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

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The new ligand *tris*(*p*-carboxyphenylethynyl)phosphine ($P\{C\equiv CC_6H_5\text{-}4\text{-}CO_2H\}_3$) was used to synthesize a permanently porous Mn(II)-based acetylenic phosphine coordination material, PCM-48. This triply-interpenetrated MOF contains 1-D microchannels that are decorated with electron-rich and adsorbate-accessible acetylenic moieties and phosphine lone pairs. PCM-48 has a moderate room-temperature C_2H_2 adsorption capacity (25.54 cm^3 g^{-1}) and displays high separation selectivities for C_2H_2 over CH_4 (C_2H_2/CH_4 = 23.3), CO_2 (C_2H_2/CO_2 = 4.3), and N_2 (C_2H_2/N_2 = 76.9) at 296 K.

Acetylene (C_2H_2) is a valuable feedstock that has several major applications, including the preparation of acrylates and vinyl intermediates,[1] in polymer synthesis[2] and in metal welding and cutting. Acetylene is primarily obtained as a by-product of ethylene (C_2H_4) synthesis (*i.e.*, steam reforming, cracking). The separation of C_2H_2 from C_2H_4 and other gases present (*e.g.*, CO_2, CH_4) is an important industrial problem because C_2H_2 is explosive in low concentrations and is a poison to C_2H_4 polymerization catalysts. However, because C_2H_2 and C_2H_4 have similar physical properties and molecular sizes, separation using a stationary phase is ineffective; instead, more energy-intensive and expensive separation processes such as cryogenic distillation or partial hydrogenation are required.[3] The identification of simpler and more cost-effective ways to separate C_2H_2 from other gases is therefore an important area of research.

Microporous metal-organic frameworks (MOFs) are attracting increasing interest for the selective capture of C_2H_2;[4] their pore dimensions and chemical compositions can be tailored more precisely than zeolites, by rational chemical modification of the ligand precursors.[4,5] For example, it has been shown that decoration of MOF pore surfaces with particular organic functional groups can encourage stronger physisorption of adsorbates with similar chemical characteristics, *via* enhancement of host-guest dipolar and/or van der Waals interactions.[6] For example, since C_2H_2 contains polar C–H groups and an electron-rich C≡C core, it has been shown that MOFs decorated with abundant polarizing moieties[7] (*e.g.*, hydrogen bond acceptors) or acetylenic groups[8] enable enhanced C_2H_2 sorption capacities and selectivities.[7–9] Such properties are apparent at room temperature and relatively low partial pressures, which is attractive from an industrial perspective. In addition, MOFs containing open metal sites (*i.e.*, vacant coordination sites) that can coordinate C_2H_2 *via* α-donation have been found to further enhance the sorption characteristics.[10] [Co_2(DHTP)] based on Co(II) and DHTP (DHTP = 2,5-dihydroxyterephthalate by Xiang et al. is amongst the leading examples reported to-date and has achieved a C_2H_2 sorption capacity of 230 cm^3 g^{-1} at 295 K and 1 atm.[11]

Triarylphosphines (Ar_3P) are unique building blocks for the preparation of functional MOFs; their trigonal pyramidal geometry encourages the formation of robust materials with 3-D networks. Our earlier work has involved the use of structurally simple Ar_3P ligands such as $P\{C_6H_4\text{-}4\text{-}CO_2H\}_3$, which has resulted in a diverse family of PCMs (phosphine coordination materials).[12] A key characteristic of the PCMs is the presence of structurally well-defined Lewis basic phosphine sites inside the micropores. Post synthetic modification of such materials is possible *via* direct coordination of low-valent metals to Ar_3P: sites as a means to tune the host/guest interactions within the pores,[12b] or to promote solid-state reactivity (*i.e.*, catalysis).[12c,d] As part of our continued studies, we recently began to investigate the use of acetylenic phosphines as a means to prepare PCMs with larger pores by using acetylene moieties to extend the distance between the P nodes and carboxylic acid termini, while retaining the inherent rigidity of the ligand. In doing so, we hoped that acetylene-functionalized PCMs might also display enhanced sorption properties of unsaturated hydrocarbons.

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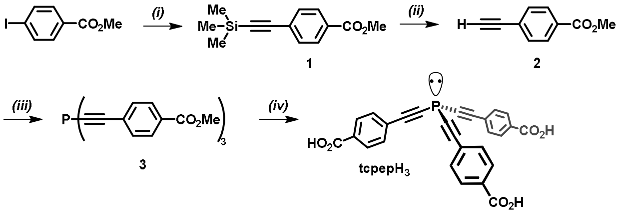
† *Electronic supplementary information (ESI) available: Full experimental procedures for tcpepH$_3$ and PCM-48; characterizing data for the ligands and PCM-48: NMR, FT-IR, TGA, ICP-OES; additional BET & PXRD data. CCDC-1846945 contains the CIF data for PCM-48; this information* is available free of charge at: www.ccdc.cam.ac.uk. *For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/x0xx00000x*

As shown in Scheme 1, a convenient 4-step synthetic route was determined for the preparation of gram quantities of *tris*(4-carboxyphenylethynyl)phosphine, ($P\{C{\equiv}CC_6H_4\text{-}4\text{-}CO_2H\}_3$; tcpep$H_3$; Figures S1–S14). In comparison to $P\{C_6H_4\text{-}4\text{-}CO_2H\}_3$, the distance between P and carboxylate-*C* atoms is extended by approximately 2.5 Å, from *ca.* 6.1 to 8.6 Å. The ^{31}P-NMR spectrum of the free triacid recorded in *per*-deutero dimethylsulfoxide (d_6-DMSO) gave a single resonance *ca.* –88 ppm (Figure S13). This indicated a significant shielding effect due to the three ethynyl π-systems positioned α- to the P(III) centre, and is significantly upfield-shifted compared to $P\{C_6H_4\text{-}4\text{-}CO_2H\}_3$ (δ= –6 ppm).[13] Unlike the triarylphosphine, tcpepH_3 was found to undergo partial hydrolysis when exposed to strong bases: initial attempts to form new PCMs with tcpepH_3 under mild solvothermal conditions at elevated pH yielded undesired coordination polymers based on the P(V) phosphinic acid species, $P(=O)(OH)\{C{\equiv}CC_6H_4\text{-}4\text{-}CO_2H\}_2$, which was formed *in situ* (not reported in this work).



Scheme 1. Synthesis scheme of *tris*(4-carboxyphenylethynyl)phosphine (tcpepH_3). Conditions: ***(i)*** TMS-acetylene, $PdCl_2(PPh_3)_2$, CuI, TEA/THF, 298 K, overnight; ***(ii)*** K_2CO_3 in MeOH, 298 K, 1.5 h, then quenched with HCl; ***(iii)*** PCl_3, TEA, CuI, in toluene, 298 K, 1 h; ***(iv)*** THF/0.5 M KOH, 298 K, 24 h, then acidified with 2 M HCl to precipitate.

Under modified solvothermal conditions at lower pH, we were able to obtain a new PCM in which the tcpepH_3 ligand remained intact. Reaction of 3 eq. of $MnCl_2$ with 1 eq. of tcpepH_3 and 3 eq. of CsF (added as a crystallising agent) at 75 °C over 3 days in a *N,N*-dimethylformamide:ethanol:H_2O (1:1:1, v/v) solvent mixture produced yellow prismatic crystals. Single crystal X-ray diffraction (SCXRD) analysis revealed a new 3-D MOF, referred to as PCM-48. The structure was solved in the monoclinic space group $C2/c$ (Z = 4). The framework of PCM-48 is net monoanionic, having the repeat unit, $[H_{1.1}F_{0.5}Na_{0.3}K_{0.1}][Mn_3(\mu_3\text{-}F)(\text{tcpep})_2(\text{DMF})(OH_2)_2]\cdot 9H_2O\cdot 2\text{DMF}$, supported by % C, H, N, F, Na & K elemental analyses and thermogravimetric analysis (TGA; *vide infra*).

Inspection of the asymmetric unit of PCM-48 reveals a single crystallographically unique tcpep^{3-} ligand that is coordinated to six Mn(II) equivalents *via* six similar *syn,syn*-bridged carboxylate modes (Figure 1). The tcpep ligand adopts a trigonal pyramidal geometry with an uncoordinated P(III) atom and C–P–C angles ranging between 99.0(3) and 103.7(3)°; the bond angles subtended at the α-C atoms are significantly distorted away from a linear arrangement (P1–C1–C2 = 174.1(7); P1–C10–C11 = 165.5(7); P1–C19–C20 = 165.3(7)°), resulting in a flattening of the ligand. This observation is consistent with soli-state SCXRD structures of known $P\{C{\equiv}CR\}_3$ molecules and complexes thereof.[14] Notably, in contrast to previous PCMs based on $[P\{C_6H_5\text{-}4\text{-}CO_2\}_3]^{3-}$ building blocks, the aryl substituents are significantly rotated out-of-plane, presumably because the aromatic π-system is not able to conjugate with the central P-atom. As a result, the ancillary *p*-carboxylate groups are oriented closer to perpendicular with respect to the ligand plane (Figure 1). The inorganic nodes in PCM-48 are regular Mn_3 triangles consisting of three octahedral Mn(II) ions bridged by a single μ_3-F^-. Mn1 and F1 reside on a mirror plane. The octahedral Mn(II) centres Mn1 and Mn2 are coordinated by one F^- and four carboxylate-*O* ligands, as well as one axially-coordinated OH_2 or DMF solvent ligand (O7 and O50, respectively; Figure 1).

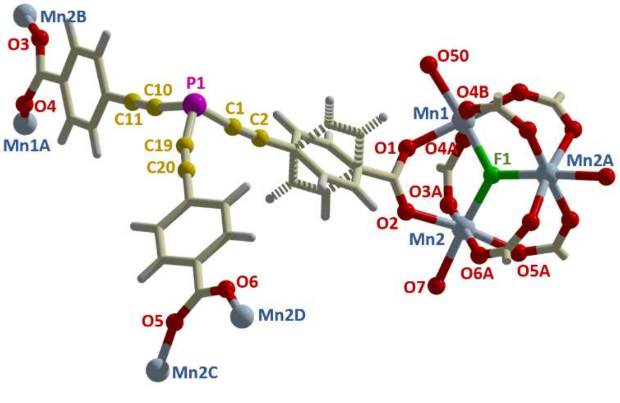


Figure 1. The extended asymmetric unit of PCM-48, showing the completed coordination environment of a single tcpep^{3-} ligand, and one complete $[Mn_3(\mu_3\text{-}F)]^{5+}$ inorganic cluster node. The positional disorder of the aryl rings is shown with broken bonds (25% occupancy *versus* the primary orientation).

Each $[Mn_3(\mu_3\text{-}F)]^{5+}$ unit acts as a trigonal prismatic 6-connected node; combined with the 3-connected tcpep^{3-} ligands, the extended structure of PCM-48 is based on triply-interpenetrated 6,3-connected nets (Figure 2A). The pore network in PCM-48 consists of 1-D channels with diamondoid shape, lying parallel to the crystallographic *c*-axis (Figure 2B). The micro-channel openings have a maximum van der Waals accessible opening of 13.7 Å. The channels of the as-synthesized material are filled with a combination of DMF and H_2O solvent of crystallization along with disordered Na^+, K^+ and F^- species, as determined by combustion analysis and inductively coupled plasma optical emission spectroscopy (ICP-OES; Table S1). TGA data of as-synthesized PCM-48 showed a mass loss of 26% below 215 °C, corresponding to the loss of 10 H_2O and 3 DMF molecules,

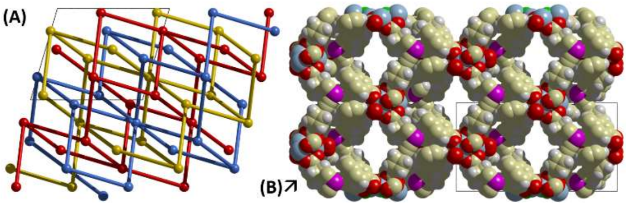


Figure 2. **(A)** Triply-interpenetrated 6,3-c nets in PCM-48 viewed in in the crystallographic *ac*-plane. **(B)** Space-filling representation of PCM-48 showing the diamondoid 1-D channel openings in the *ab*-plane.

after which the material remained thermally stable until the onset of framework degradation *ca.* 340 °C (Figure S16). In comparison, TGA of a sample of PCM-48 that was pre-evacuated at 150 °C over 12 h showed minimal mass loss (Figure S16); combustion analysis also confirmed that all DMF had been removed from the structure upon desolvation *in vacuo*, since no N was detected. It should also be noted that the thermal stability of PCM-48 is significantly higher than Cu(II)-based MOFs, which are prevalent in the realm of acetylene uptake.[7a,8,10] The triple interpenetration in PCM-48 is also likely to engender stability and permanent porosity upon removal of solvent.

Bulk phase purity of as-synthesized PCM-48 was confirmed by powder X-ray diffraction (PXRD) in comparison to the simulated PXRD pattern obtained from the SCXRD solution (Figure S17); the patterns were in close agreement and no additional reflections that could correspond to additional minority phases were found. In addition, PXRD analysis of PCM-48 samples after solvent exchange treatment (using acetone or methanol) and evacuation confirmed that the same crystalline phase was retained in all instances (Figures S17 & S20). The removal of the higher boiling point solvents of synthesis (DMF, H_2O) by solvent exchange was used in the pre-activation of PCM-48 samples prior to gas sorption analyses.

In initial studies, the bulk textural properties of acetone- or methanol-exchanged PCM-48 were assessed as a function of the evacuation temperature. Individual samples were evacuated at 296, 333, and 373 K over 12–24 h and then their total CO_2 and C_2H_2 sorption capacities were measured. It was found that the total adsorbed amount of C_2H_2 and CO_2 at 760 mmHg were both marginally diminished at higher activation temperatures, so 296 K activation was used in all subsequent studies (Figures S21 & S22). The cryogenic (77 K) N_2 surface area of an acetone-exchanged PCM-48 activated at 296 K was 300 $m^2\ g^{-1}$ (BET method) and 468 $m^2\ g^{-1}$ (Langmuir method), with a corresponding pore volume of 0.17 $cm^3\ g^{-1}$. In comparison, a methanol-exchanged sample gave a surface area 397 $m^2\ g^{-1}$ (BET method) and 593 $m^2\ g^{-1}$ (Langmuir method) with a pore volume of 0.20 $cm^3\ g^{-1}$ under otherwise identical activation conditions. However, the differences in measured gas capacities for C_2H_2, and CO_2 were largely negligible at ambient temperature (296 K) for acetone- *vs.* methanol-exchanged samples. Using CO_2 as the analyte, acetone pre-treated PCM-48 had a measured Langmuir surface area of 575 $m^2\ g^{-1}$ at 196 K (Figure S24).

The unique microchannel environment of PCM-48 due to the acetylenic phosphine ligands employed led us to investigate the gas sorption properties for C_2H_2 and related C_2 hydrocarbons. Sorption isotherms for C_2H_2, C_2H_4 and C_2H_6 were collected at 273 K and 296 K in order to obtain zero coverage isosteric heats of adsorption (Q_{st})[15] and Ideal Adsorbed Solution Theory (IAST)[16] values (*vide infra*). At 760 mmHg and 296 K, the measured uptakes were: C_2H_2, 25.54; C_2H_4, 19.61; C_2H_6, 21.40 $cm^3\ g^{-1}$ (Figure 3A). All three gases showed Type-I adsorption behavior with no evidence of desorption hysteresis. The observed order of sorption capacity $C_2H_2 > C_2H_6 > C_2H_4$ is interesting not only in that acetylene was most preferentially adsorbed inside PCM-48, but that the saturated C_2 hydrocarbon showed a greater saturation capacity than for ethylene (Figure 3A).

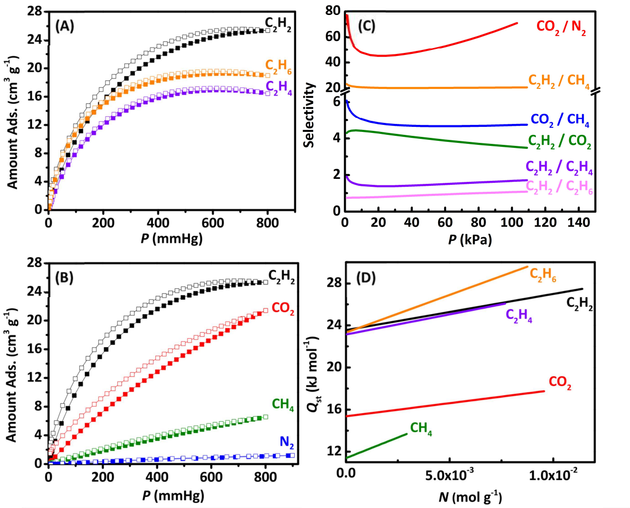


Figure 3. (A) Comparison of C_2-hydrocarbon adsorption-desorption isotherms for PCM-48 at 296 K (closed symbols = adsorption; open symbols = desorption). **(B)** Gas adsorption isotherms for PCM-48 at 296 K. **(C)** Comparison of IAST selectivities of C_2H_2/CH_4 (50:50, v/v), C_2H_2/C_2H_4 (1:99, v/v), C_2H_2/C_2H_6 (50:50, v/v), CO_2/N_2 (15:85, v/v), and C_2H_2/CO_2 (50:50, v/v) mixtures of PCM-48 at 296 K. **(D)** Q_{st} plots for CO_2, C_2H_2, C_2H_4, C_2H_6, and CH_4 obtained from virial calculations based on isotherms recorded at 273 and 296 K.

Next, we assessed the sorption selectivity of PCM-48 for C_2H_2 *versus* CH_4 and CO_2 separations, since these are common impurities found in industrial gas mixtures. In terms of industrial applications of MOFs for C_2H_2 purification, selectivity is more important that total uptake capacity; in this regard, PCM-48 shows appreciable selectivity for C_2H_2 sorption over both CO_2 and CH_4 at 296 K, with an order of selectivity = $C_2H_2 > CO_2 > CH_4$ (Figure 3B). The IAST method was implemented to assess the separation performance of PCM-48 for different binary mixtures of gases as a function of pressure (Figure 3C). IAST selectivity values were calculated and plotted for a 1:99 v/v binary mixture of C_2H_2/C_2H_4, 1:1 v/v mixtures of C_2H_2/C_2H_6, C_2H_2/CH_4, C_2H_2/CO_2 and CO_2/CH_4 and a 15:85 v/v mixture of CO_2/N_2, all at 296 K (Figure 3C). Although the selectivity for C_2H_2/C_2H_4 was only found to be 1.9, the theoretical selectivity toward C_2H_2/CH_4 in PCM-48 was 23.3; this value is comparable to leading materials such as ZJU-199,[10b] and is greater than what has been reported by most MOFs to-date (Table 1).[17] In addition, PCM-48 gave an appreciable CO_2/CH_4 separation factor of 6.1, which is greater than for ZJU-199 and PMOF-3 (Table 1).[8b,10b] The calculated selectivity for C_2H_2/CO_2 = 4.3 was also comparable to several other MOFs that are proficient in C_2H_2 sorption, but is lower than in MIL-100(Fe).[18] Notably, PCM-48 also achieved an IAST value of 76.9.

Table 1. Pertinent C_2H_2 and CO_2 separation selectivities *versus* PCM-48.

MOF	*C_2H_2/C_2H_4*	*C_2H_2/CH_4*	*C_2H_2/CO_2*	*CO_2/CH_4*	*Ref.*
PCM-48	**1.9**	**23.3**	**4.3**	**6.1**	-
ZJU-199	—	33.5	—	5.8	[10b]
UTSA-300a	75	—	21	—	[20]
$[Co_6(OH)_4]$	—	9.6	3.4	—	[17b]
MIL-100(Fe)	3.4	—	18.2	—	[18]
M'MOF-74	2.1	700	13	—	[4b,5b]
PMOF-3	—	156	—	5.1	[8b]

for CO_2/N_2 at 296 K, which is outstanding *versus* other MOFs that are proficient in C_2H_2 sorption; this level of CO_2/N_2 selectivity is comparable to LIFM-26, which has a selectivity of 93.[19]

The Q_{st} values obtained for C_2H_2, C_2H_4, C_2H_6, CO_2 and CH_4 in PCM-48 help us to better understand the observed sorption selectivity from a thermodynamic perspective (Figure 3D). The values were obtained by fitting the 273 K and 296 K adsorption isotherms of each gas to a virial-type equation, followed by the calculation of Q_{st} vales using the Clausius−Clapeyron equation.[15] In order of increasing binding affinity, the calculated values were: CH_4, 11.4; CO_2, 15.4; C_2H_4, 23.2; C_2H_6, 23.4; C_2H_2, 23.6 kJ mol^{-1}. All gases yielded sorption energies with positive slopes, which is indicative of increasingly energetically-favourable host-guest and guest-guest interactions, as more guest molecules become adsorbed inside the microchannels.[15] The Q_{st} values obtained for PCM-48 are within the normal range of magnitudes observed previously for other MOFs.[7-11,17-20] The measured Q_{st} value for CO_2 is likely due to the presence of abundant polarizing acetylenic and phosphine moieties inside the channels. Similarly, the observed sorption preference for C_2H_2 is likely due to a combination of this effect and enhanced acetylene polarization at the $[Mn_3(\mu_3\text{-}F)]^{5+}$ nodes. From an application standpoint, Q_{st} = 23.6 kJ mol^{-1} for C_2H_2 is well-suited for reversible C_2H_2 sorption, in that the desorption step would not incur a large energy penalty.

In conclusion, we have demonstrated how a rationally-designed MOF based on a novel acetylenic phosphine ligand was able to preferentially adsorb C_2H_2 over related C_1 and C_2 gases at room temperature. The inherent polarity of the microchannels in PCM-48 also engendered high CO_2 selectivity over N_2, also at room temperature. In future studies, we plan to utilize the available phosphine lone pairs inside the PCM-48 channels as sites to *post*-synthetically anchor low-valent metals as a means to further tune the sorption selectivity.

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Conflicts of interest

The authors declare no conflicts of interest.

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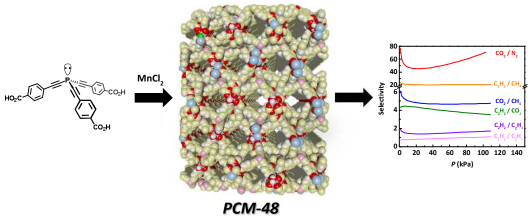
HO2C
CO2H
CO2H
P
MnCl2
PCM-48
Selectivity
80
60
40
20
6
4
2
0
0
20
40
60
80
100
120
140
P (kPa)
CO2 / N2
C2H2 / CH4
CO2 / CH4
C2H2 / CO2
C2H2 / C2H4
C2H2 / C2H4