Electronic Supplementary Information

Phosphonium zwitterions for lighter and chemically-robust MOFs: Highly reversible H_2S capture and solvent-triggered release

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Contents

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. Phosphorous trichloride (PCl_3) was purchased from Sigma Aldrich and was then purified through distillation. *N*-butyllithuim (*n*-BuLi) (2.48 M, hexanes) was purchased from Acros and titrated in house. $Pd(OAc)_2$ was purchased from Oakwood Products. 1,4-dibromobenzene was purchased from Chem-Impex International Inc. 4-iodobenzoic acid was purchased from Matrix Scientific. All organic solvents were purchased from Fischer Scientific. Tetrahydrofuran (THF) was prepared by distillation (Na/benzophenone) 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

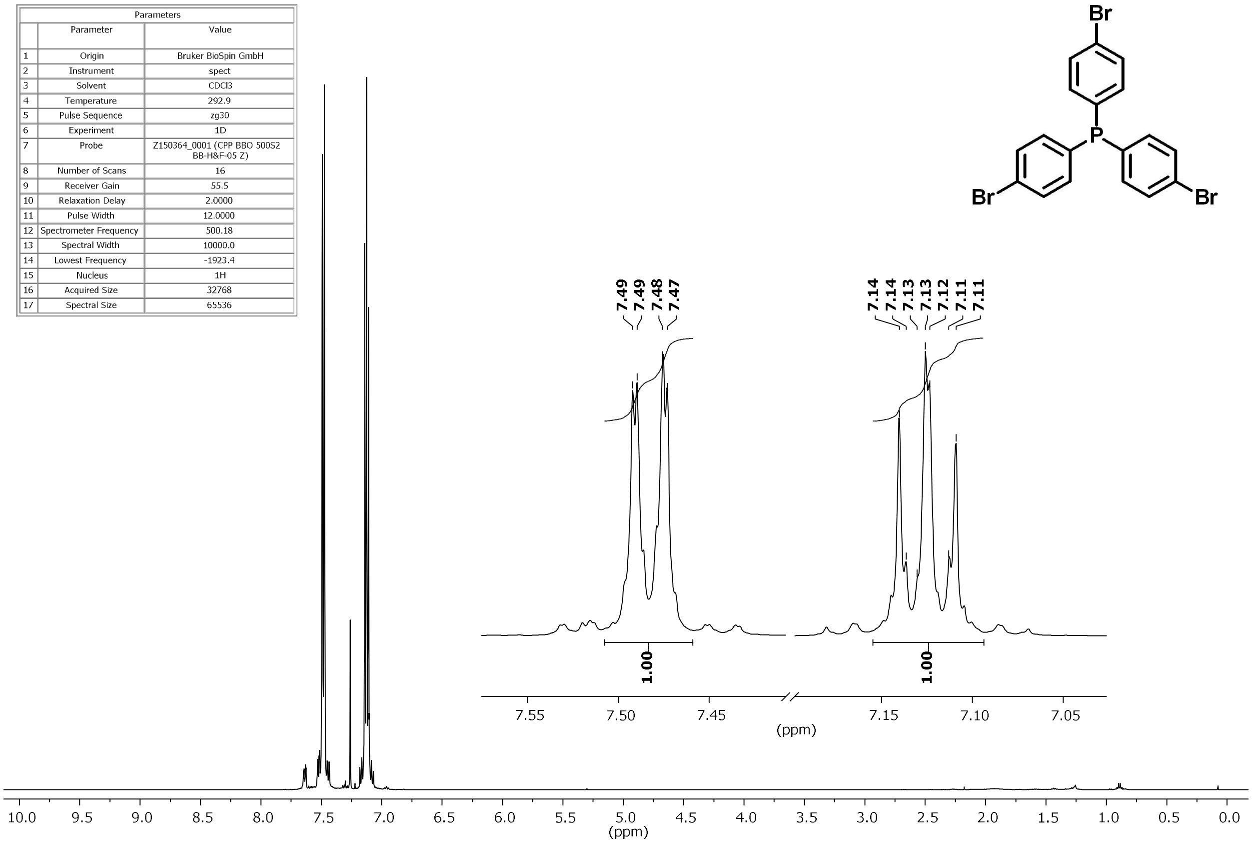
All analyses were performed in house. All nuclear magnetic resonance (NMR) shifts were software standardized and are expressed as δ in parts per million (ppm). Coupling constants (J) are reported in Hz and apparent peak multiplicities are noted. ^1H, ^{13}C, and ^{31}P NMR analysis were performed on a Varian NMRS 400 MHz NMR spectrometer, Varian NMRS 600 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 with an attached ATR apparatus. For Single Crystal X-Ray Crystallography (SCXRD), suitable crystals were mounted on a thin glass fiber using perfluoropolyether oil, which was frozen in situ by a nitrogen gas cryostream flow. Data collection was performed on a Rigaku Saturn CCD diffractometer using MoKα (0.709 Å) equipped with an Oxford 600 series Cryostream (iPCM-1). All other structures were collected on an Agilent Super Nova diffractometer equipped with an AtlasS2 CCD, and Oxford 700 low-temperature attachment, using CuKα radiation (1.7902 Å). Powder X-ray Diffraction (PXRD) were recorded for iPCM-1 and In-PCM-66 on a Stoe Stadi-P diffractometer, with a

Debye-Scherrer geometry detector using Co Kα radiation (1.7902 Å). Data was collected in the range 5.0–40.0° 2θ using multiple scans, which were subsequently averaged. Powder X-ray Diffraction (PXRD) for Mg-PCM-75 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. Elemental microanalyses were performed by Midwest Microlab LLC (Indianapolis). Quantachrome Autosorb-1 system at 77 K (N_2, H_2, O_2) or 196 K (CO_2, CH_4) and all gases (99.995+%) were purchased from Praxair. Gas sorption studies on Mg-PCM-75 were carried out using a volumetric sorption analyzer (Micromeritics 3Flex 3500). Gas adsorption-desorption isotherms for these samples were collected at 77 K (N_2, H_2, O_2) or 196 K (CO_2, CH_4) after dehydration under vacuum (< 10─5 Torr) at 200 °C for 12 hours. The H_2S determination was made using a HP 5890 GC, by continuous injections of the system exhaust, of each injection we obtained a chromatogram. From the corresponding chromatogram we integrate the H_2S signal to obtain the abundance. Knowing the H_2S concentration from the feed, we can calculate the H_2S concentration in each one of the injections, as the saturation concentration is the original feed concentration. From this data we can obtain the corresponding breakthrough plots, C/C_f vs time. In this system it is necessary carry out a Blank, because the system can adsorb H_2S by itself. H_2O vapor isotherms were recorded by a dynamic method in a DVS Advantage 1 instrument from Surface Measurement System (mass sensitivity: 0.1 µg; RH accuracy: 0.5% RH, vapor pressure accuracy: 0.7% P/P_0. PCM-75 samples were activated at 200 °C for 1 hour under flowing N_2 prior to H_2O adsorption experiments.

Synthetic Details

Synthesis of *tris*(4-bromophenyl)phosphine (1).

In a 500 mL 3-neck round bottom flask, 1,4-dibromobenzene (20.0 g, 84.7 mmol) was dissolved in dry THF (~ 250 mL). The solution was cooled down to −78 °C (acetone/dry ice bath). To the cooled solution, *n*-BuLi (34.2 mL of 2.48 M in hexanes, 84.7 mmol) was added dropwise *via* addition funnel over 30 minutes giving a white slurry. After stirring at −78 °C for an additional 1.5 hours, PCl_3 (2.47 mL, 28.2 mmol) was diluted in THF (10 mL) and added dropwise over 30 minutes forming a light-yellow solution. The light-yellow solution was then allowed to stir overnight to slowly acclimate to room temperature. Degassed D.I. water (100 mL) was added to the reaction flask slowly. The product was then phase extracted with dichloromethane (DCM), and the aqueous layer was washed with additional DCM (3 x 50 mL). The organic layers were combined, washed with brine, dried over $MgSO_4$, filtered and dry loaded onto silica gel (18.0 g). The crude product was then purified using column chromatography (eluted with hexanes on silica gel) affording 9.77 g (69 %) of a colorless crystalline solid. ^{1}H NMR ($CDCl_3$, 500.18 MHz) δ = 7.48 (dd, 6H), 7.13 (dt, 6H); $^{13}C\{^1H\}$ NMR ($CDCl_3$, 125.78 MHz) δ = 135.34 (d), 135.13 (s), 132.07 (d), 124.10 (s); $^{31}P\{^1H\}$ NMR ($CDCl_3$, 202.47 MHz) δ = -8.60. FT-IR (ATR): ν_{max} (cm^{-1}) = 1920 (vw), 1567 (w), 1472 (m), 1381 (m), 1298 (w), 1177 (w), 1093 (w), 1065 (s), 1006 (vs), 947 (vw), 815 (s), 806 (s), 722 (s), 627 (vw), 565 (m), 506 (vs), 471 (m).



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17	Spectral Size	65536

Figure S1. ^{1}H NMR spectrum of *tris*(4-bromophenyl)phosphine.

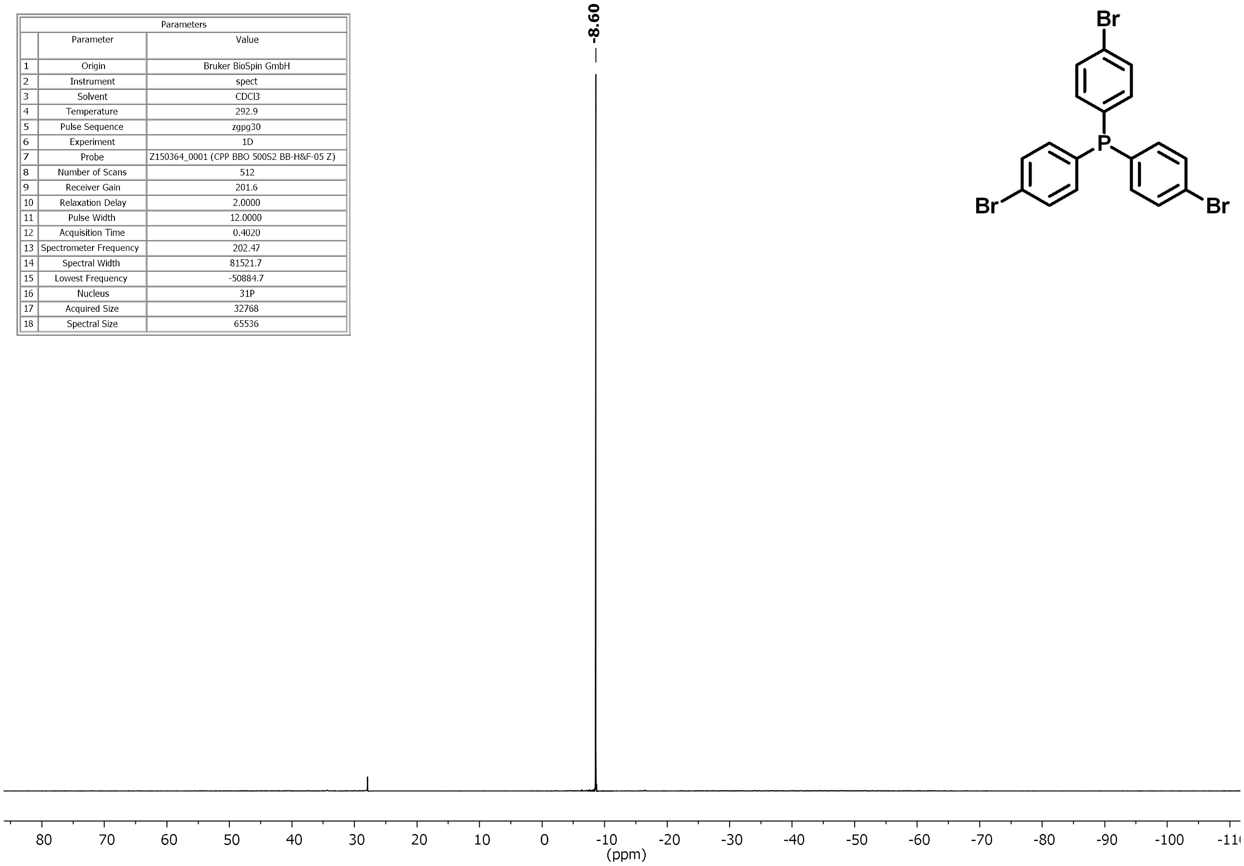

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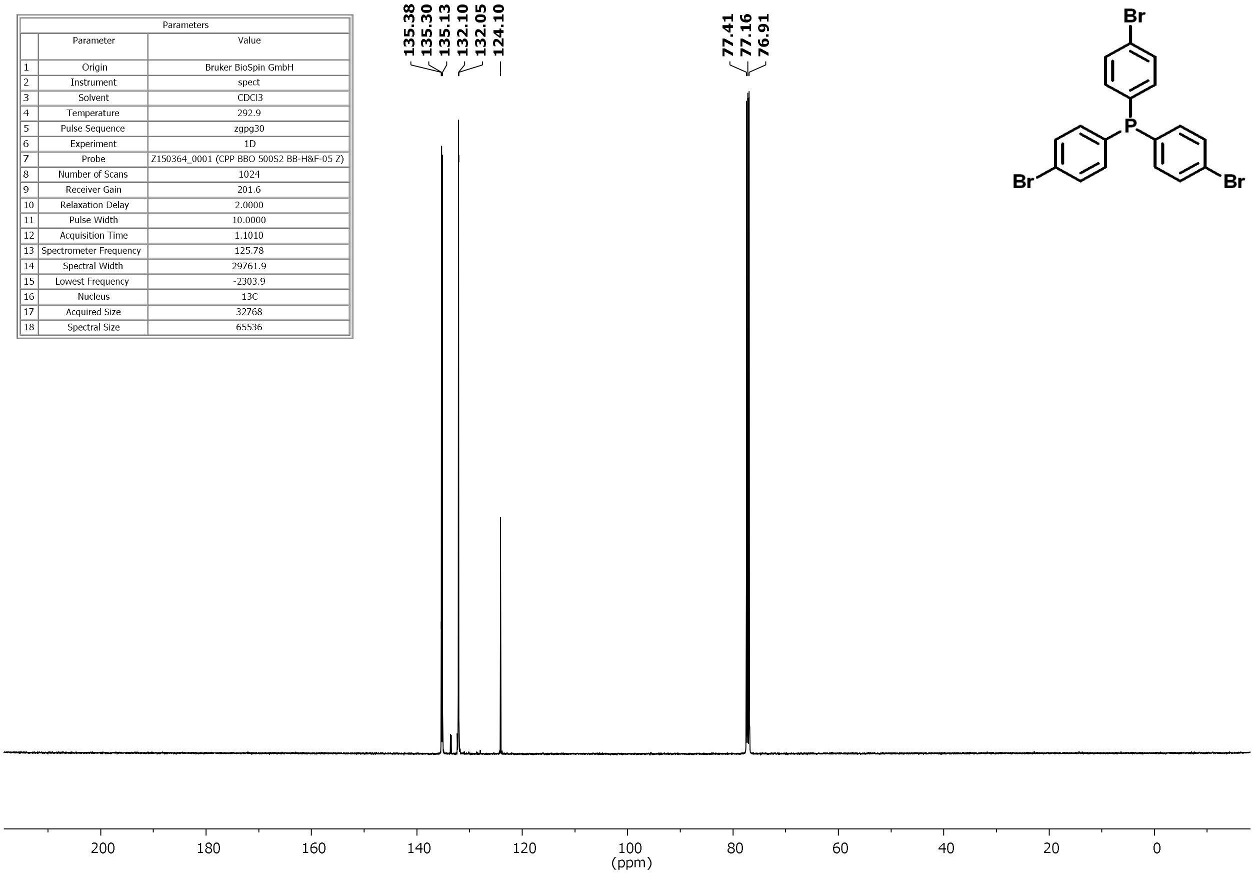
Figure S2. ^{31}P NMR spectrum of *tris*(4-bromophenyl)phosphine.



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8	Number of Scans	1024
9	Receiver Gain	201.6
10	Relaxation Delay	2.0000
11	Pulse Width	10.0000
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13	Spectrometer Frequency	125.78
14	Spectral Width	29761.9
15	Lowest Frequency	-2303.9
16	Nucleus	13C
17	Acquired Size	32768
18	Spectral Size	65536

Figure S3. ^{13}C NMR spectrum of *tris*(4-bromophenyl)phosphine.

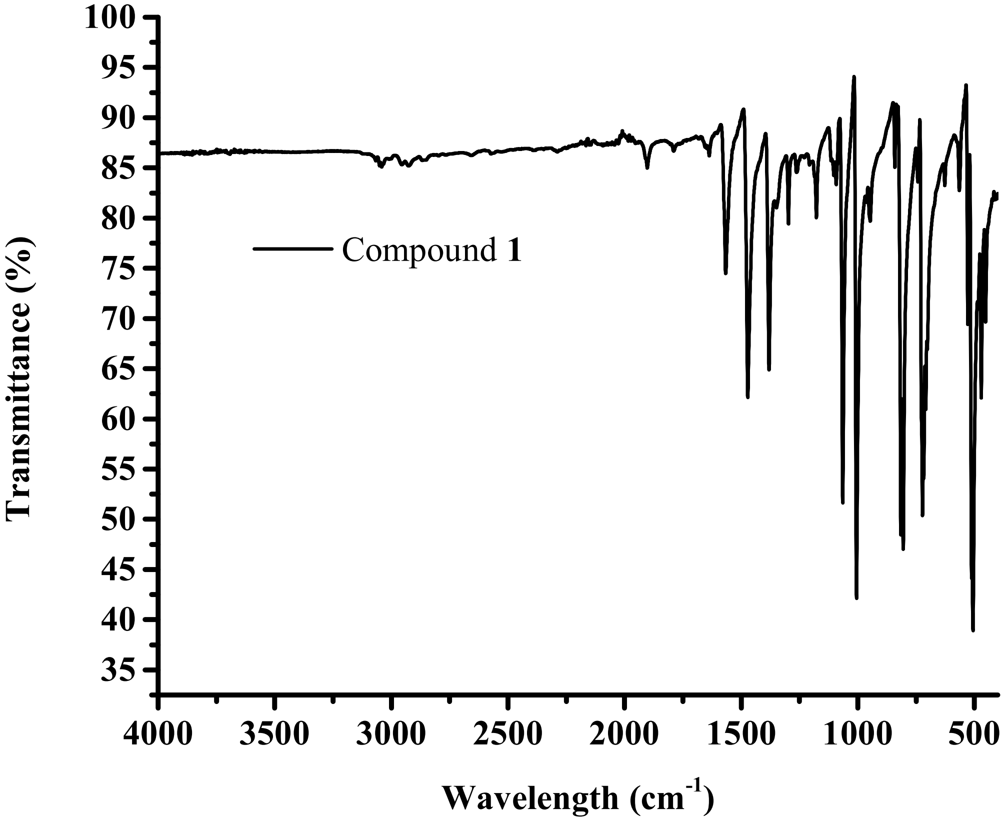

Figure S4. Infrared spectrum of *tris*(4-bromophenyl)phosphine.

Synthesis of *tris*(4-carboxyphenyl)phosphine (2).

In a 500 mL 3-neck round bottom flask, *tris*(4-bromophenyl)phosphine (**1**) (2.50 g, 5.01 mmol) was dissolved in dry THF (250 mL). The solution was cooled down to −78 °C (acetone/dry ice bath). To the cooled solution, *n*-BuLi (6.67 mL of 2.48 M in hexanes, 16.5 mmol) was added dropwise *via* syringe over 30 minutes giving an orange/red suspension. After stirring at −78 °C for an additional 2 hours, excess crushed CO_2(s) was added to the lithiated phosphine resulting in a white suspension. The suspension was then allowed to stir overnight to slowly acclimate to room temperature. The lithium salt was then collected by centrifugation and dried under vacuum. The lithium salt was further dissolved in degassed H_2O (30 mL) and cooled in an ice bath. HCl (2 M) was added dropwise until the pH of the suspension was ~ 2 – 3. The white precipitate was collected by centrifuge and the pellet was washed with addition amounts of H_2O. The pellet was dried under vacuum affording 1.67 g (84 %) of a white solid. ^{1}H NMR (DMSO-d_6, 500.18 MHz) δ = 13.12 (s), 7.97 (d, 6H), 7.38 (t, 6H); ^{13}C{^{1}H} NMR (DMSO-d_6, 125.78 MHz) δ = 166.92 (s), 140.97 (d), 133.51 (d), 131.60 (s), 129.67 (s); ^{31}P{^{1}H} NMR (DMSO-d_6, 202.47 MHz) δ = −6.38. FT-IR (ATR): ν_{max} (cm^{-1}) = 3375 (m, br), 2538 (w, br), 1685 (s), 1594 (m), 1557 (w), 1415 (m), 1393 (m), 1311 (w), 1285 (m, br), 1181 (m), 1128 (w), 1085 (w), 1016 (m), 908 (w, br), 850 (m), 807 (w), 759 (m), 693 (m), 513 (m), br), 471 (w).

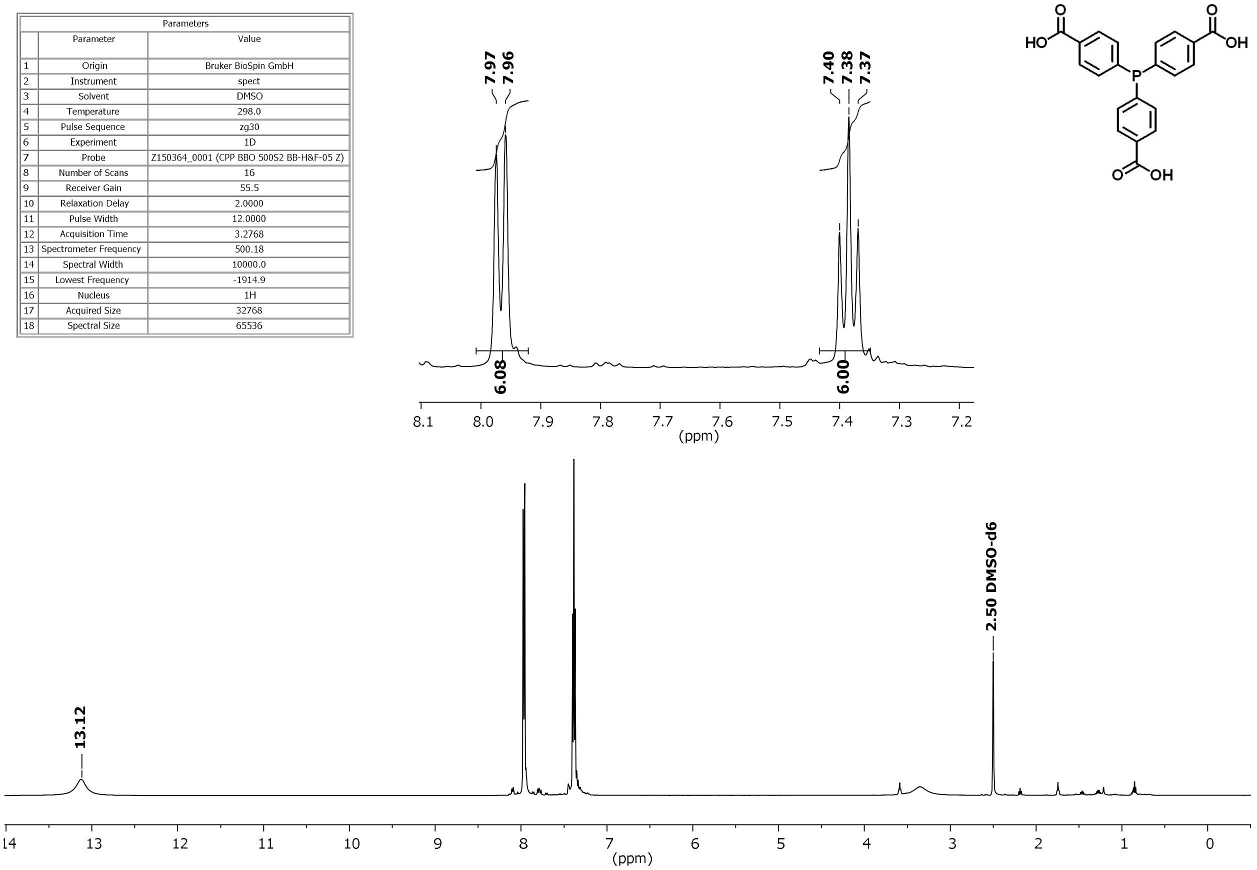

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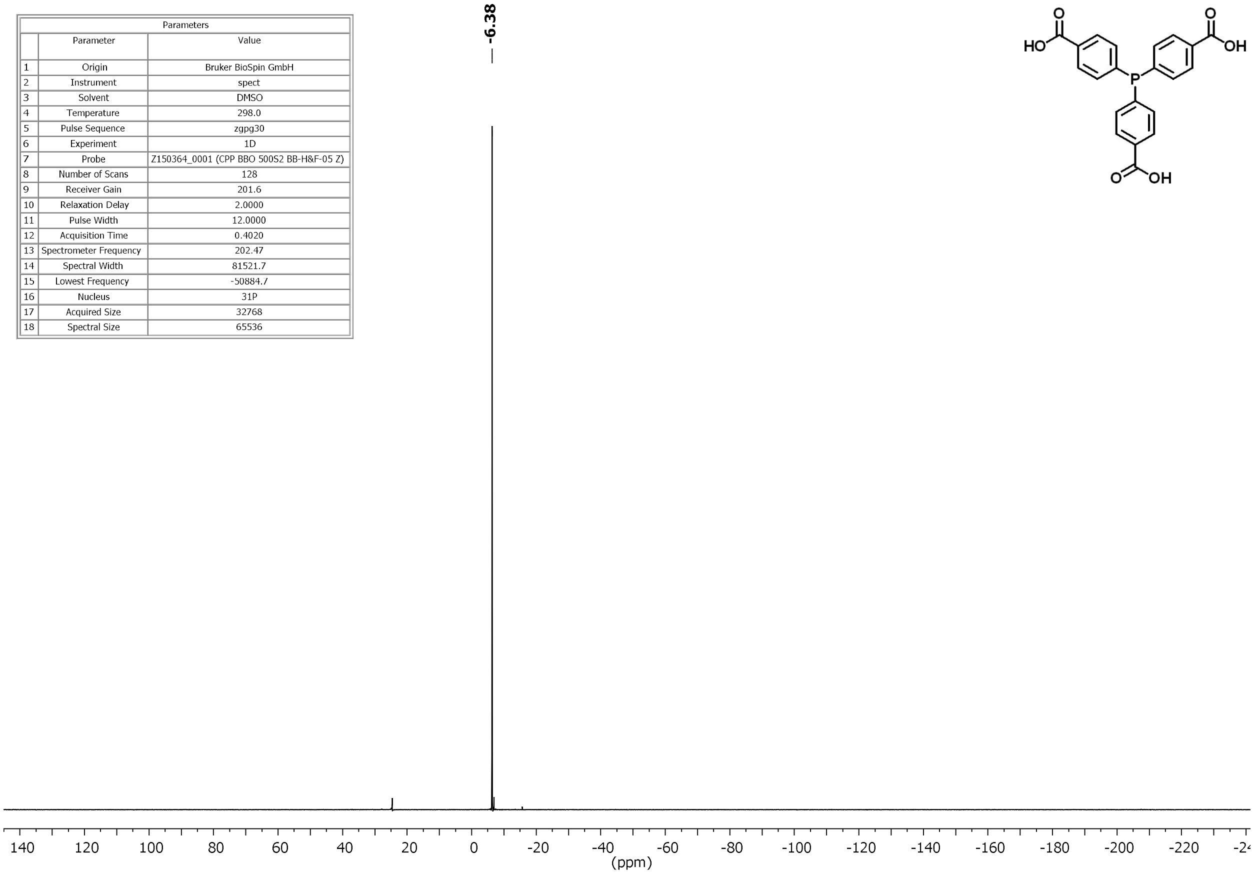
Figure S5. ^{1}H NMR spectrum of *tris*(4-carboxyphenyl)phosphine.



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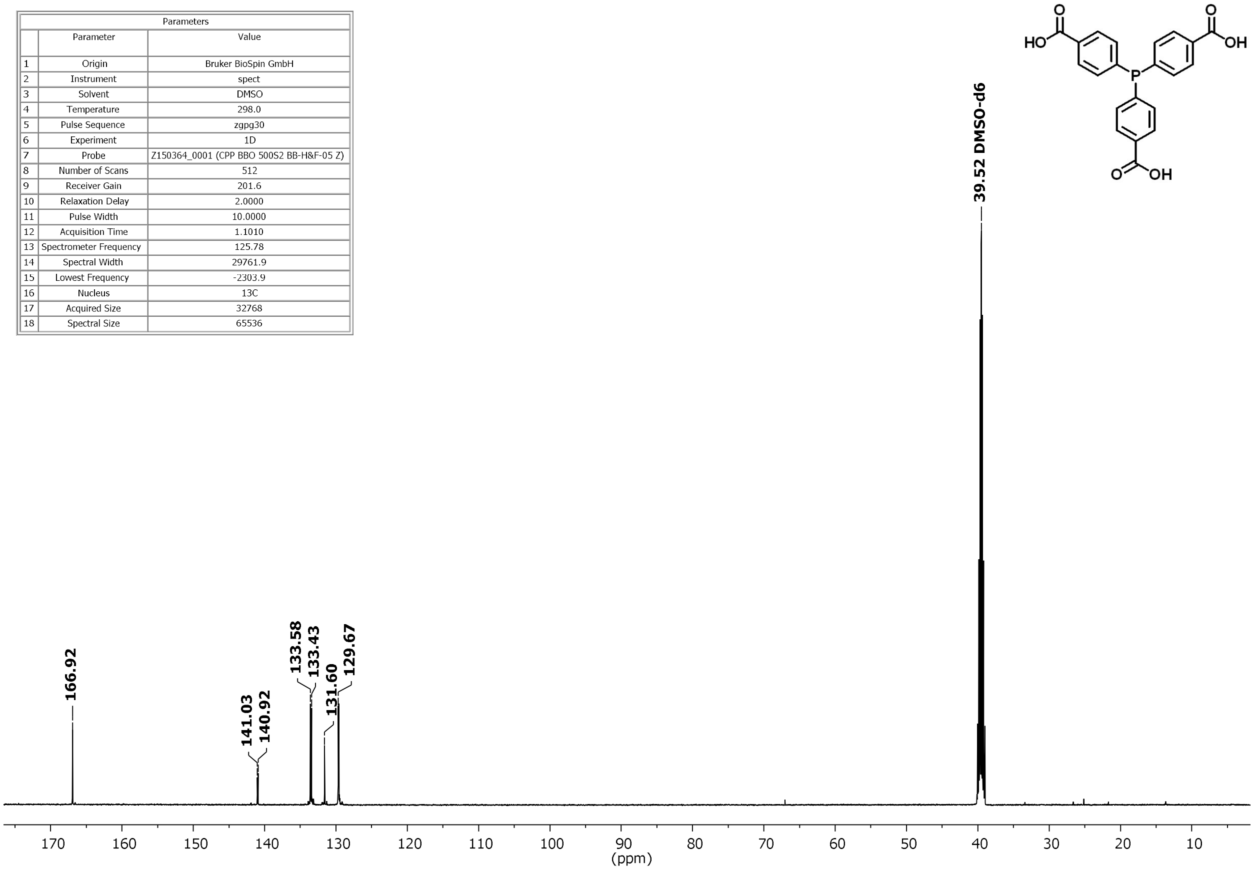
11	Pulse Width	12.0000
12	Acquisition Time	0.4020
13	Spectrometer Frequency	202.47
14	Spectral Width	81521.7
15	Lowest Frequency	-50884.7
16	Nucleus	31P
17	Acquired Size	32768
18	Spectral Size	65536

Figure S6. ^{31}P NMR spectrum of *tris*(4-carboxyphenyl)phosphine.



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6	Experiment	1D
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9	Receiver Gain	201.6
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14	Spectral Width	29761.9
15	Lowest Frequency	-2303.9
16	Nucleus	13C
17	Acquired Size	32768
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Figure S7. ^{13}C NMR spectrum of *tris*(4-carboxyphenyl)phosphine.

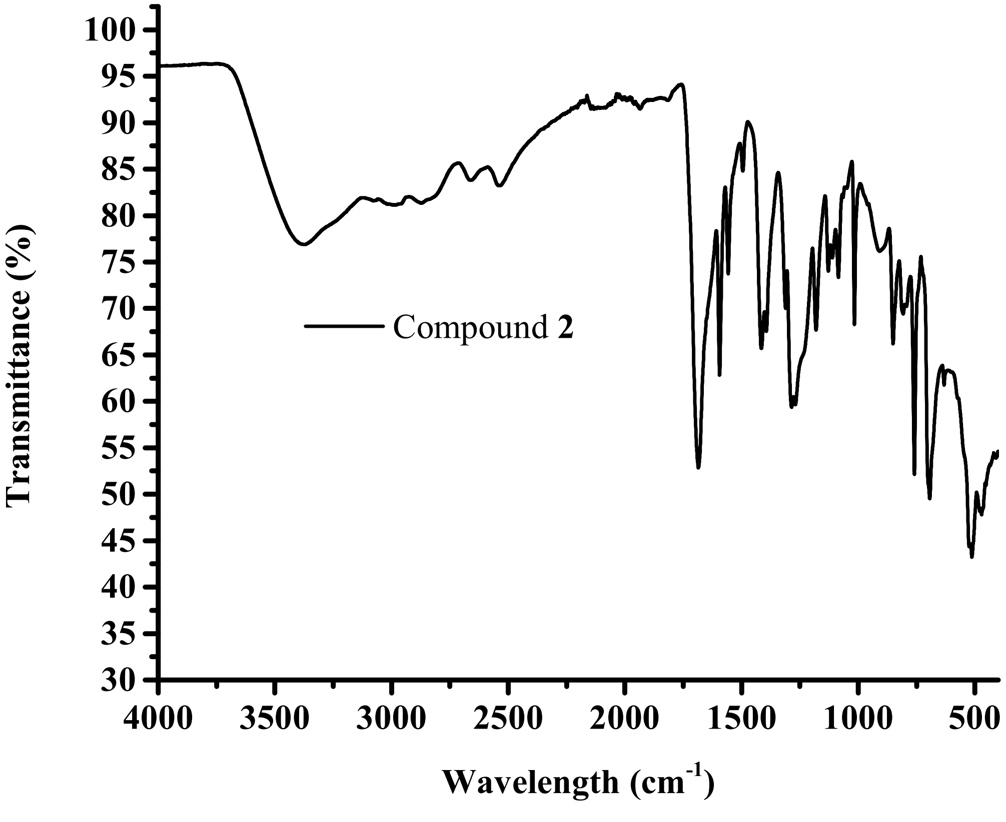

Figure S8. Infrared spectrum of *tris*(4-carboxyphenyl)phosphine.

Synthesis of *tetrakis*(4-carboxyphenyl)phosphonium (tpcppH$_3^+$,iPCM-1).

Tris(4-bromophenyl)phosphine (0.20 g, 0.51 mmol), 4-iodobenzoic acid (0.14 g, 0.56 mmol), and palladium (II) acetate (6 mg, 0.025 mmol) were dissolved in degassed DMF (20 mL) in a 50 mL round bottom flask with a side arm. The resulting yellow solution was stirred under nitrogen at room temperature for 12 hours. The solution was heated to 160 °C until the solution turned a deep red/brown color (4 - 8 hours). The reaction was then cooled to room temperature and reduced (~30 % original volume) and added to ice water (~75 mL) resulting in the formation of a precipitate. The solid was collected and washed with acetone (3 x 15 mL) and dried to afford 0.15 g (57 %) of a beige powder. Crystallizes when concentrated from hot DMF. ^{1}H NMR (DMSO-d_6, 100 °C, 599.68 MHz) δ = 8.24 (dd, 8H), 7.85 (dd, 8H); ^{13}C{^{1}H} NMR (DMSO-d_6, 100 °C, 150.81 MHz) δ = 165.44 (d), 139.86 (s), 134.19 (d), 129.99 (d), 119.52 (d); ^{31}P{^{1}H} NMR (DMSO-d_6, 161.92 MHz) δ = 22.47. FT-IR (ATR): ν_{max} (cm^{-1}) = 3449 (br), 3041 (w), 2800 (w), 2607 (w), 2489 (w), 1702 (s), 1600 (w), 1561 (w), 1545 (w), 1494 (w), 1392 (s), 1313 (w), 1244 (m), 1182 (w), 1128 (w), 1097 (s), 1012 (m), 859 (m), 813 (w), 763 (m), 709 (s), 690 (w), 632 (m), 567 (s), 512 (w), 476 (w), 384 (s), 314 (w), 271 (s), 177 (w), 138 (w), 122 (m). HRMS (ESI+) m/z: [M + H]$^+$ Exact mass calculated for [$C_{28}H_{20}O_8P$]$^+$: 515.0890; Found: 515.0899. Elem. Anal. Calcd. for activated iPCM-1, $C_{28}H_{19}O_8P \cdot H_2O$ requires: C 63.16, H 3.98. Found: C 62.78, H 3.59.

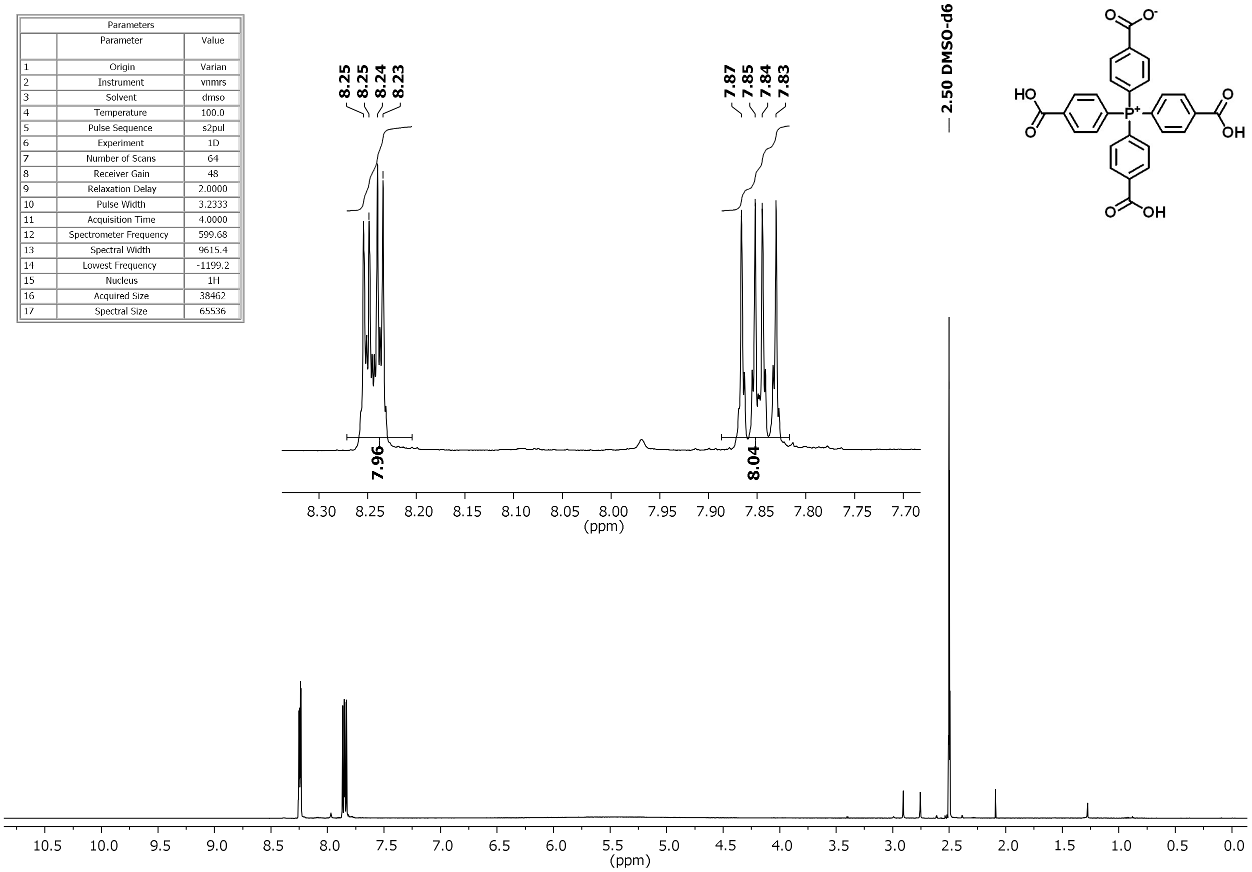

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Figure S9. ^{1}H NMR spectrum of *tetrakis*(4-carboxyphenyl)phosphonium.

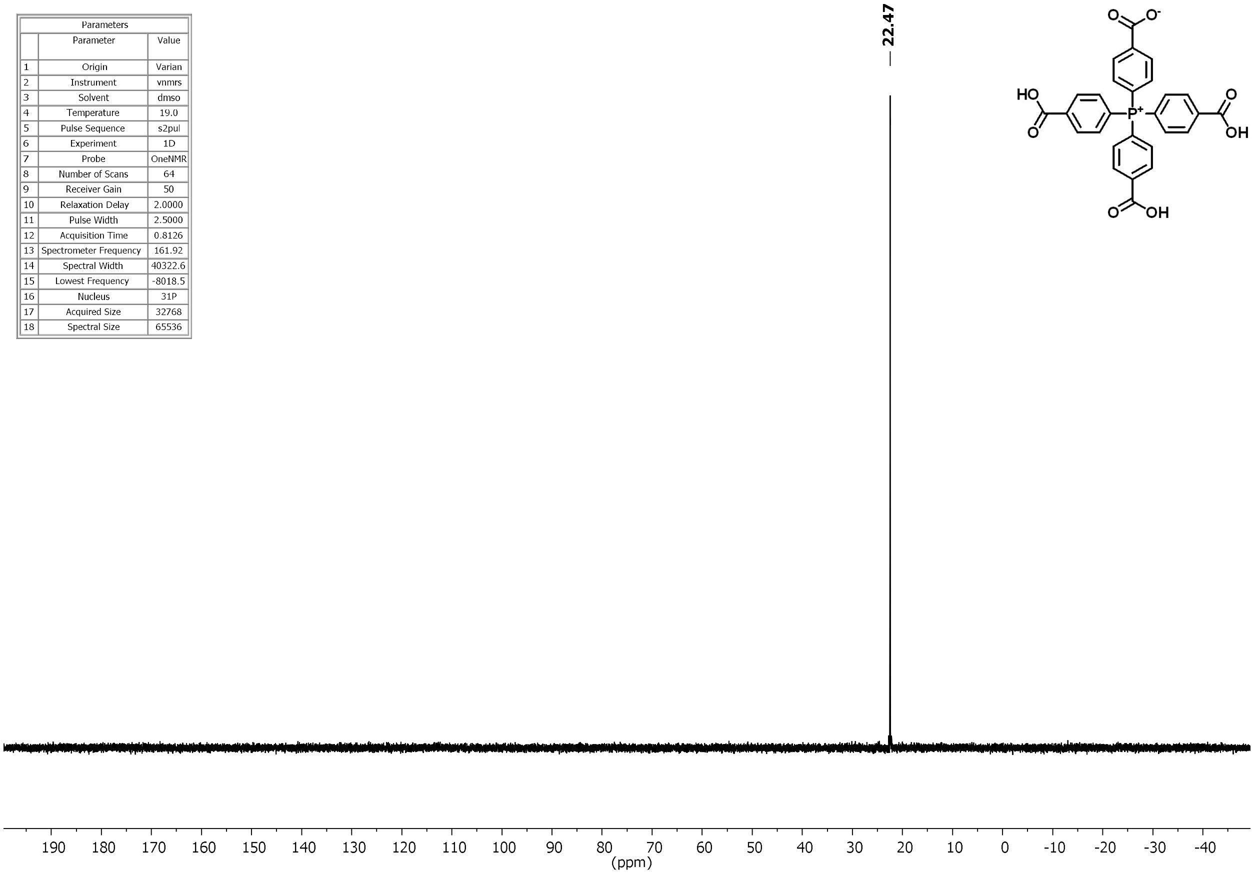

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Figure S10. ^{31}P NMR spectrum of *tetrakis*(4-carboxyphenyl)phosphonium.

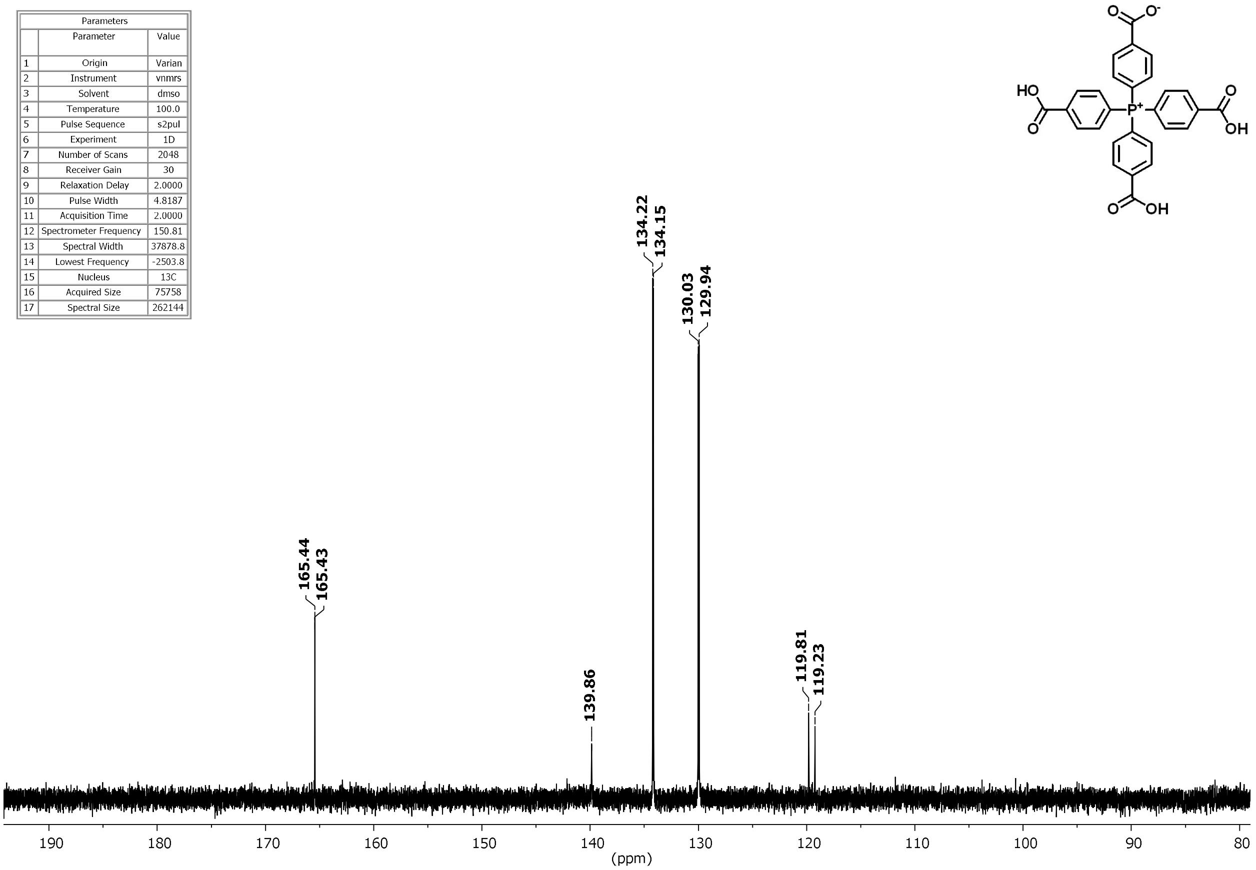

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Figure S11. ^{13}C NMR spectrum of *tetrakis*(4-carboxyphenyl)phosphonium.

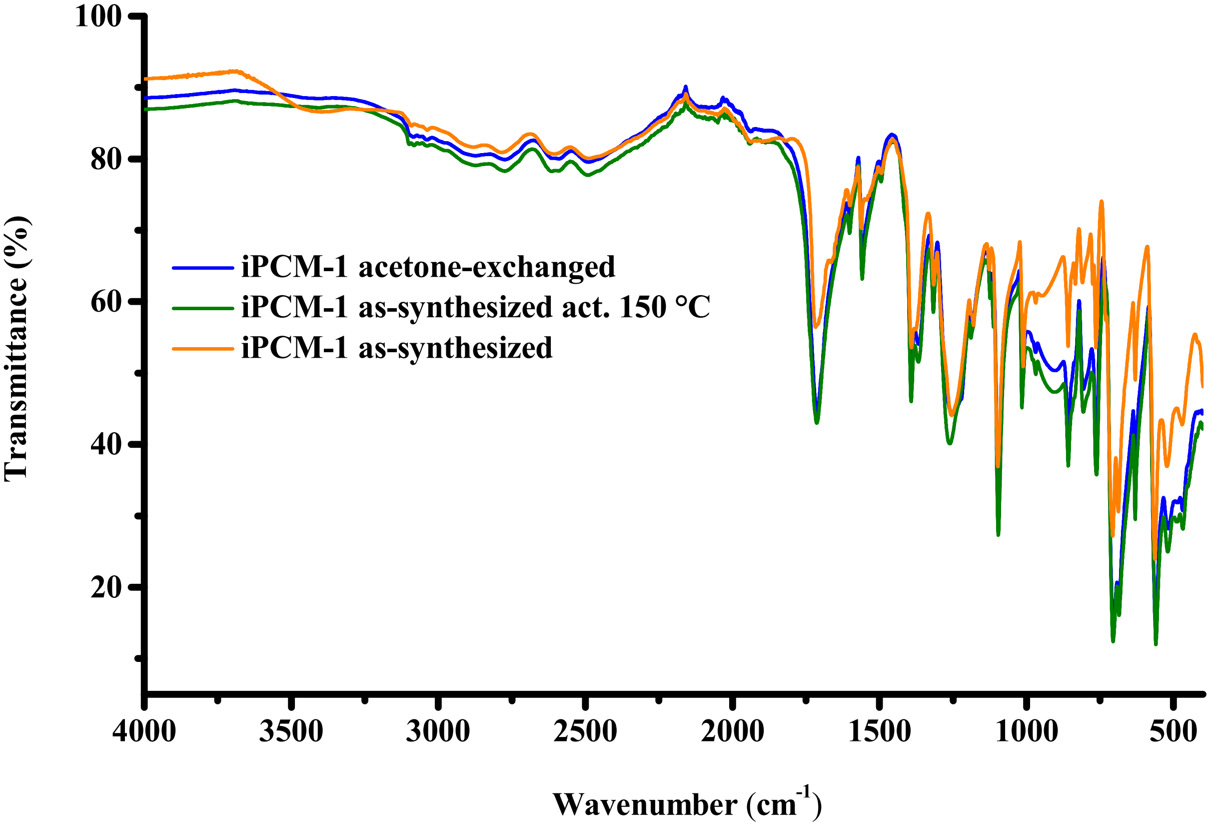


Figure S12. Infrared spectrum of *tetrakis*(4-carboxyphenyl)phosphonium (iPCM-1).

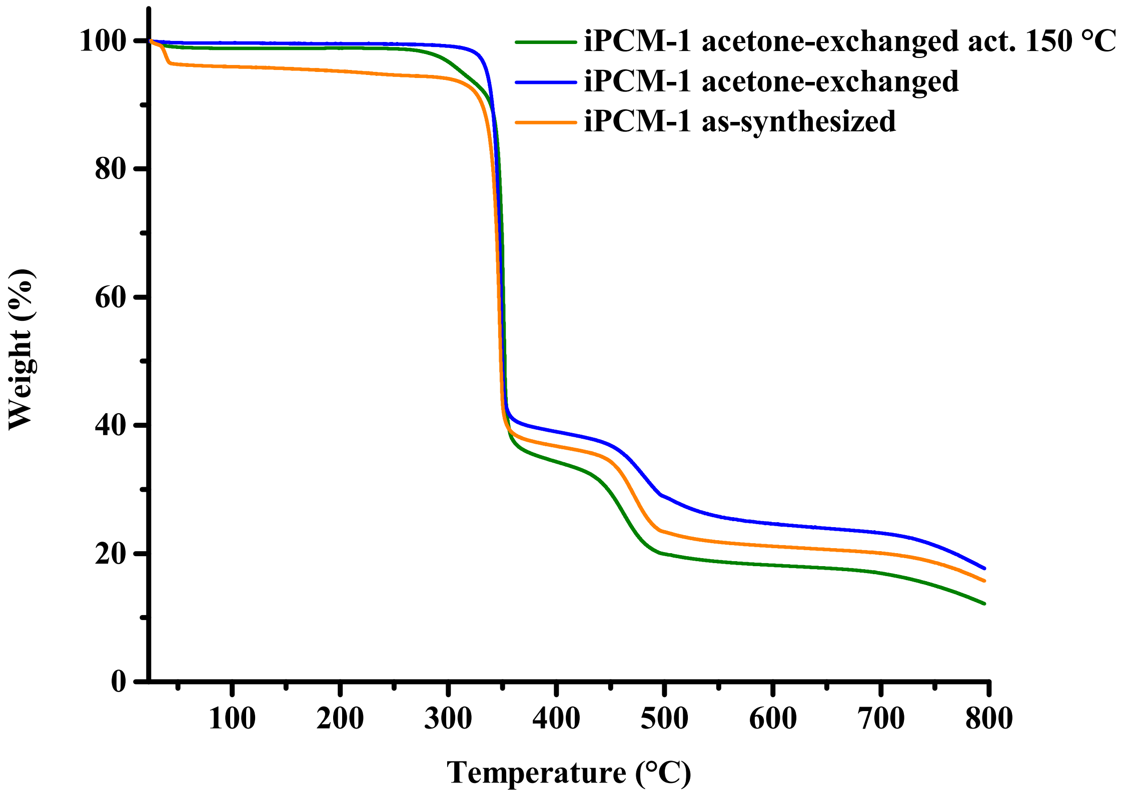


Figure S13. Thermogravimetric analysis (TGA) profiles of iPCM-1.

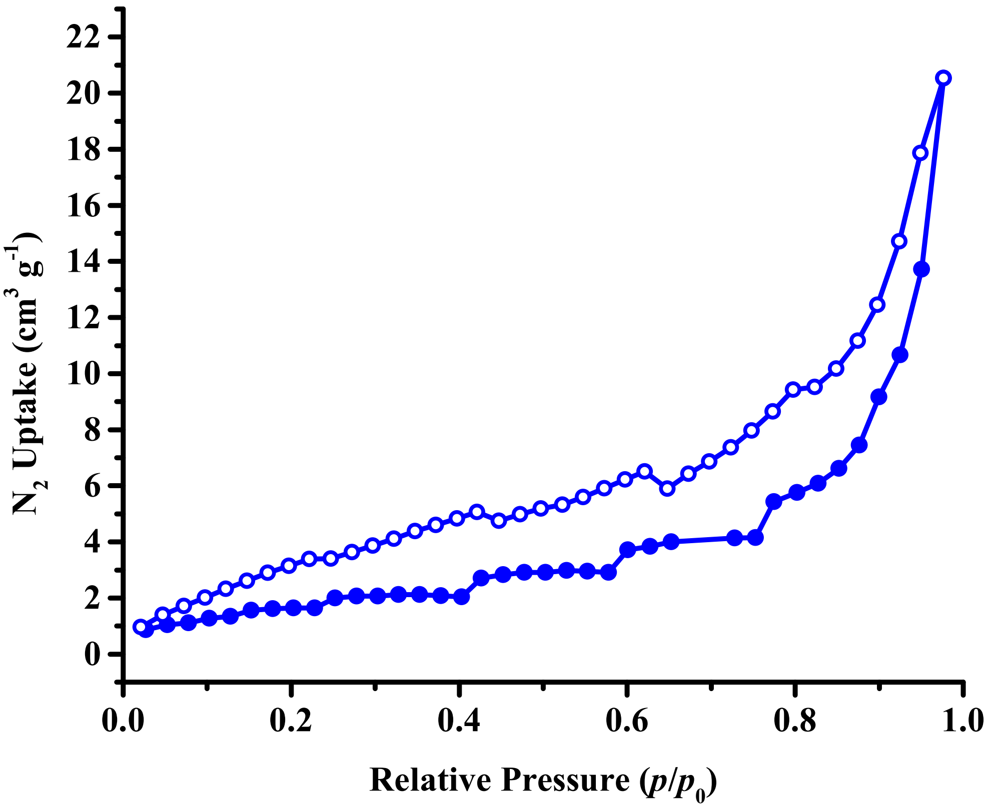


Figure S14. N_2 sorption isotherm of iPCM-1 acetone exchanged and activated at 100 °C and collected at 77 K.

Synthesis of In-PCM-66 [In(tpcpp)].

Tetrakis(4-carboxyphenyl)phosphonium (26 mg, 0.05 mmol) and $In(NO_3)_3$ (15 mg, 0.05 mmol) were suspended in 10 mL of H_2O inside of a 23 cm^3 Teflon-lined autoclave (Parr Corp.), heated at 160 °C for 18 hours, and cooled to room temperature. Once cooled, the crystallites were purified by 3 cycles of sonication and decanting the supernatant affording 7 mg (17% crystalline yield) of a beige microcrystalline powder. FT-IR (ATR): v_{max} (cm^{-1}) = 1729 (w), 1596 (w), 1497 (vw), 1393 (m), 1251 (w), 1101 (m), 1015 (m), 871 (m), 770 (w), 745 (s), 693 (s), 634 (w), 571 (w), 507 (w), 745 (w), 410 (m). Elem. Anal. Calcd. for activated In-PCM-66, $C_{28}H_{16}O_8PIn$ requires: C 53.53, H 2.89. Found: C 53.18, H 2.87.

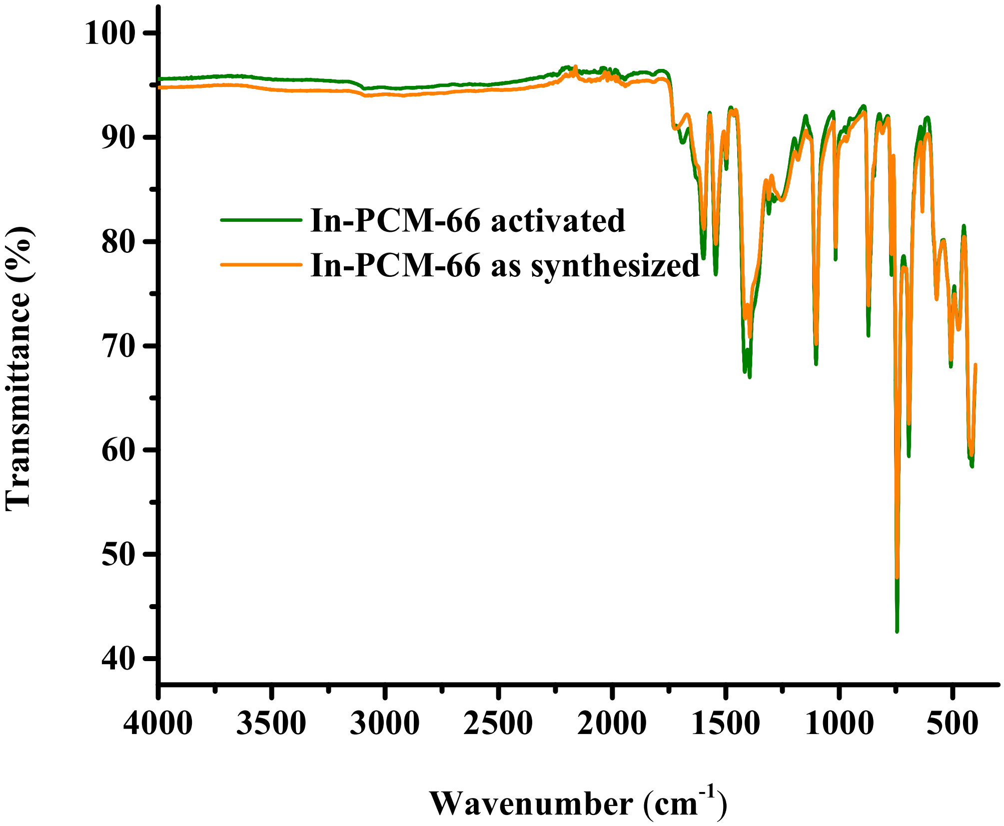


Figure S15. Infrared spectrum of PCM-66.

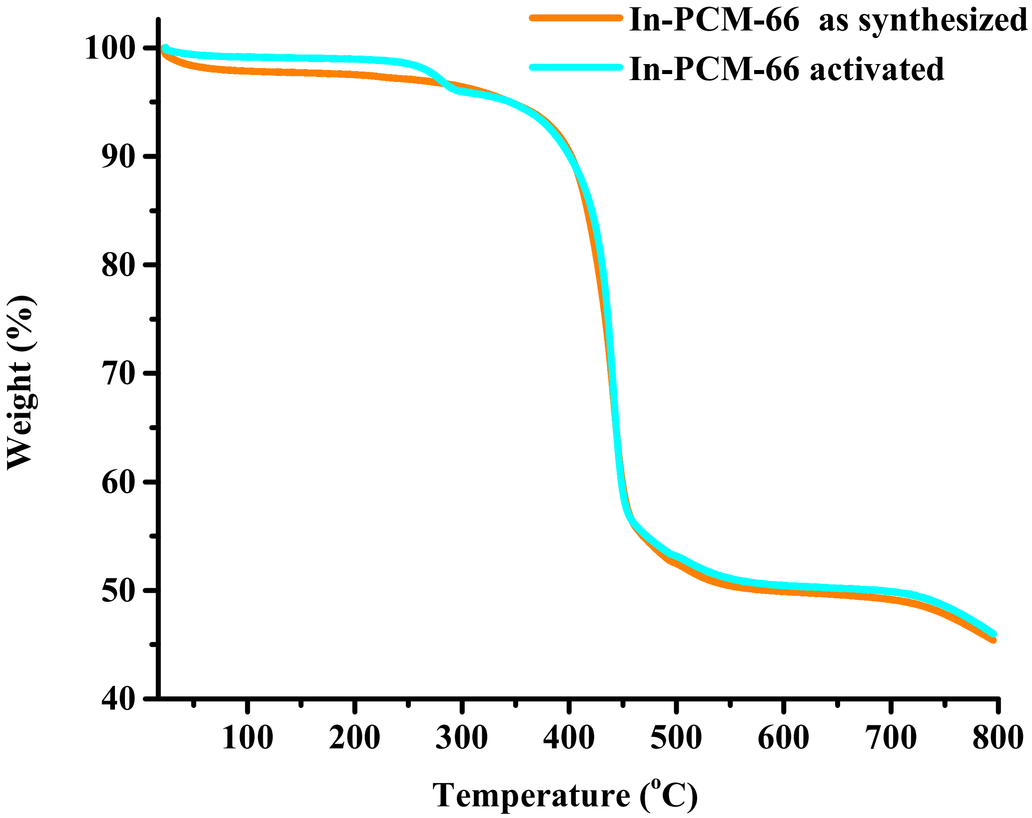


Figure S16. Thermogravimetric analysis (TGA) profiles of PCM-66.

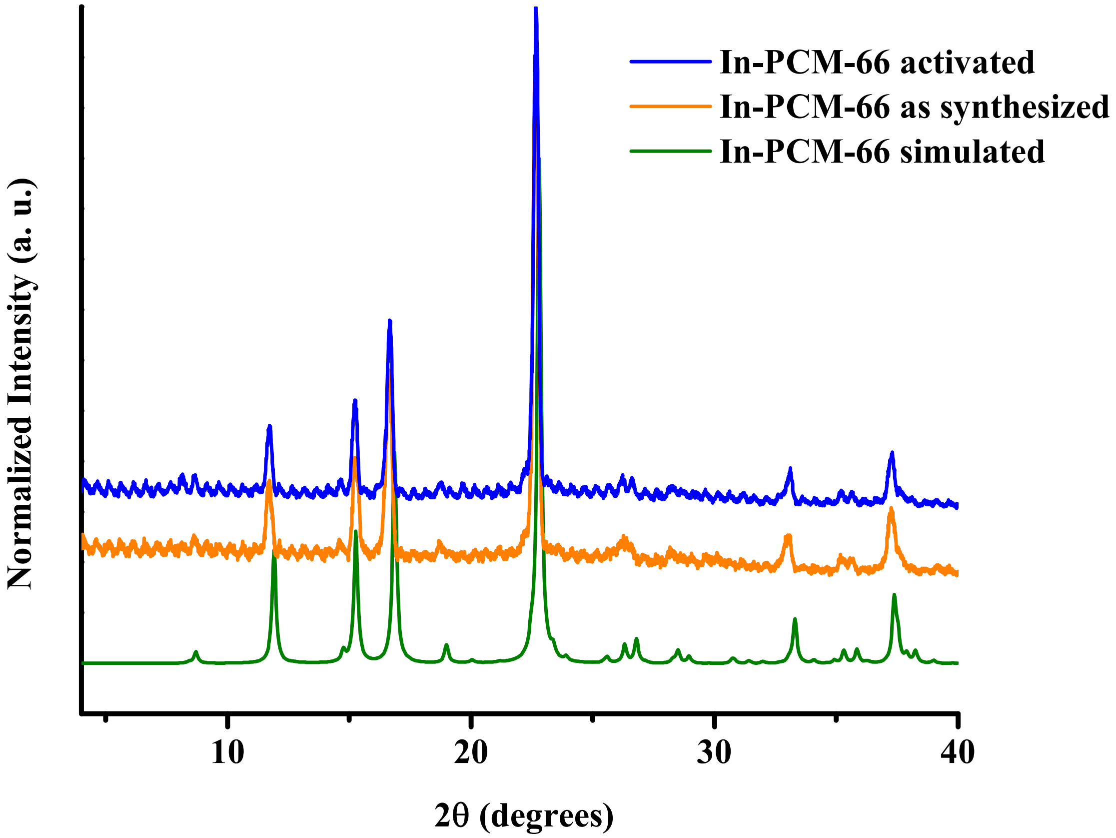


Figure S17. PXRD patterns of PCM-66.

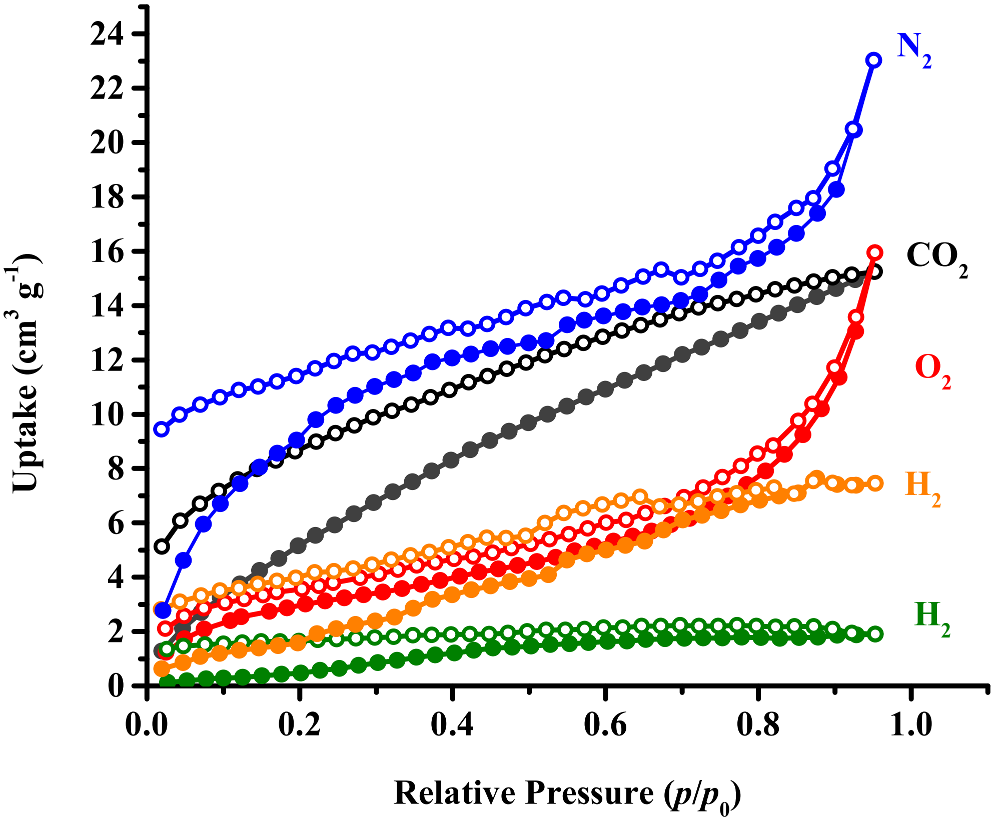


Figure S18. Sorption isotherms of PCM-66 activated at 100 °C.

Synthesis of Mg-PCM-75.

Tetrakis(4-carboxyphenyl)phosphonium (10 mg, 0.02 mmol) and $Mg(NO_3)_2 \cdot 6\ H_2O$ (15 mg, 0.06 mmol) were combined in a 20 mL scintillation vial with 5 mL of DMF: MeOH: H_2O (5:2:1, v:v). The vial was placed inside an oven at 85 °C for 12 hours. The crystalline material was washed with fresh solvent and filtered affording 8 mg (53% crystalline yield) of colorless rod-like prisms. FT-IR (ATR): ν_{max} (cm^{-1}) = 3207 (m, br), 1644 (w), 1588 (s), 1536 (s), 1375 (vs), 1097 (s), 1000 (w), 766 (m), 721 (m), 684 (w), 565 (m), 472 (w). Elem. Anal. Calc. for $[Mg_3(tpcpp)_2(H_2O)_{12}]$ $C_{56}H_{56}Mg_3O_{28}P_2$ requires: C 51.27, H 4.30, N 0.00. Found: C 51.10, H 3.96, N 0.00. Elem. Anal. found post H_2S C 46.99, H 4.24 , N 0.87, S 0.79.

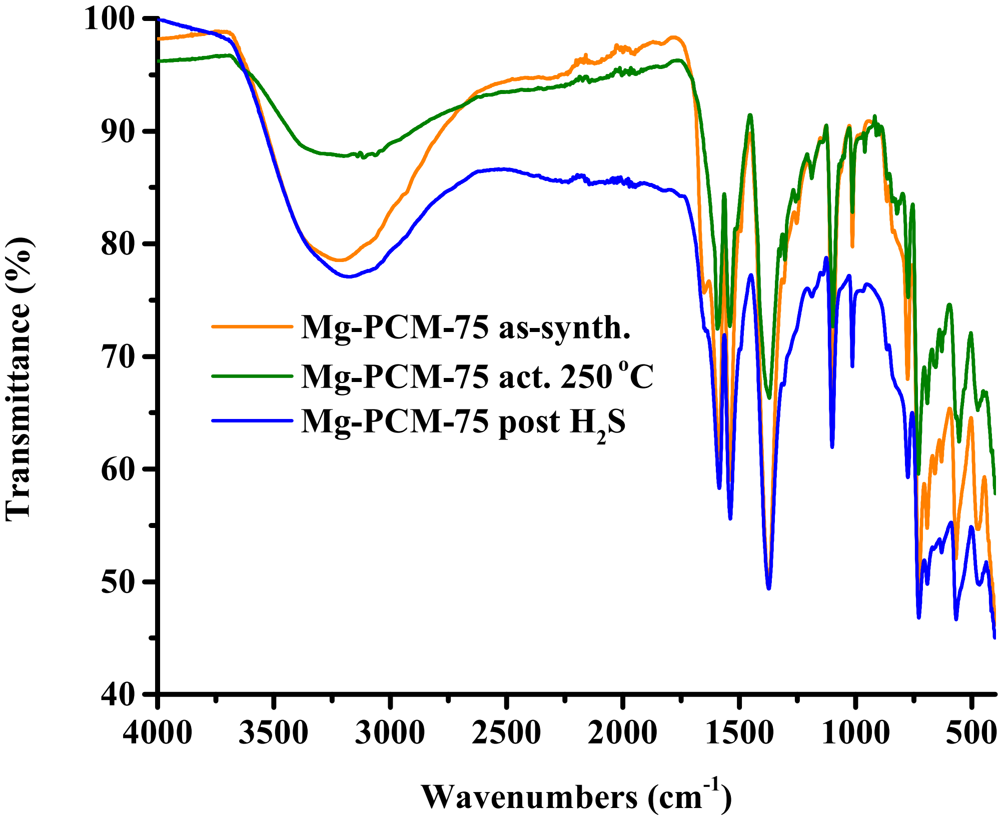


Figure S19. Infrared spectrum of PCM-75.

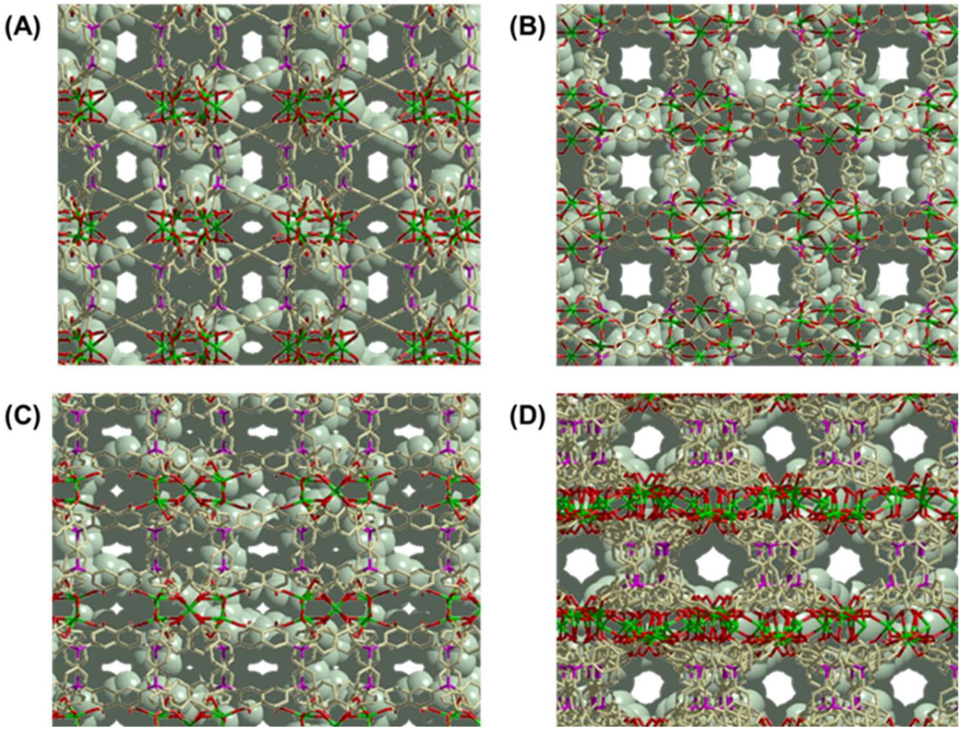


Figure S20. (A) View along the *a*-axis of PCM-75; (B) view along the *b*-axis of PCM-75; (C) view along the *c*-axis of PCM-75; (D) view along the *a,b*-bisector of PCM-75.

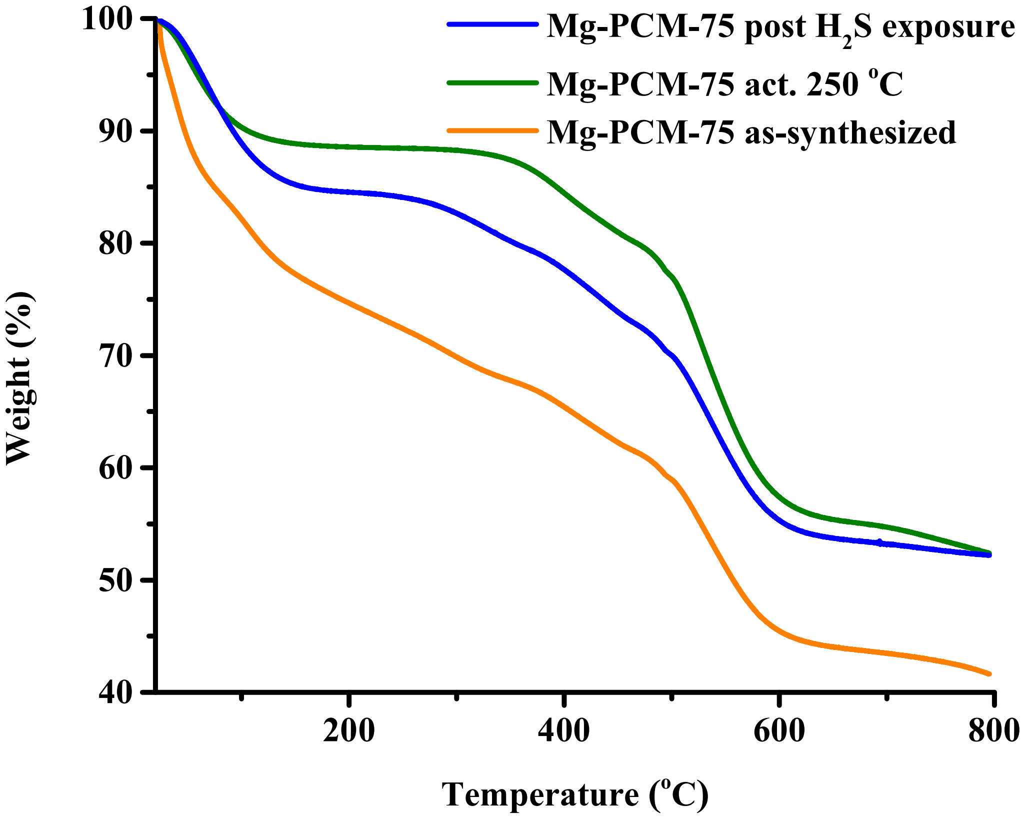


Figure S21. Thermogravimetric analysis (TGA) profiles of PCM-75.

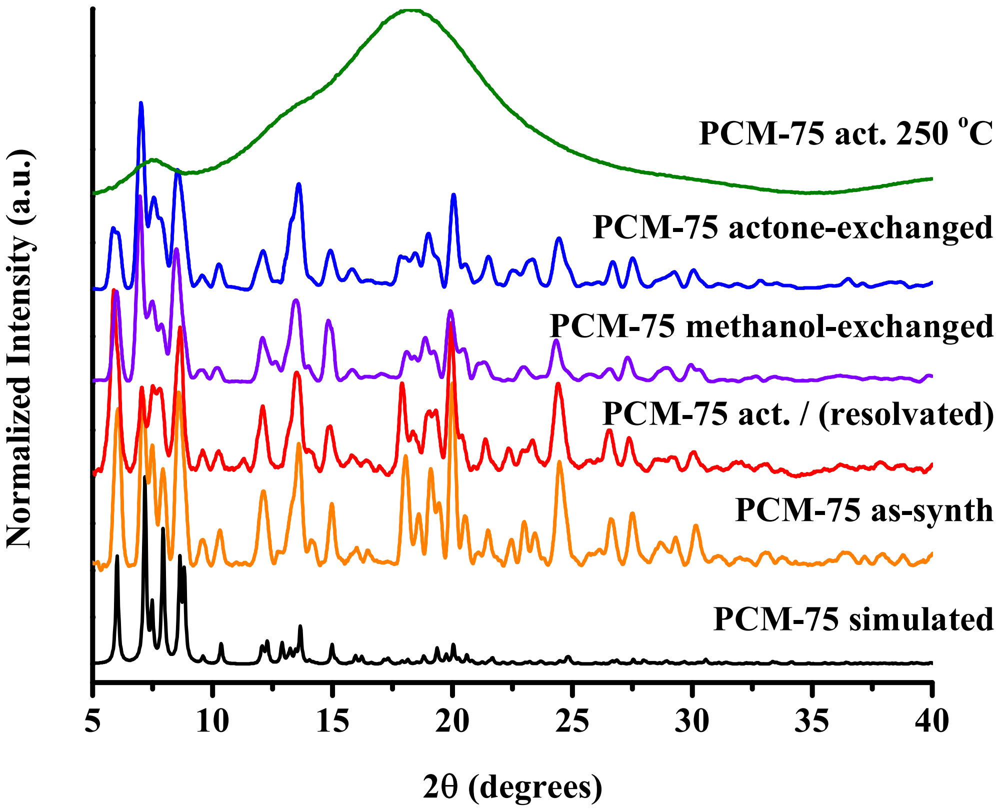


Figure S22. PXRD patterns of PCM-75 as synthesized and exchanged.

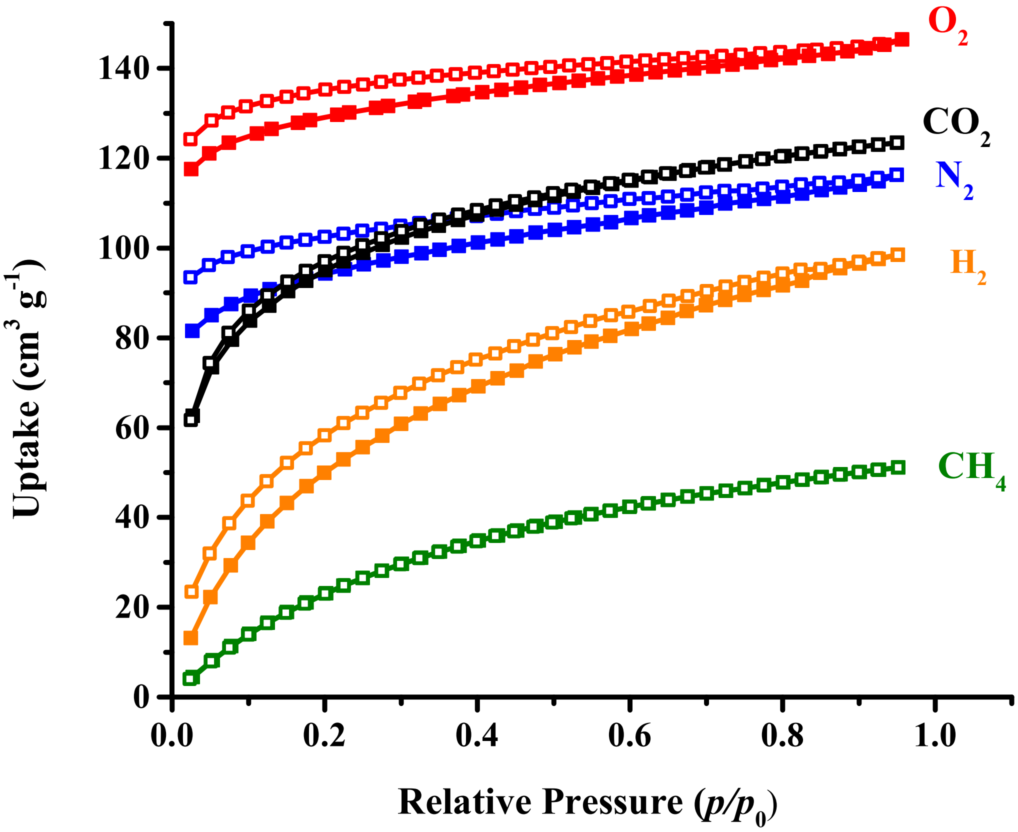


Figure S23. Sorption isotherms of Mg-PCM-75 activated at 75 °C.

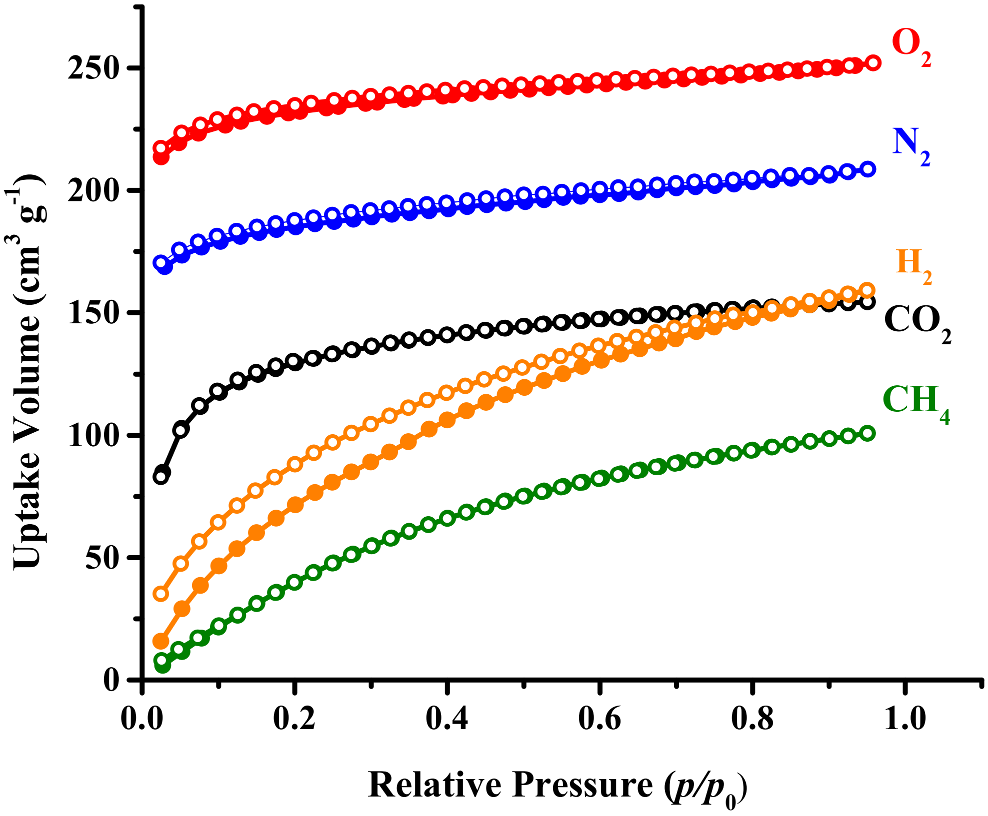


Figure S24. Sorption isotherms of Mg-PCM-75 activated at 150 °C.

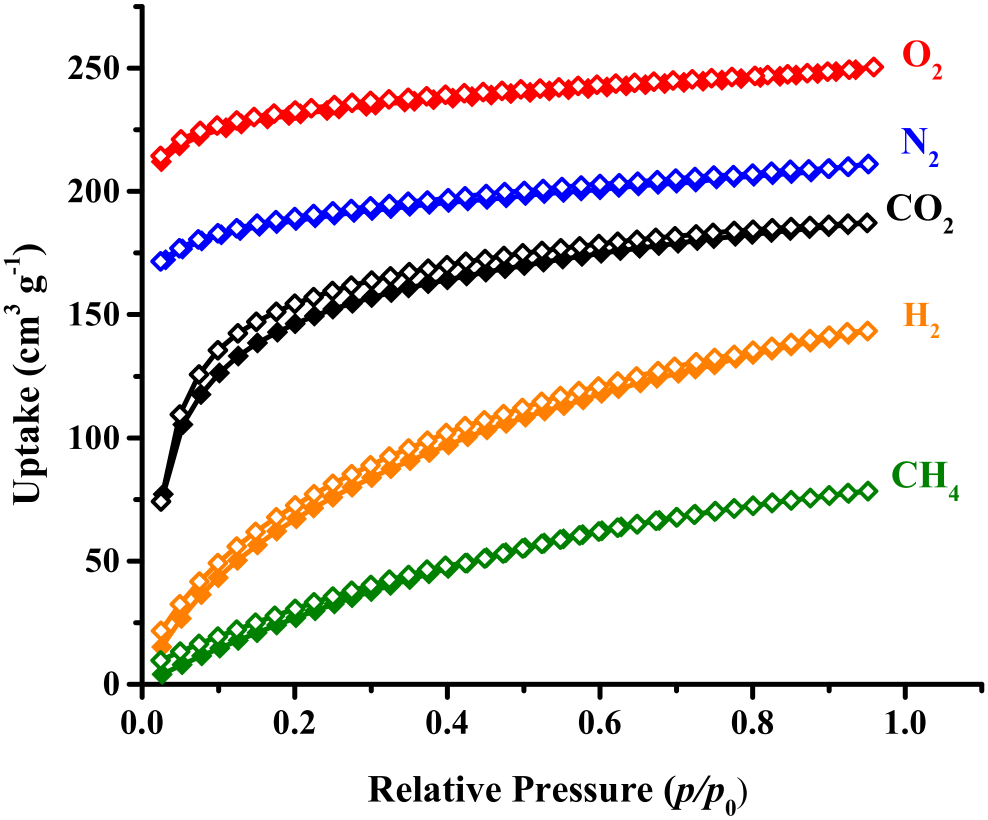


Figure S25. Sorption isotherms of Mg-PCM-75 activated at 250 °C.

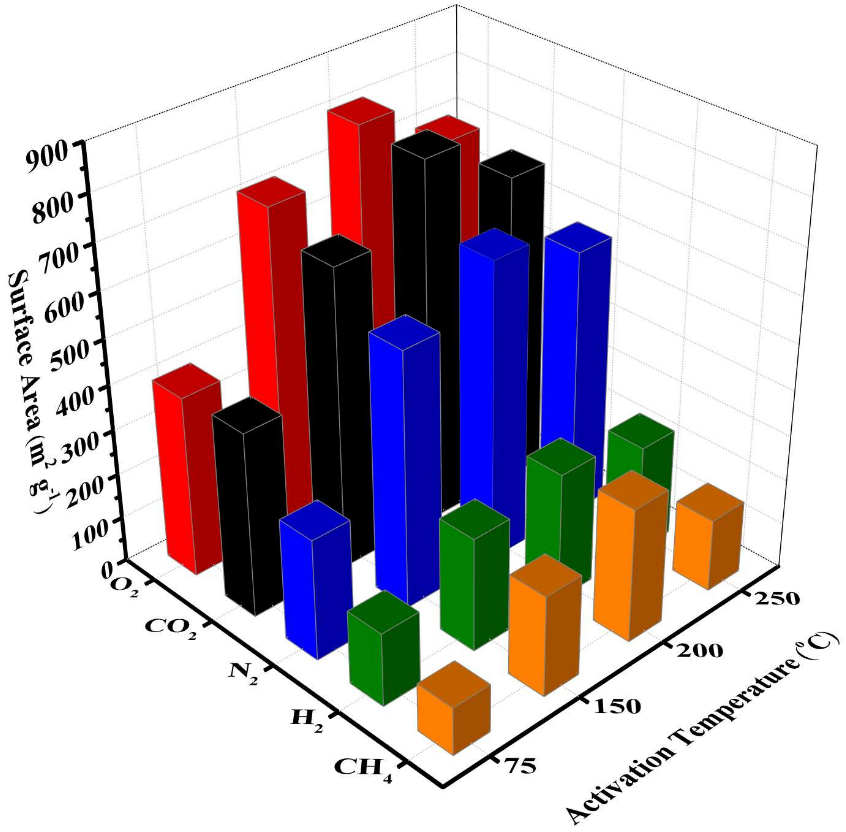


Figure S26. A graphical representation of the surface area for PCM-75 based on different probe gasses and activation conditions.

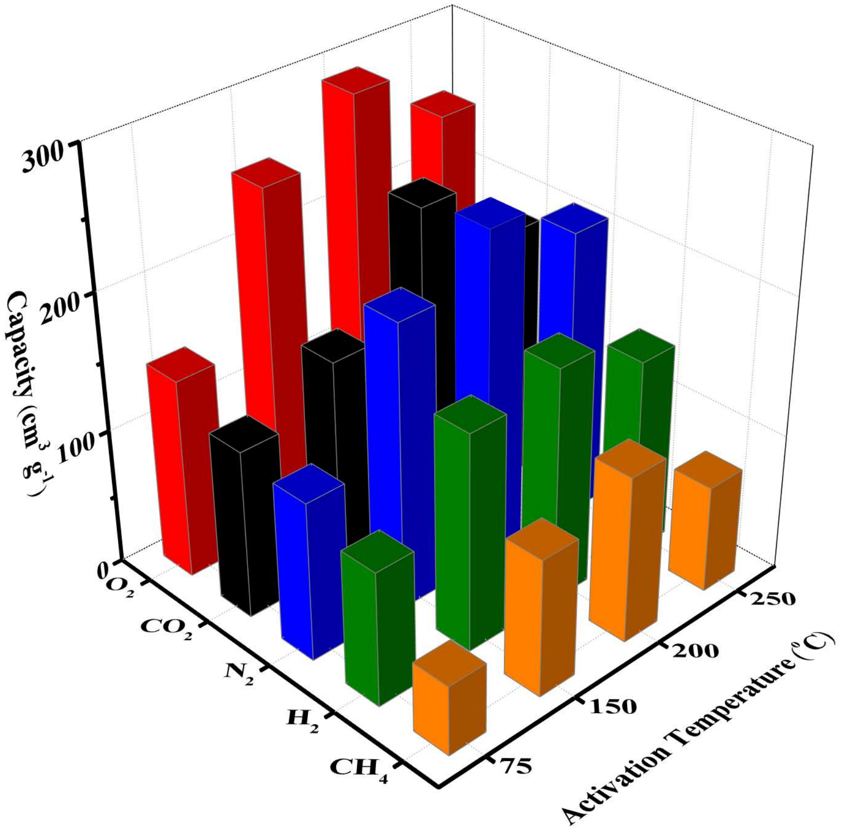


Figure S27. A graphical representation of the volumetric capacity for PCM-75 based on different probe gasses and activation conditions.

Table S1. Tabulated gas sorption data for PCM-75

Activation Temperature (°C)	***75***	***150***	***200***	***250***
N_2 *SA_{BET} (m^2 g^{-1})/Capacity (cm^3 g^{-1})*	296 / 116.3	567 /208.6	661 / 241.7	592 / 211.1
N_2 *Pore Volume (cm^3 g^{-1})*	0.18	0.32	0.37	0.33
CO_2 *SA_{BET} (m^2 g^{-1})/Capacity (cm^3 g^{-1})*	410 /123.4	663 / 154.4	800 / 233.7	684 /187.2
CO_2 *Pore Volume (cm^3 g^{-1})*	0.23	0.29	0.44	0.35
O_2 *SA_{BET} (m^2 g^{-1})/Capacity (cm^3 g^{-1})*	403 / 146.4	717 / 252.0	808 / 290.3	698 / 250.5
H_2 *SA_{BET} (m^2 g^{-1})/Capacity (cm^3 g^{-1})*	163 / 98.5	252 / 159.1	283 / 171.0	238 / 143.4
CH_4 *SA_{BET} (m^2 g^{-1})/Capacity (cm^3 g^{-1})*	106 / 51.1	233 / 100.7	297 / 122.0	161 / 78.5

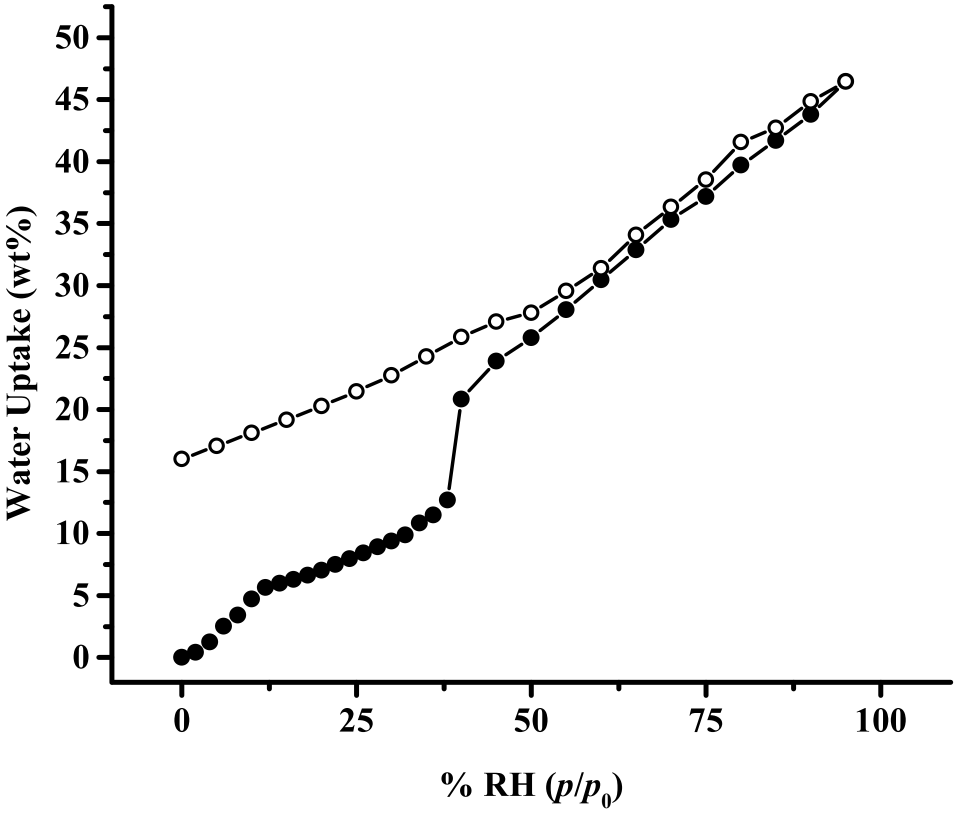


Figure S28. Water sorption isotherm of PCM-75 collected at 20 °C.

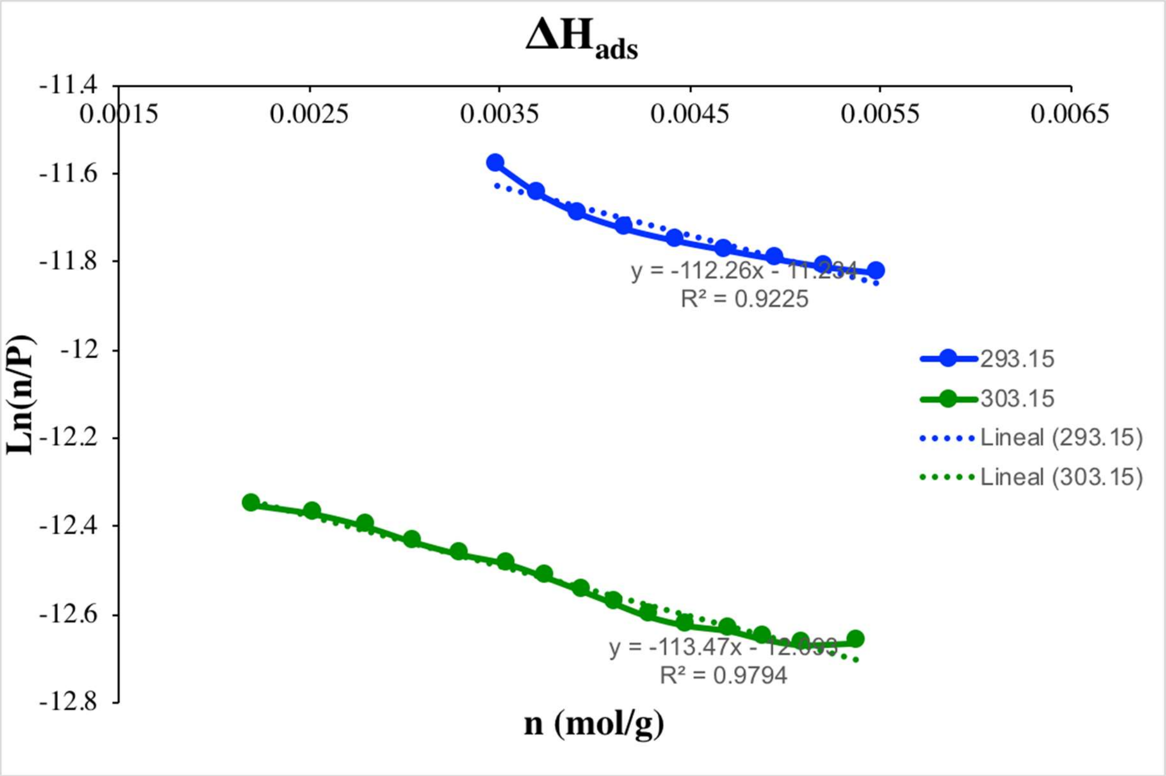


Figure S29. Fitting of the Clausius–Clapeyron equation to calculate the isosteric heat of adsorption (ΔH_{ads}) for water.

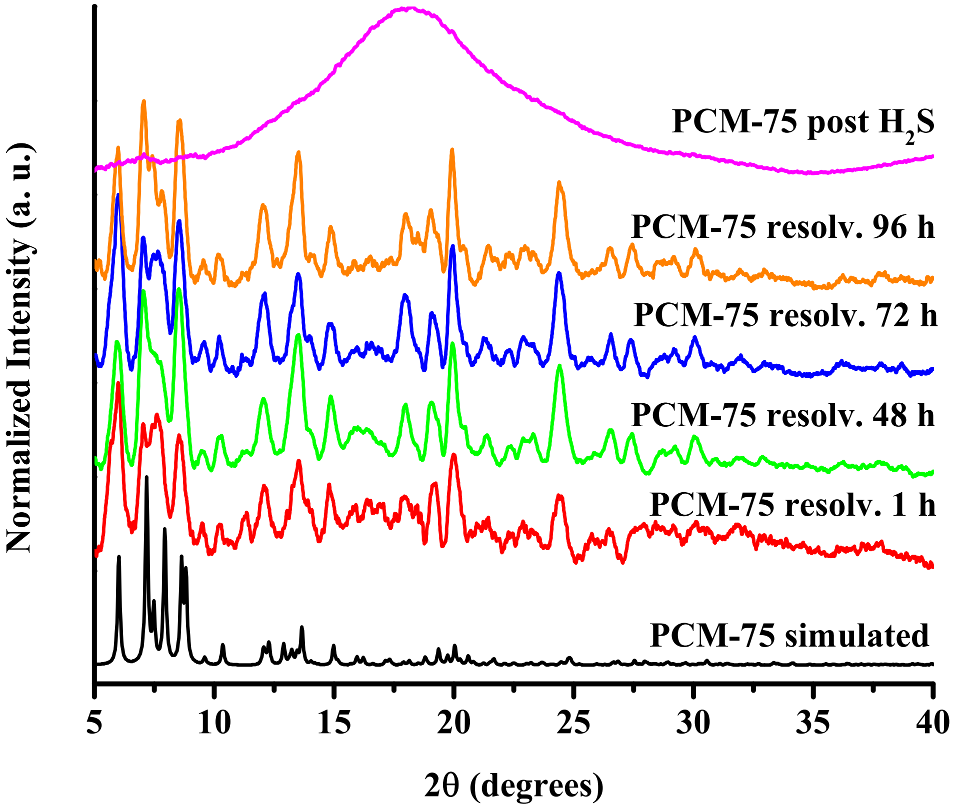


Figure S30. PXRD patterns of PCM-75 after exposure to H_2S (top) and resolvated.

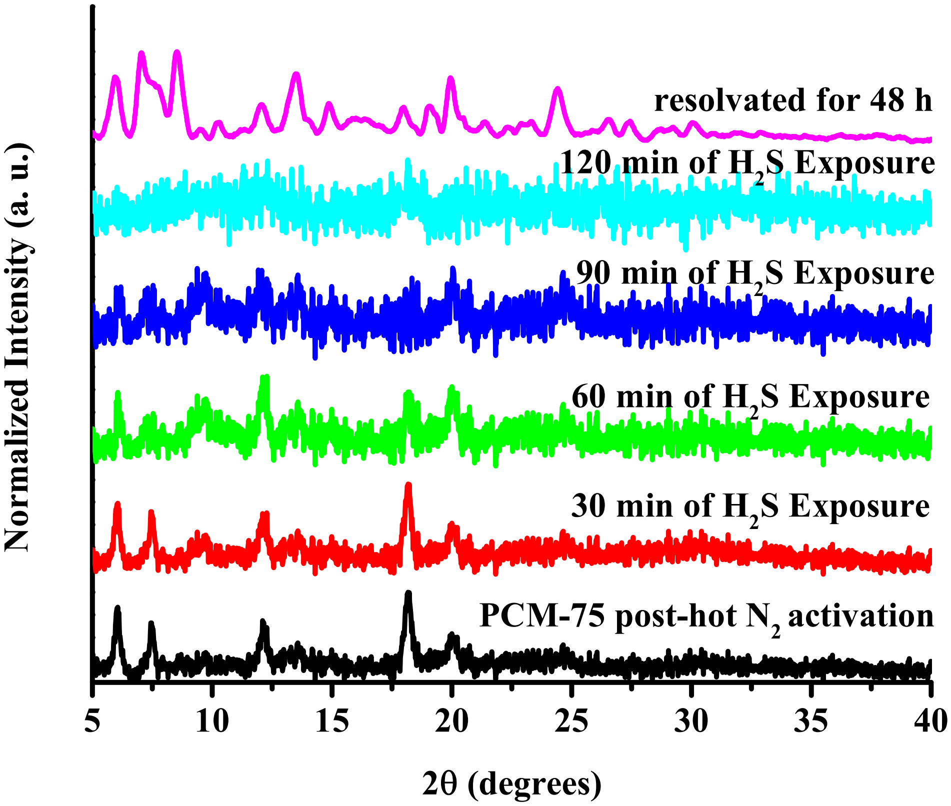
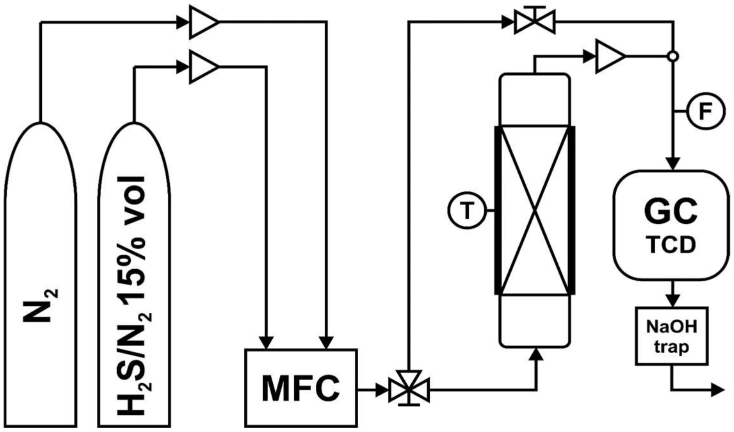


Figure S31. *In situ* PXRD patterns of PCM-75 under an atmosphere of H_2S as a function of time.

H_2S Adsorption Experimental

Dynamic breakthrough experiments were carried out in a home-made system (Scheme S1). The adsorption column was made from quartz glass with an internal diameter of 7 mm, with a porous glass bed to hold the sample. The adsorption column was covered with a temperature-controlled heating jacket. The column downstream was monitored with a gas chromatograph (HP-5890) equipped with a HP-PLOT 1 column and a thermal conductivity detector (TCD). The GC is equipped with an automatic injection valve.

Samples were activated *in situ* at 200 °C for 12 hours with a constant flow of dry N_2 and then slowly cooled to 30 °C. Then the H_2S concentration was adjusted with a mass flow controller fed with two lines: dry N_2 and H_2S/N_2 15:85 v/v mixture (Scheme S1). The breakthrough experiments were carried out at 30 °C and the downstream flow was analysed with a GC, the complete breakthrough of H_2S was indicated by the downstream gas concentration reaching the initial feed.



Scheme S1. Representation of breakthrough system. The H_2S/N_2 mixture passed through a mass flow controller (MFC) which feeds the adsorption column, and a gas chromatograph with a thermal conductivity detector (GC TCD) was used to measure the H_2S downstream.

The H_2S adsorption capacity was calculated using Eq. S11.1, where 'V_{H2S}' represents the H_2S volumetric capacity ($cm^3\ g^{-1}$), 'm' the adsorbent mass (g), 'F' the input flow rate ($cm^3\ min^{-1}$), 'C_f' and 'C_t' the influent and downstream H_2S concentrations respectively (% vol), and 't' the time (min).

$$V_{H_2S} = \frac{F}{C_f \cdot m} \cdot \int_0^t (C_f - C_t)dt \qquad \textbf{Eq. S1.1}$$

As mentioned before, the adsorption column has a porous glass bed thus, a blank run before each experiment was measured to eliminate the adsorption contribution of the column. In Fig. S32 the blue circles represent the adsorption of the column, and the purple circles represent the Mg-PCM-75 adsorption. Then the Mg-PCM-75 corrected volumetric capacity '$V_{H2S,corr}$' was estimated using Eq. S1.2.

$$V_{H_2S,corr} = V_{H_2S,blank} - V_{H_2S,sample} \qquad \textbf{Eq. S1.2}$$

The H_2S adsorption capacity is often reported as 'q_{H2S}' (mol g^{-1}), this value was roughly estimated with the volumetric adsorption capacity '$V_{H2S,corr}$' (cm^3 g^{-1}) and the ideal gas law Eq. S1.3. Where 'p' is the system pressure (77.3 kPa), 'T' the measurement temperature (303 K), and 'R' the ideal gas constant (8314.4598 cm^3 kPa K^{-1} mol^{-1}).

$$q_{H_2S} = \frac{V_{H_2S,corr} \cdot p}{R \cdot T} \qquad \textbf{Eq. S1.3}$$

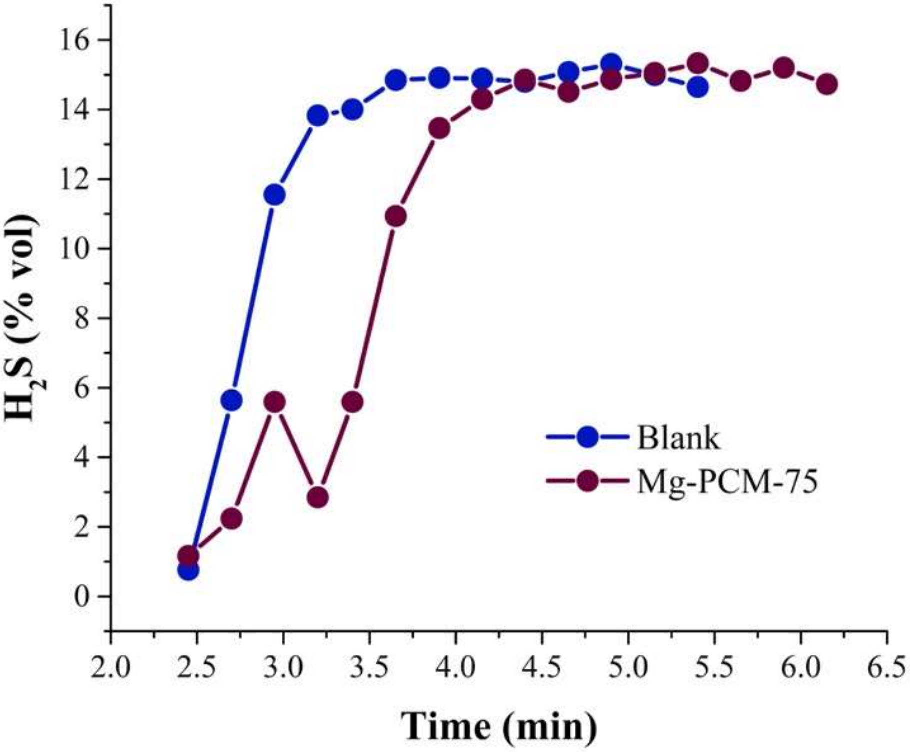


Figure S32. H_2S breakthrough experiments for PCM-75.

Table S2. H_2S breakthrough data for Mg-PCM-75

Mg-PCM-75 area	44.76 %vol*min
Blank area	50.03 %vol*min
Area difference	5.27 %vol*min
H_2S Vol ads	10.54 mL
H_2S ads	0.4308111936 mmol
Mg-PCM-75 mass	54.68 mg
H_2S ads	**7.87 mmol/g**

The breakthrough system was tested with other reported MOF materials (Fig. S33): MOF74(Zn) and HKUST-1.[1] 50 mg of each sample were activated in situ at 180 °C for 1 hour with a constant flow of dry N_2 and then slowly cooled to 30 °C. Then the H_2S desired concentration was adjusted 6 %vol. Adsorption capacity at 6 %vol of H_2S concentration for the reported materials are correspondent with the reported values (Table S3).

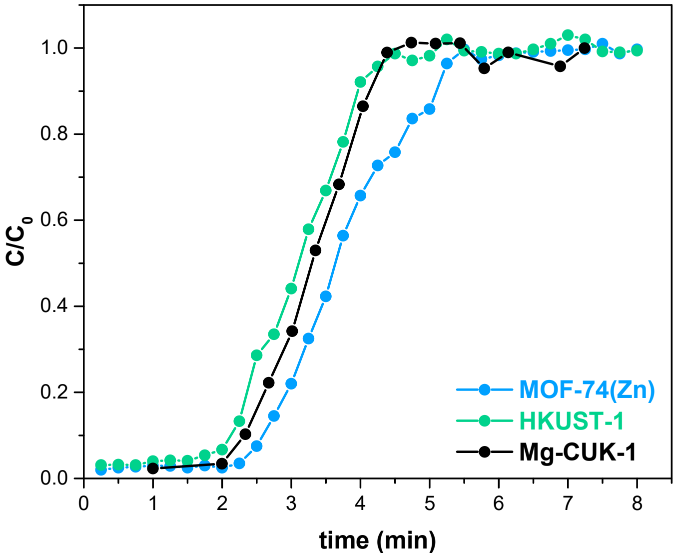


Figure S33. H_2S adsorption breakthrough curves at 30 °C for MOF-74(Zn) and HKUST-1. Measurements using 6 %vol. H_2S/N_2 feed concentration and a 30 cm^3 min^{-1} flow rate.

Table S3. H_2S adsorption capacity for some related MOFs. Breakthrough measurements using 6 %vol. H_2S/N_2 feed concentration and a 30 cm^3 min^{-1} flow rate.

Material	**H_2S uptake (mmol g^{-1})**	
	Our System[2]	**Reported**[1]
Mg-CUK-1	1.41	-
MOF-74(Zn)	1.72	1.64
HKUST-1	1.04	1.1

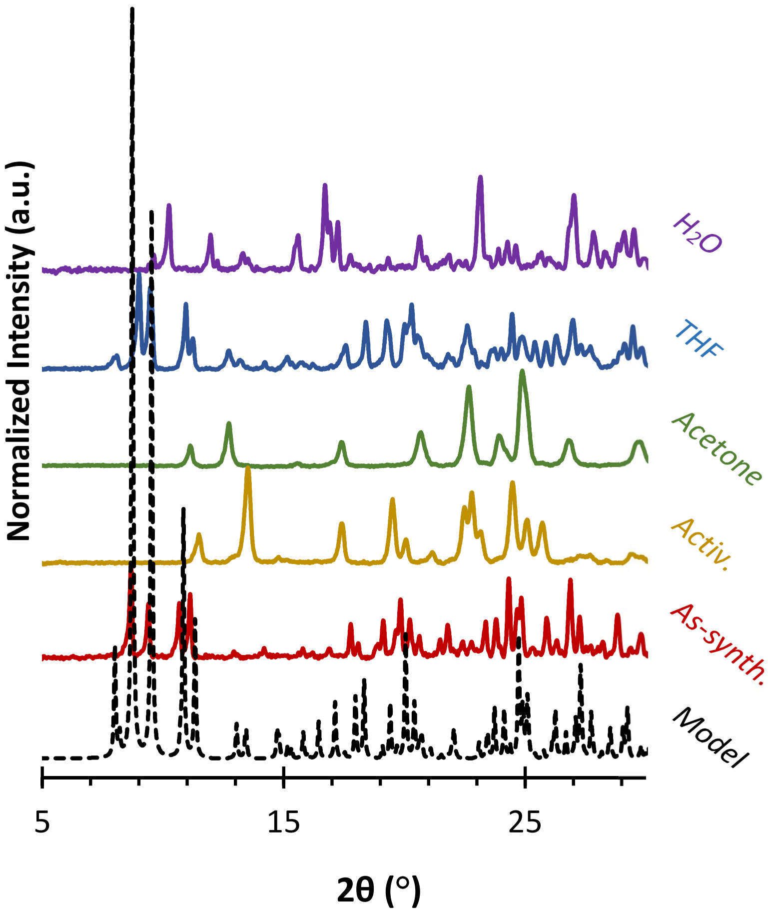


Figure S34. Comparison of PXRD data for iPCM-1 upon desolvation and re-immersion in different solvents.

References

[1] J. Liu, Y. Wei, P. Li, Y. Zhao and R. Zou, *J. Phys. Chem. C*, 2017, **121**, 13249.

[2] E. Sánchez-González, P. G. M. Mileo, M. Sagastuy-Breña, J. Raziel Álvarez, J. E. Reynolds, III, A. Villarreal, A. Gutiérrez-Alejandre, J. Ramírez, J. Balmaseda, E. González-Zamora, G. Maurin, S. M. Humphrey and I. A. Ibarra, *J. Mater. Chem. A*, 2018, **6**, 16900.