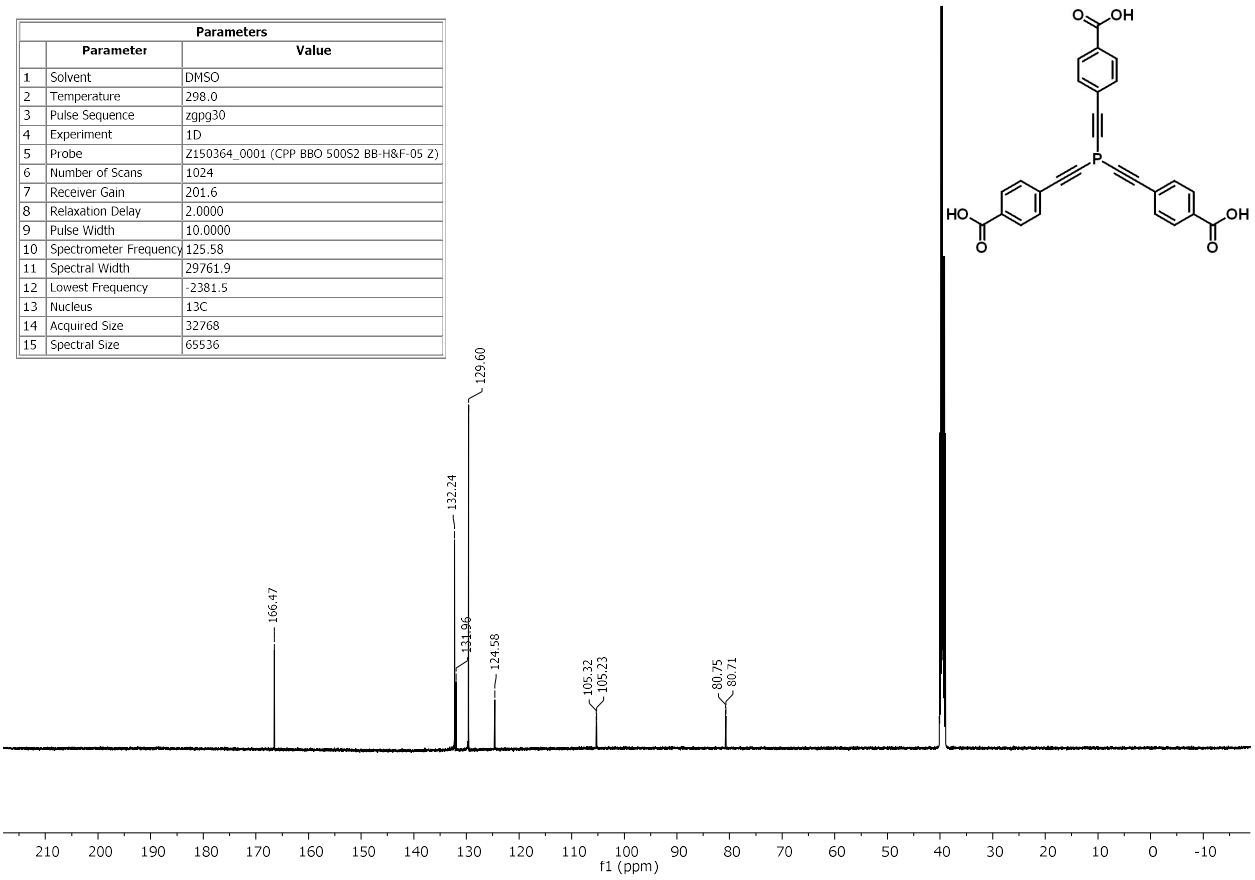

Figure S12. ^{13}C NMR spectrum of *tris*(4-carboxyphenylethynyl)phosphine

Parameters		
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2	Temperature	298.0
3	Pulse Sequence	zgpg30
4	Experiment	1D
5	Probe	Z150364_0001 (CPP BBO 500S2 BB-H&F-05 Z)
6	Number of Scans	128
7	Receiver Gain	201.6
8	Relaxation Delay	2.0000
9	Pulse Width	12.0000
10	Spectrometer Frequency	202.15
11	Spectral Width	81521.7
12	Lowest Frequency	-50868.7
13	Nucleus	31P
14	Acquired Size	32768
15	Spectral Size	65536

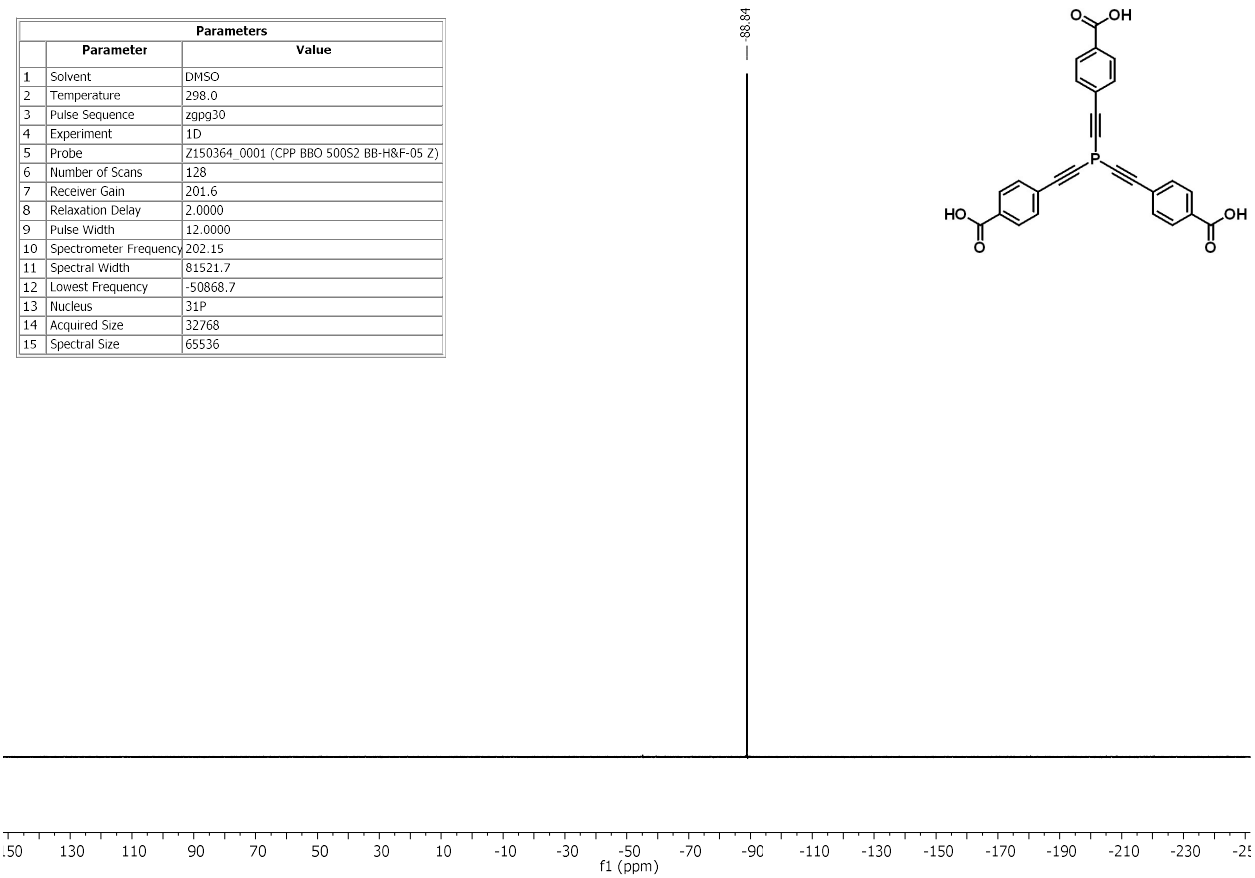

Figure S13. ^{31}P NMR spectrum of *tris*(4-carboxyphenylethynyl)phosphine

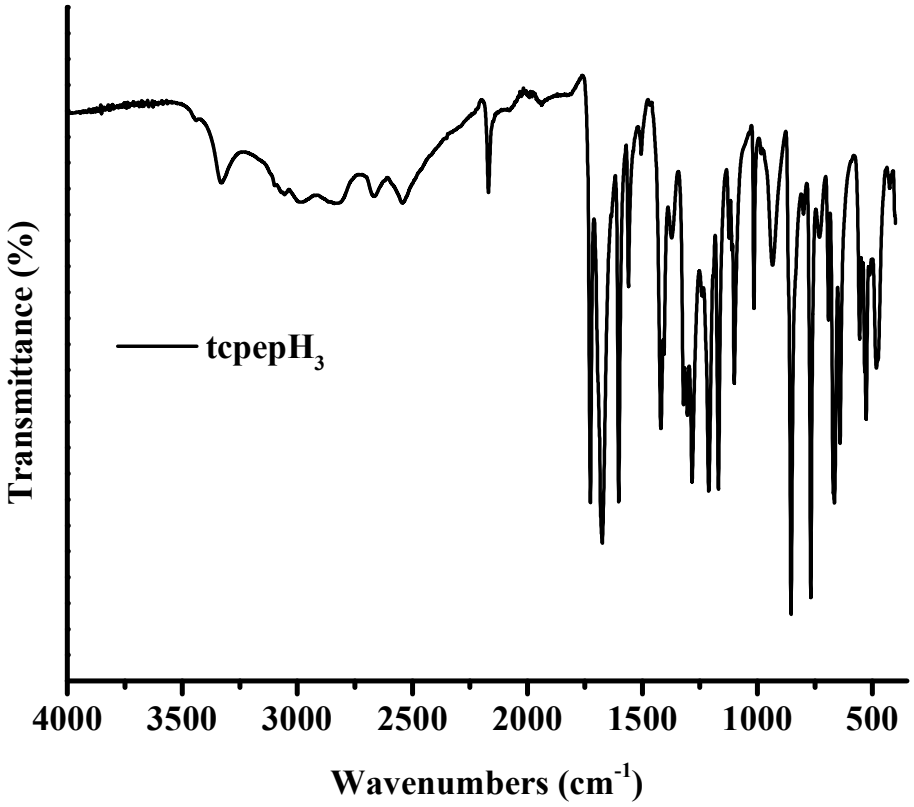

Figure S14. Infrared spectrum of *tris*(4-carboxyphenylethynyl)phosphine

Mn-PCM-48 [Mn_3(μ3-F)(tcpep)2(H_2O)$_2$(DMF)$_1$(H_3O)$_{1.1}$(F)$_{0.5}$(Na)$_{0.3}$(K)$_{0.1}$]·(H_2O)$_8$·(DMF)$_2$ synthesis. In a 20 mL glass scintillation vial, $MnCl_2 \cdot 4H_2O$ (19.1 mg, 0.10 mmol), CsF (15 mg, 0.10 mmol), and **tcpepH$_3$** (15 mg, 0.03 mmol) were dissolved in 5 mL of DMF: H_2O: EtOH (1:1:1, v:v). The vial was placed in a graphite heating bath (75℃) for 3-5 days. The crystalline material was washed with fresh solvent and filtered affording 12 mg (33% crystalline yield) of a crystalline yellow prismatic solid. IR (solid): ν_{max} (cm^{-1}) = 3275 w (br), 2162 w, 1651 m, 1600 m, 1578 m, 1530 m, 1382 s, 1175 w, 1100 w, 1015 w, 858 m, 781 m, 676 m, 528 w, 421 m. Elem. Anal. Calculated for activated PCM-48, $C_{54}P_2F_{1.5}O_{19.6}H_{40.3}Mn_3Na_{0.3}K_{0.1}$ requires: C 51.11, H 3.2, F 2.25, Na 0.54, K 0.31. Found: C 51.00, H 2.50, N none, F 2.29, Na 0.53, K 0.33.

Table S1. ICP-OES results for Mn-PCM-48

Element Analyzed	Average value found (ppm)	Mass of Mn-PCM-48 (mg)	Volume of analyte (mL)	Concentration of analyte (ppm)	Component weight (%)
K	0.638	2.0	10.24	195.3	0.33
Na	1.042	2.0	10.24	195.3	0.53

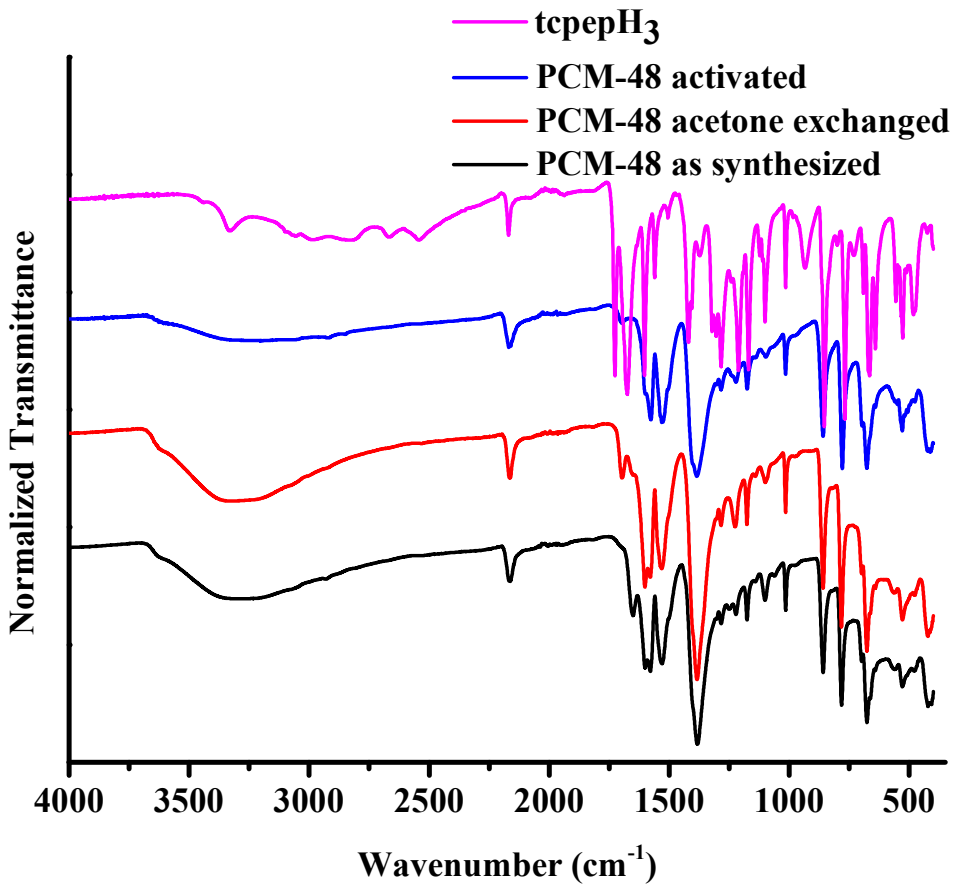

Figure S15. Infrared spectrum of Mn-PCM-48

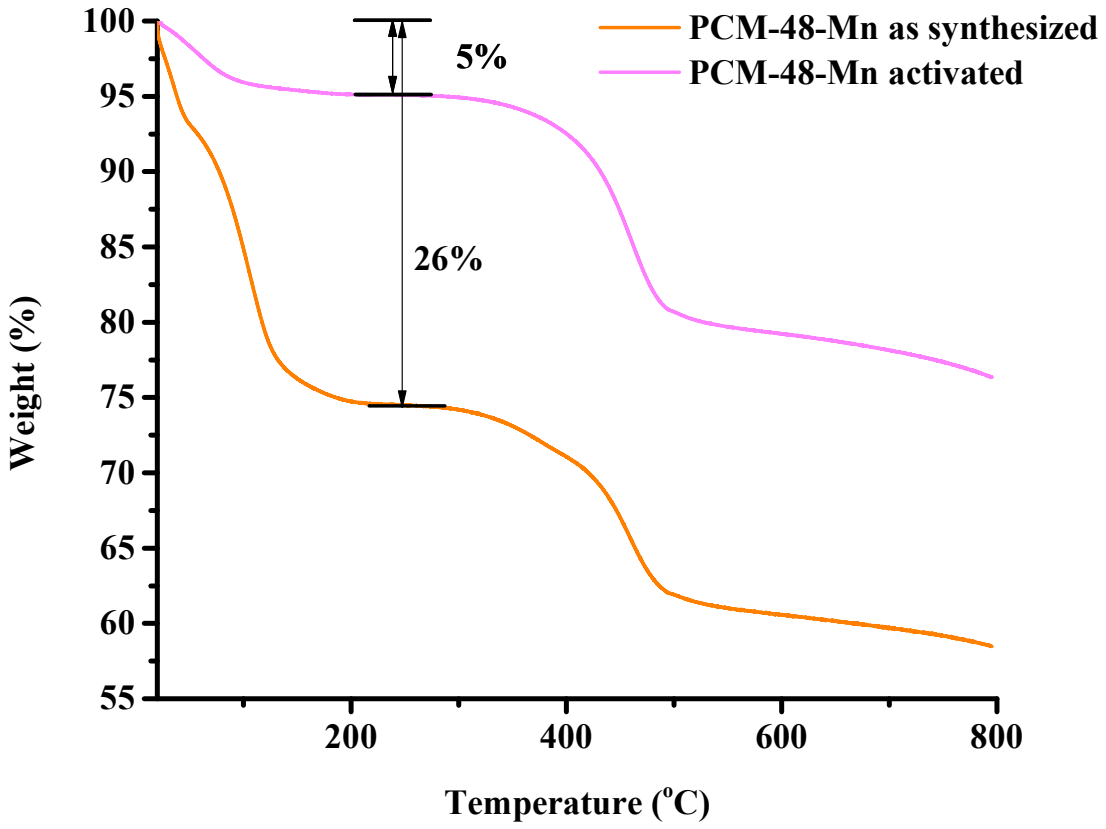

Figure S16. TGA profiles of Mn-PCM-48

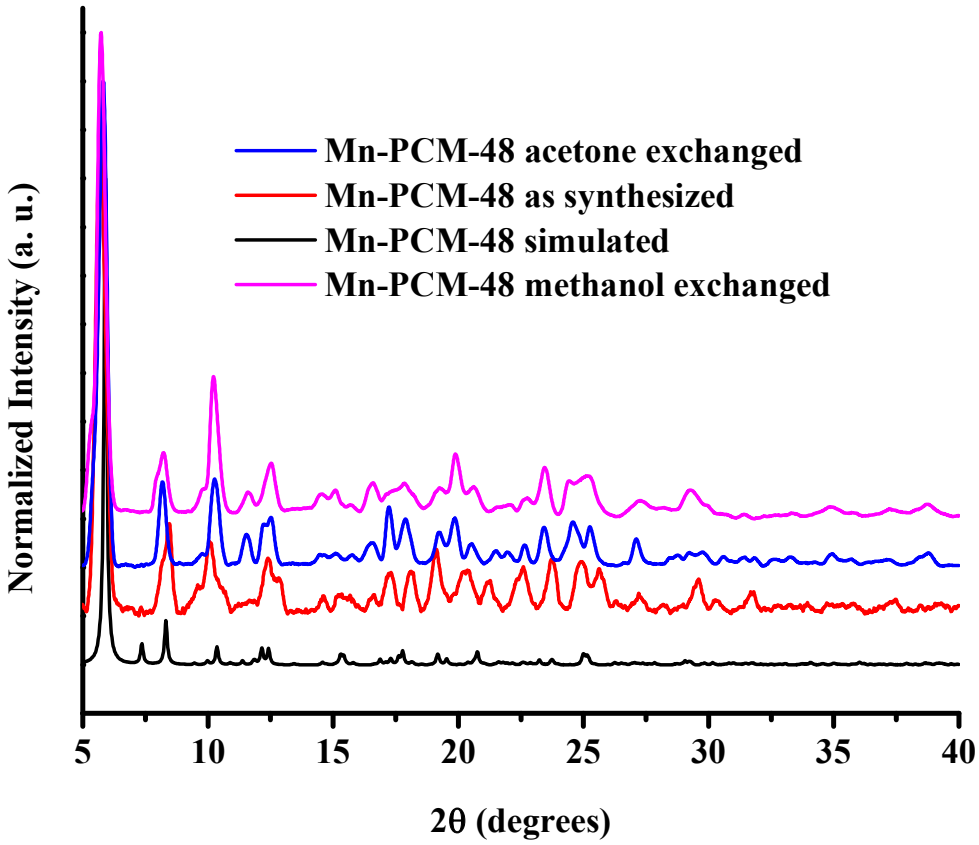

Figure S17. PXRD patterns of Mn-PCM-48

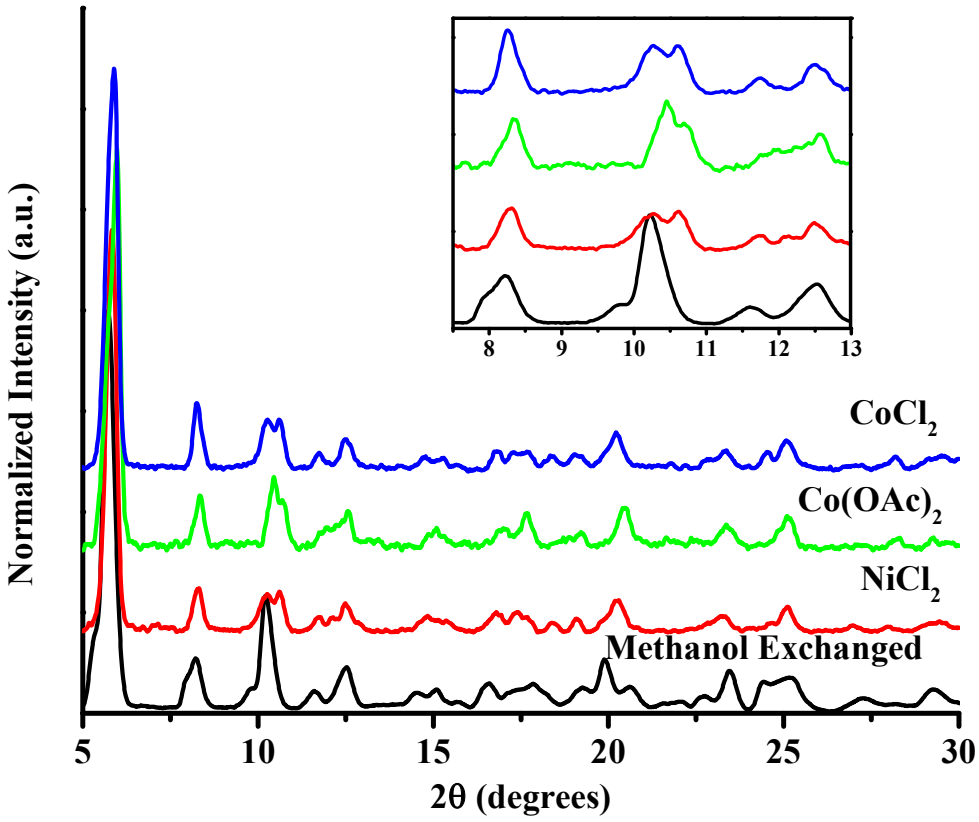

Figure S18. PXRD patterns of metal exposed Mn-PCM-48 in methanol

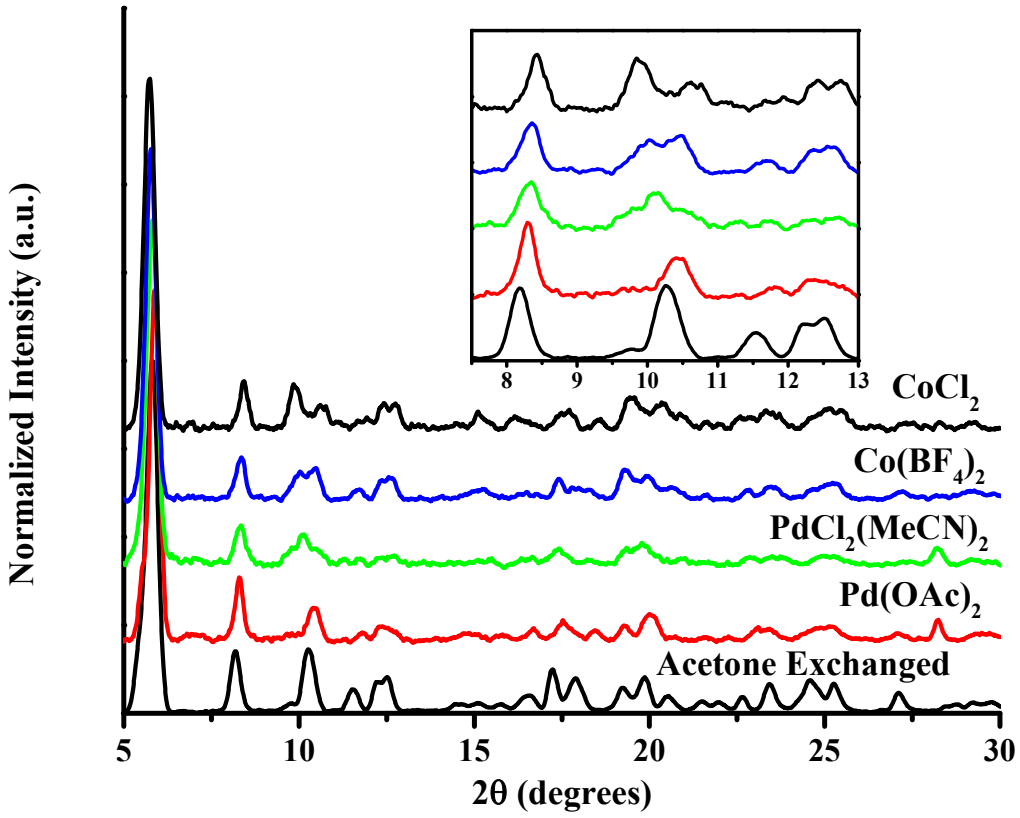

Figure S19. PXRD patterns of metal exposed Mn-PCM-48 in acetone

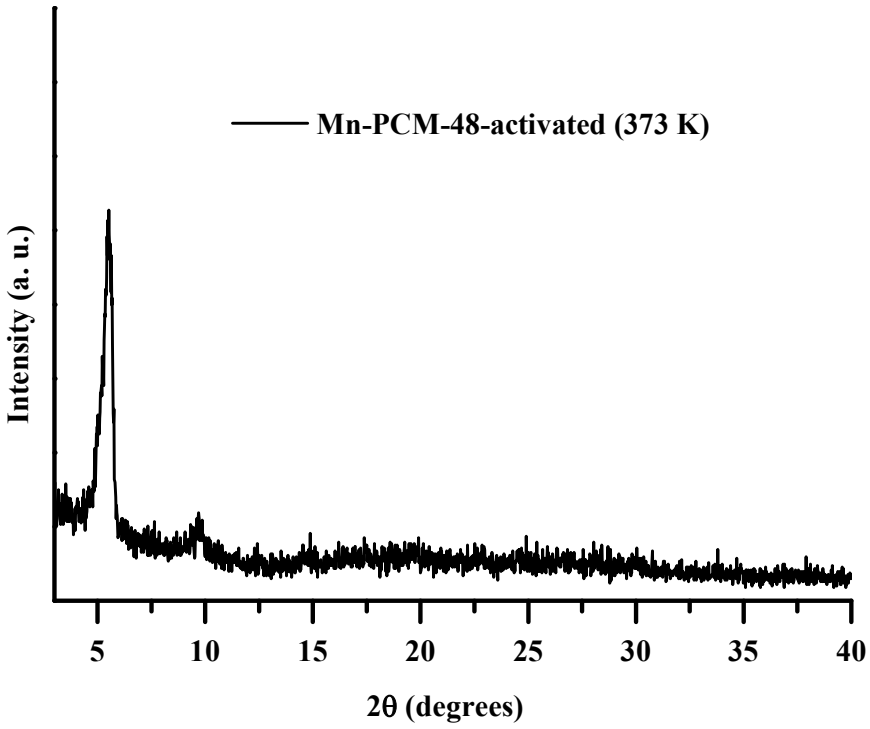

Figure S20. PXRD pattern of Mn-PCM-48 post-activation

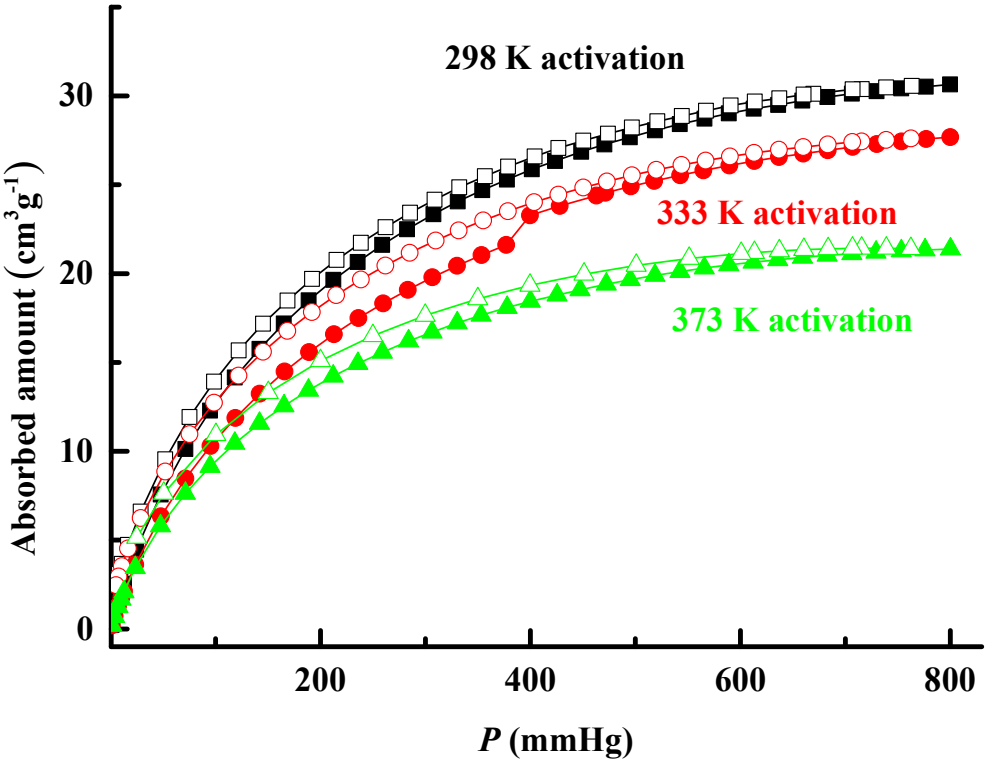

Figure S21. C_2H_2 sorption isotherms at 298 K of acetone exchanged PCM-48 at various activation temperatures

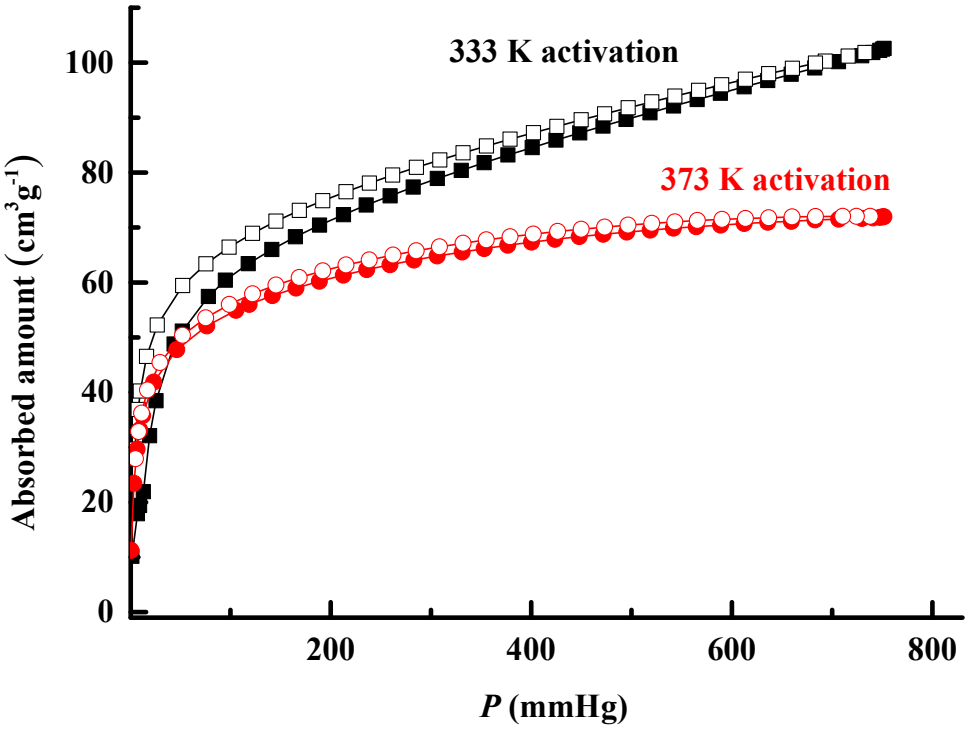

Figure S22. CO_2 sorption isotherms at 298 K of acetone exchanged PCM-48 at various activation temperatures

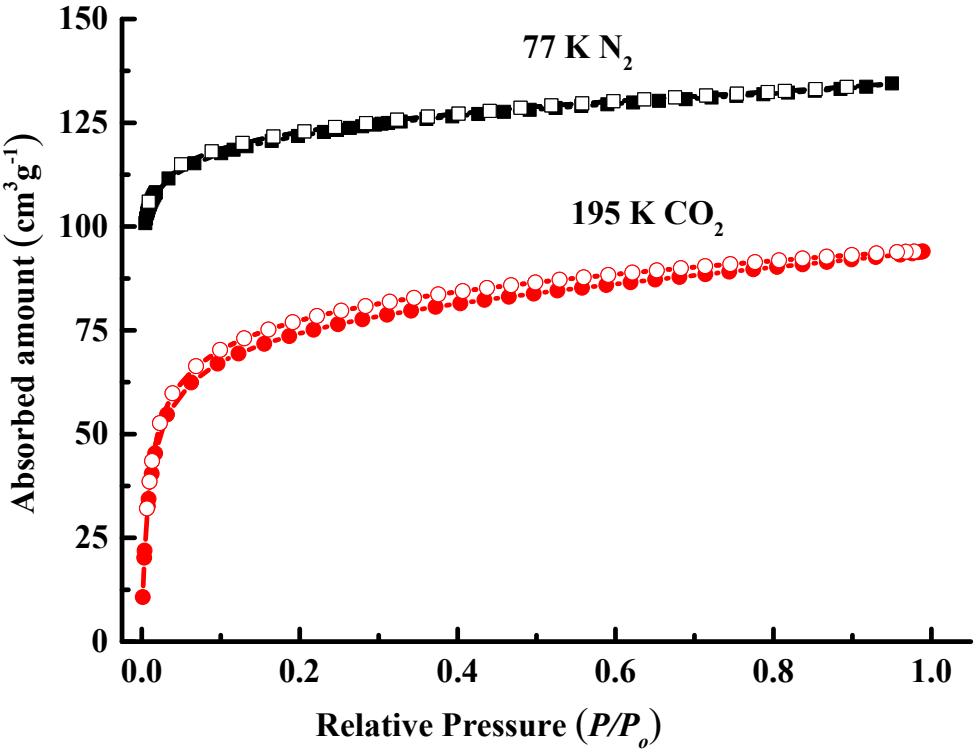

Figure S23. Gas sorption isotherms of methanol exchanged Mn-PCM-48 activated at 296 K

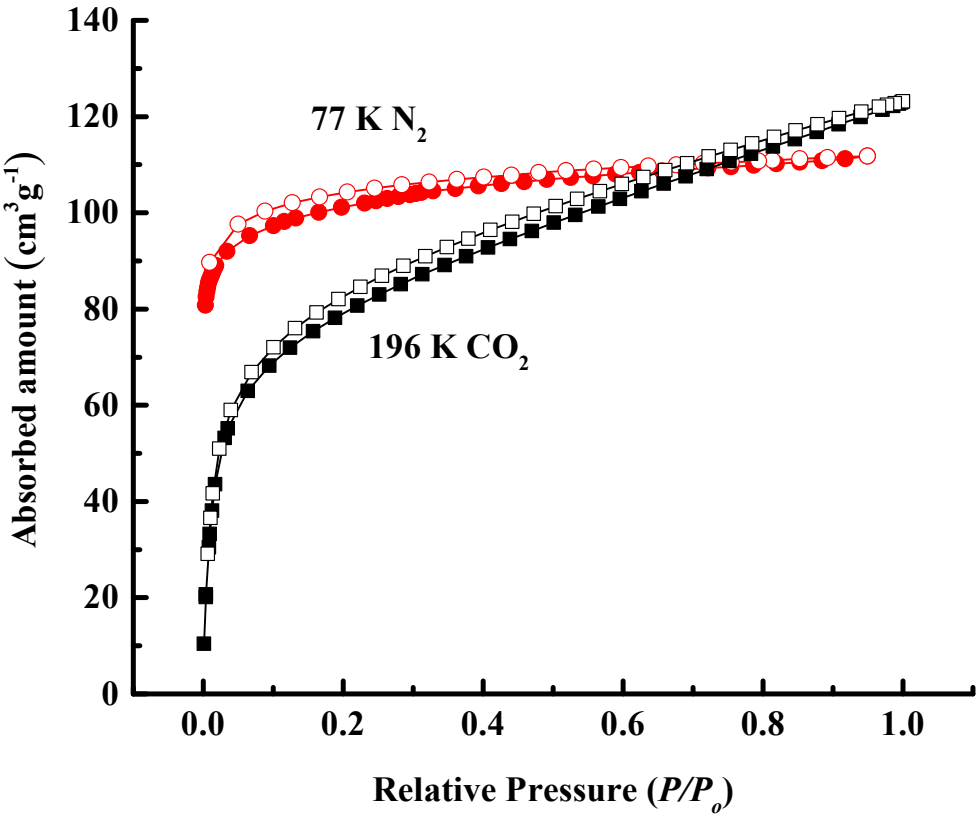

Figure S24. Gas adsorption isotherms of acetone exchanged Mn-PCM-48 activated at 296 K

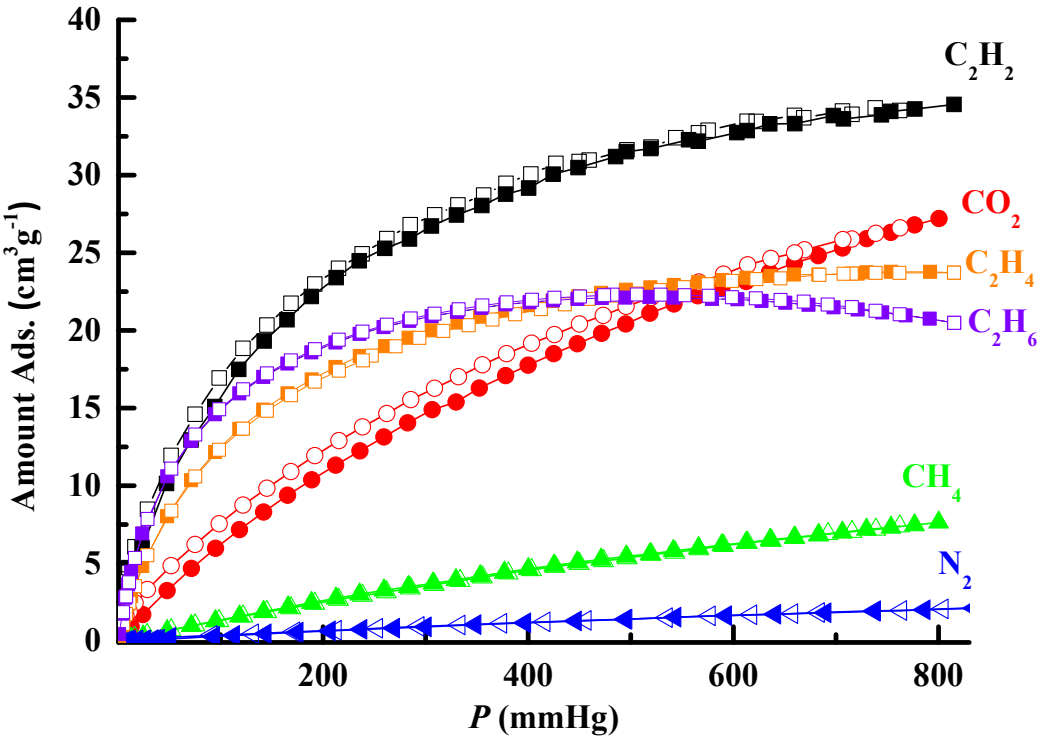

Figure S25. Gas sorption isotherms collected at 273 K of acetone exchanged Mn-PCM-48 activated at 296 K

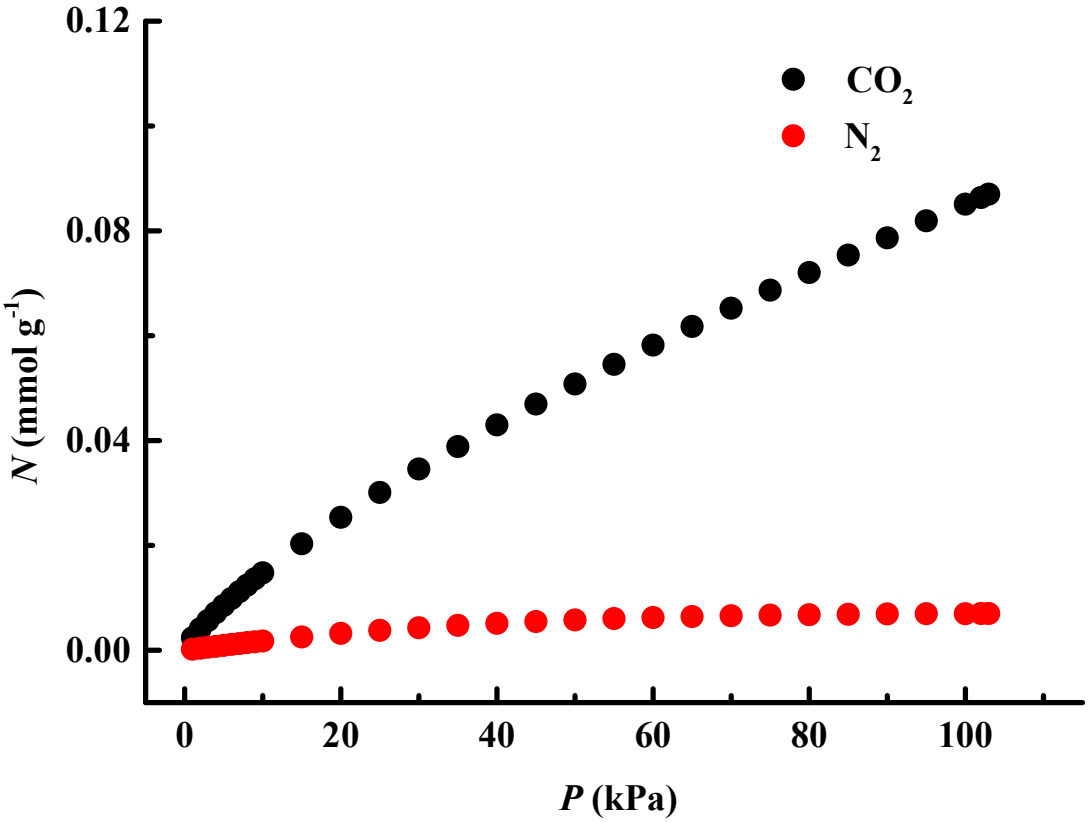

Figure S26. IAST calculation of the component molar loadings with a (15/85, v/v) CO_2/ N_2 mixture at 296 K for Mn-PCM-48

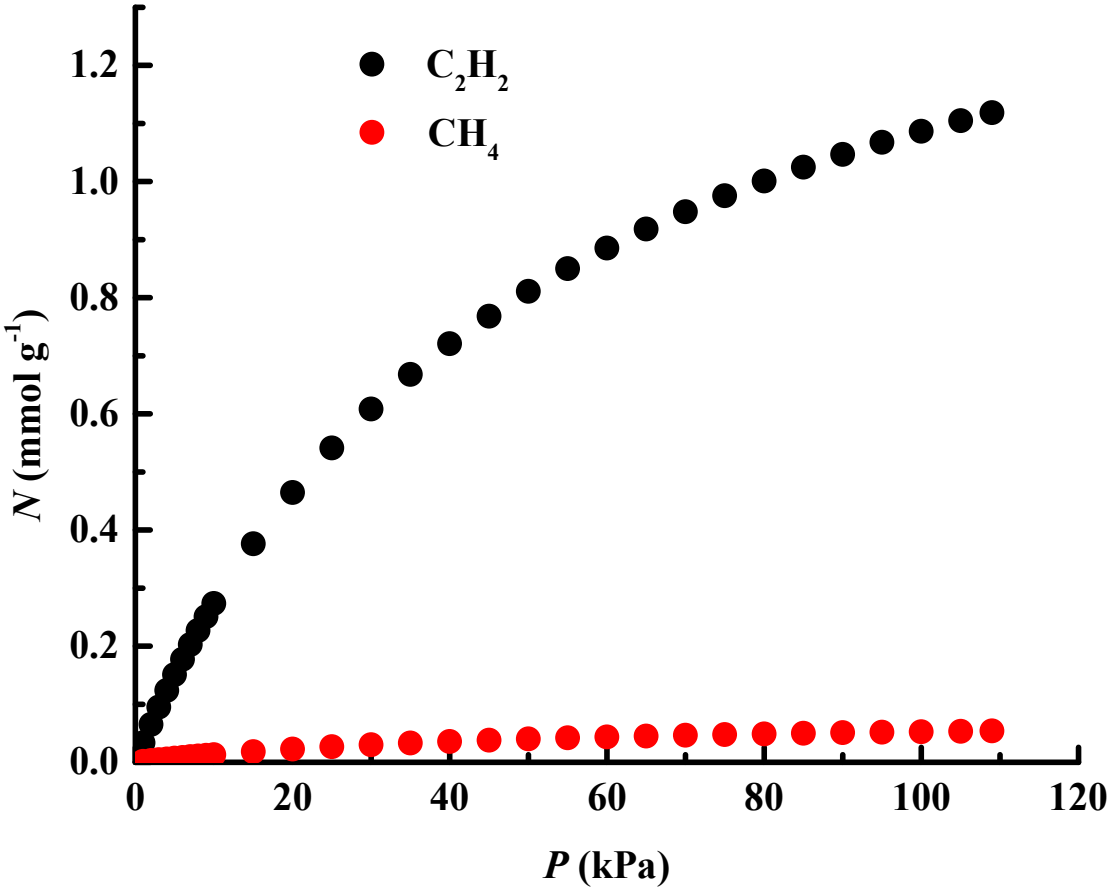

Figure S27. IAST calculation of the component molar loadings with an equimolar C_2H_2/CH_4 (50/50, v/v) mixture at 296 K for Mn-PCM-48

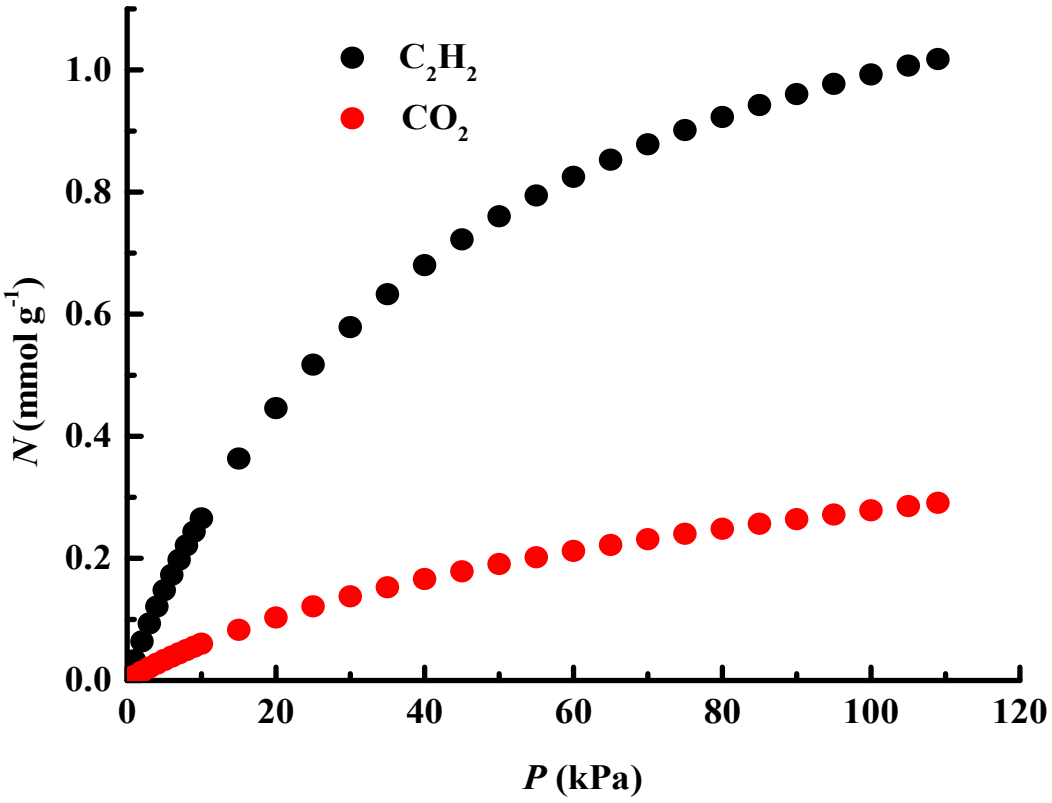

Figure S28. IAST calculation of the component molar loadings with an equimolar C_2H_2/CO_2 (50/50, v/v) mixture at 296 K for Mn-PCM-48

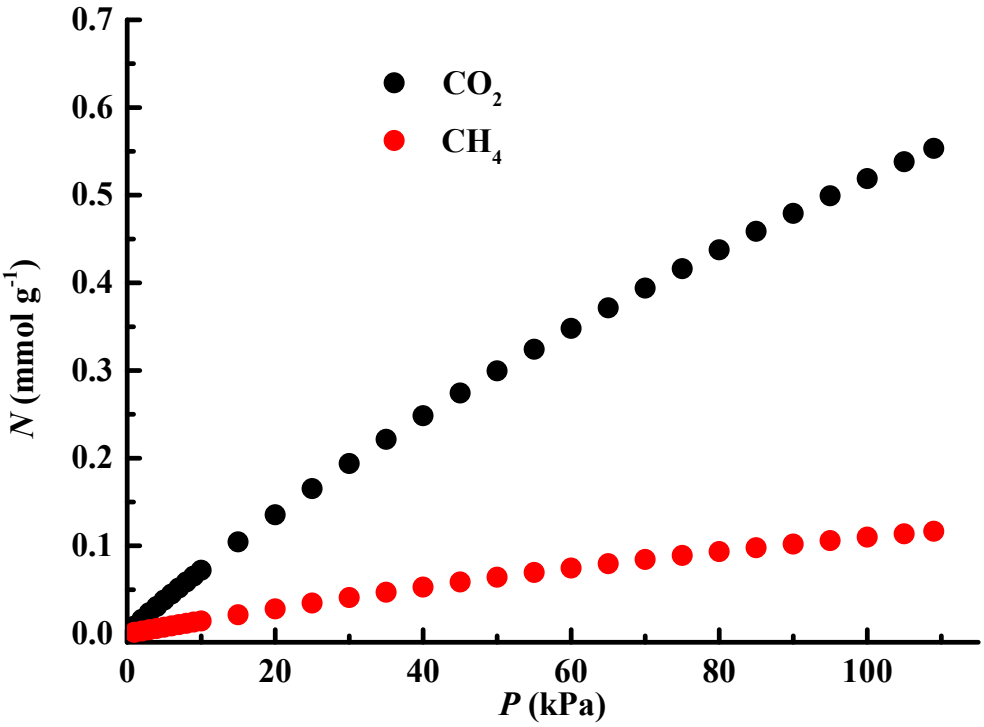

Figure S29. IAST calculation of the component molar loadings with an equimolar CO_2/CH_4 mixture at 296 K for Mn-PCM-48

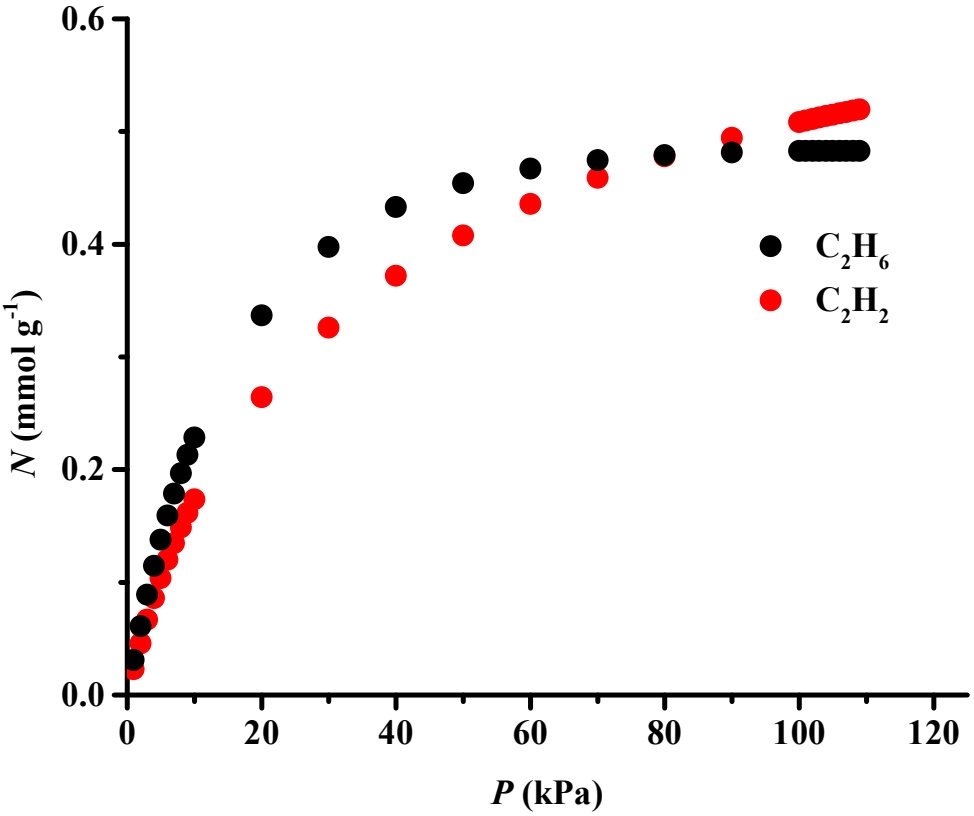

Figure S30. IAST calculation of the component molar loadings with an equimolar C_2H_2/C_2H_6 (50/50, v/v) mixture at 296 K for Mn-PCM-48

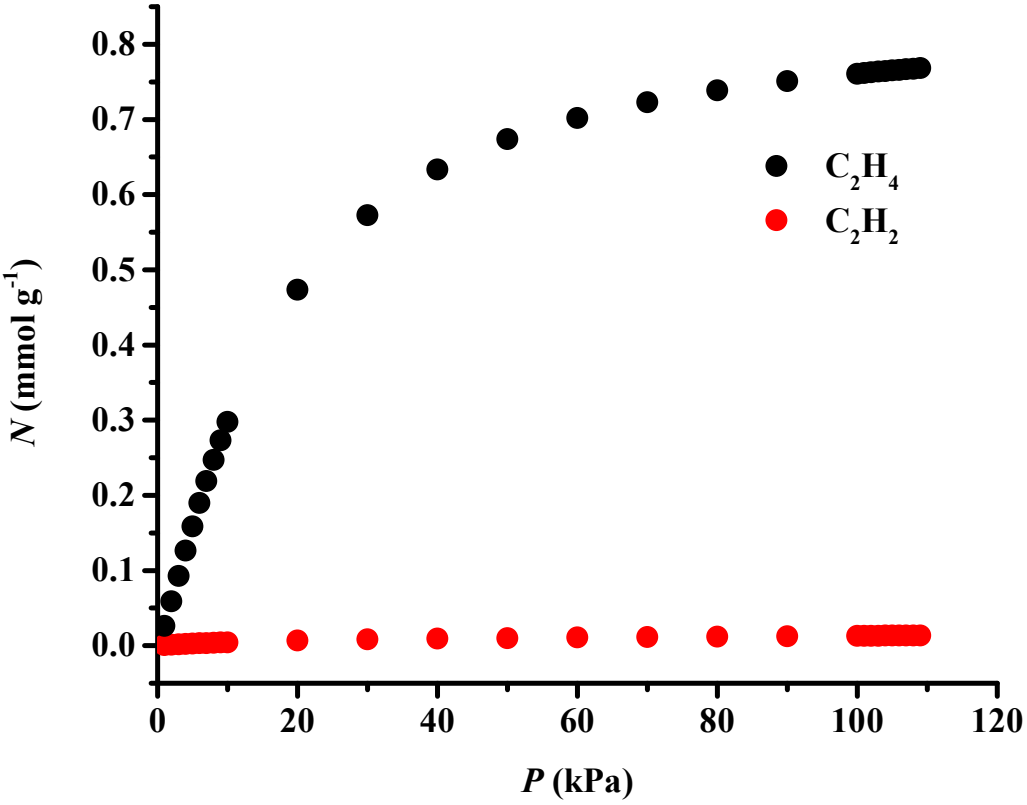

Figure S31. IAST calculation of the component molar loadings with a (1/99, v/v) C_2H_2/C_2H_4 mixture at 296 K for Mn-PCM-48

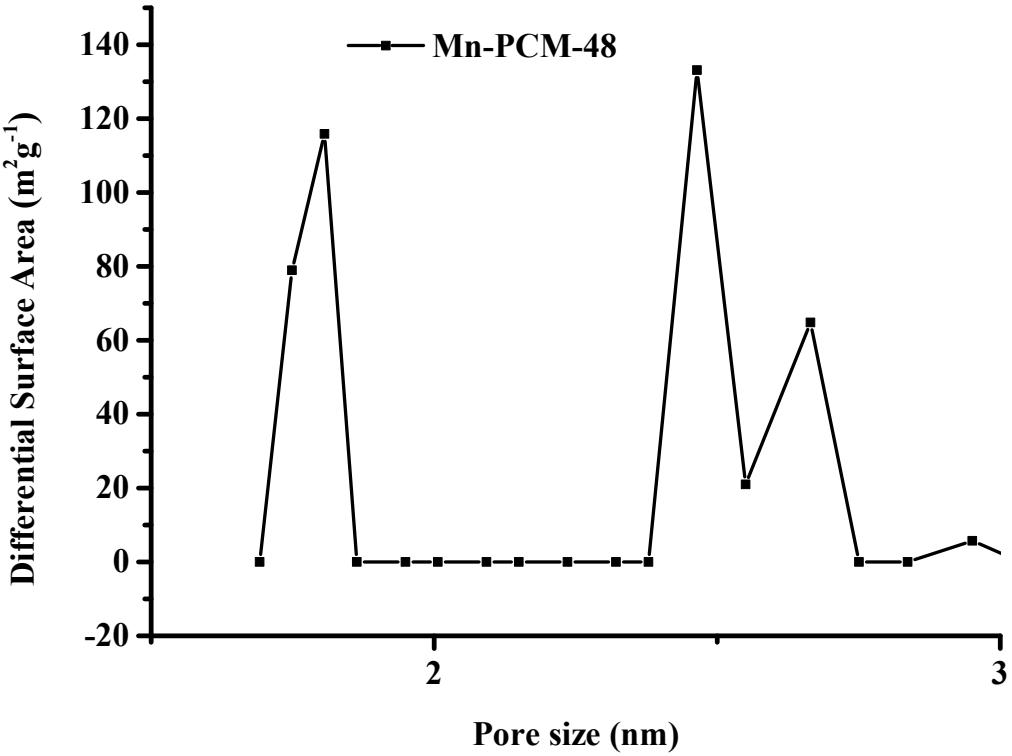

Figure S32. Pore size distribution plot of Mn-PCM-48 *via* N_2 77K isotherm

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