SUPPORTING INFORMATION

# Tuning the host-guest interactions in a phosphine coordination polymer through different types of *post*-synthetic modification

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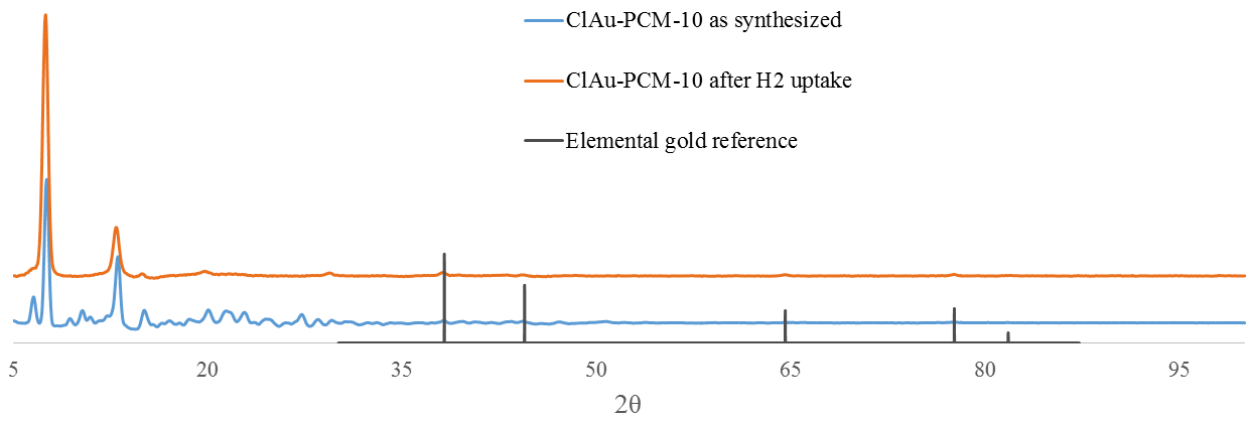



**Figure S1**: ClAu–PCM-10 PXRD, after activation and $H_2$ adsorption (orange) as synthesized (blue). Elemental gold reference (grey).

**$H_2$ isotherms**

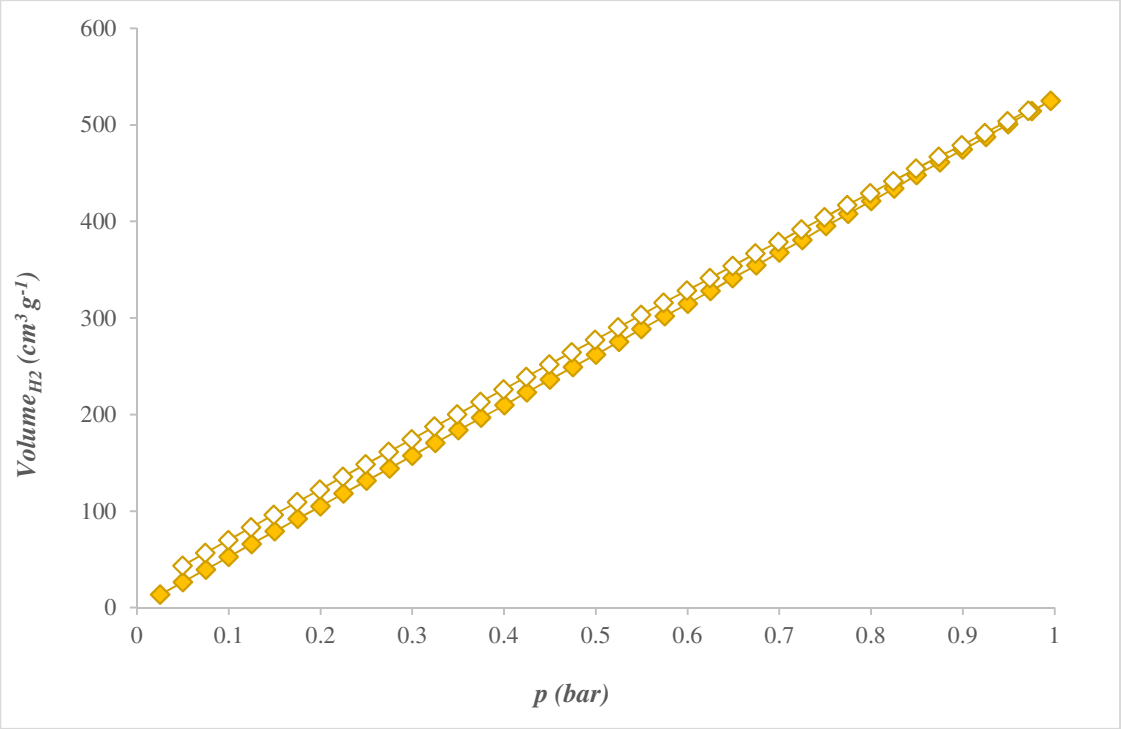



**Figure S2A**: First cycle of $H_2$ adsorption on ClAu–PCM-10. 4.72 weight % at 1 bar

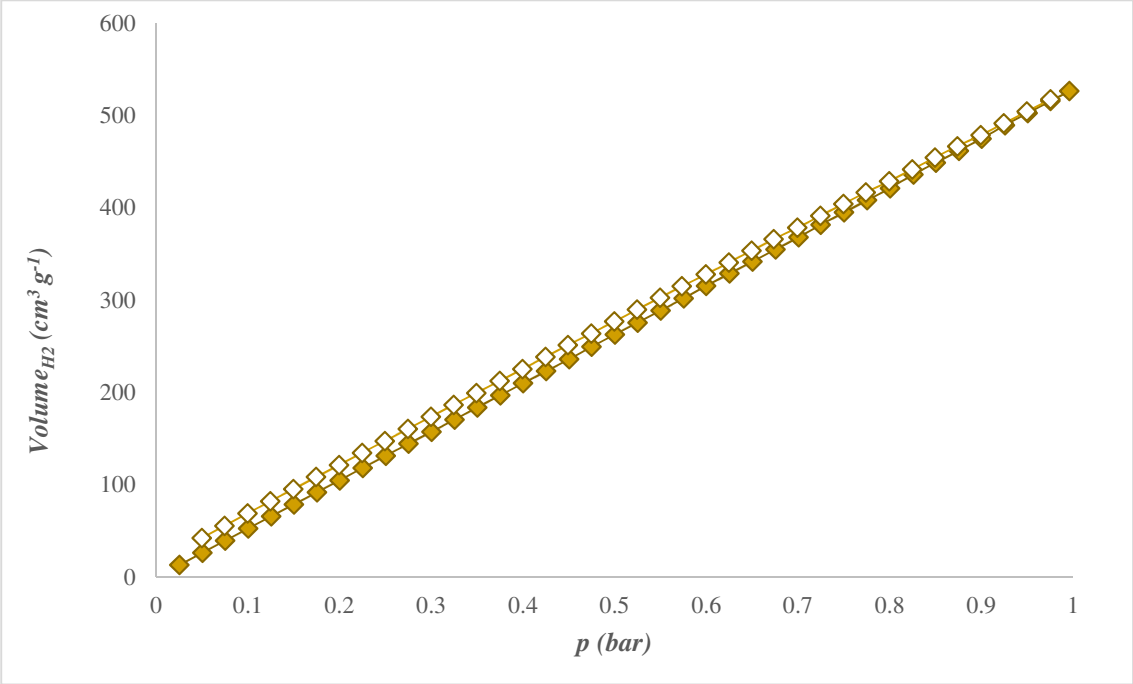



**Figure S2B**: Second cycle of $H_2$ adsorption on ClAu–PCM-10. 4.73 weight % at 1 bar

**Figures S3A-G.** Adsorption isotherms of PCM-10 and PSM composite materials at 278 K and 298 K and their corresponding $Q_{st}$ *versus* loading plots. The virial-type equation (eq.1) was used to fit the adsorption data at 278 K and 298 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.2)

$$\ln\left(\frac{n}{p}\right) = A_0 + A_1 n + A_2 n^2 + \cdots \qquad (1)$$

$$Q_{\mathrm{st}} = R \ln\left(\frac{P_1}{P_2}\right)\frac{T_1 T_2}{T_2 - T_1} \qquad (2)$$

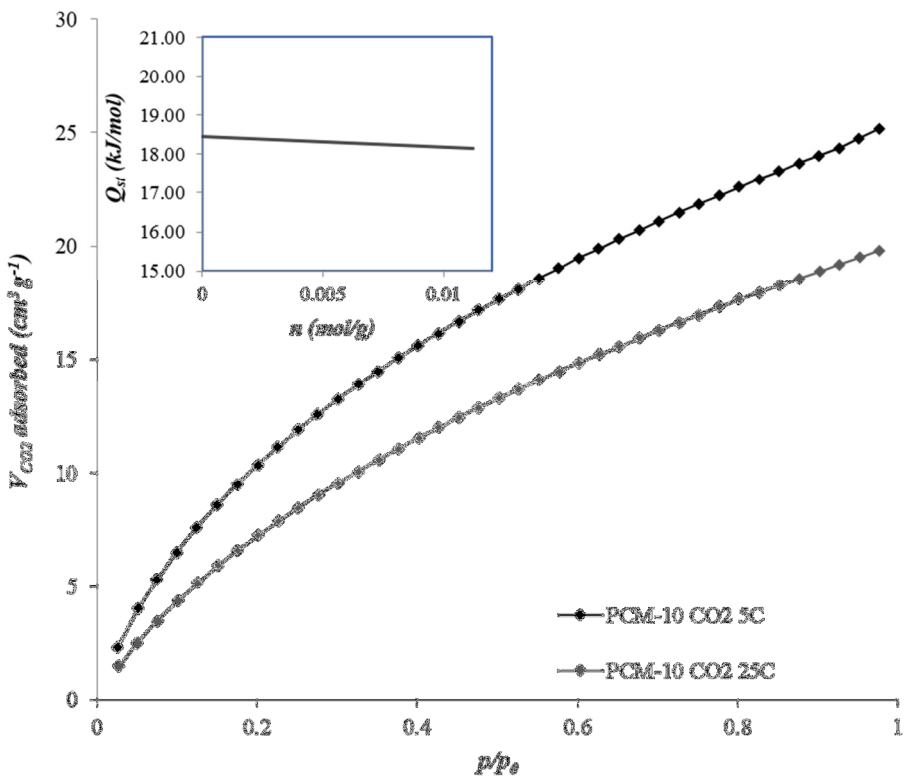



**Figure S3A.** 278 K and 298 K adsorption isotherms and $Q_{st}$ plots for PCM-10.

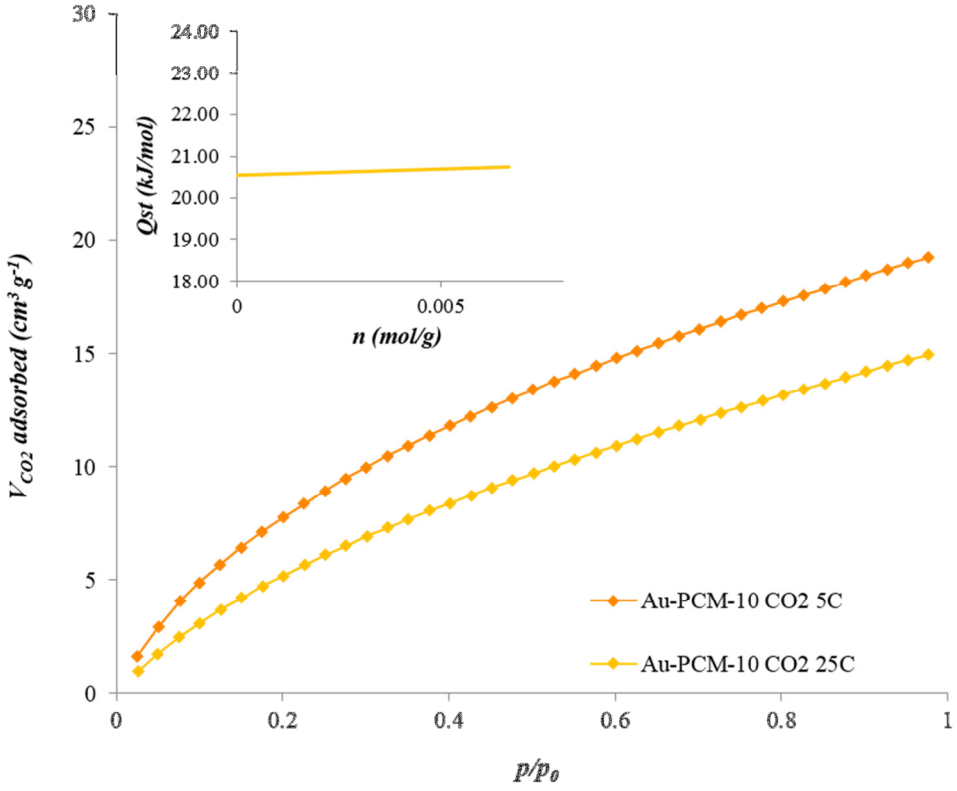



**Figure S3B.** 278 K and 298 K adsorption isotherms and $Q_{st}$ plots for ClAu–PCM-10.

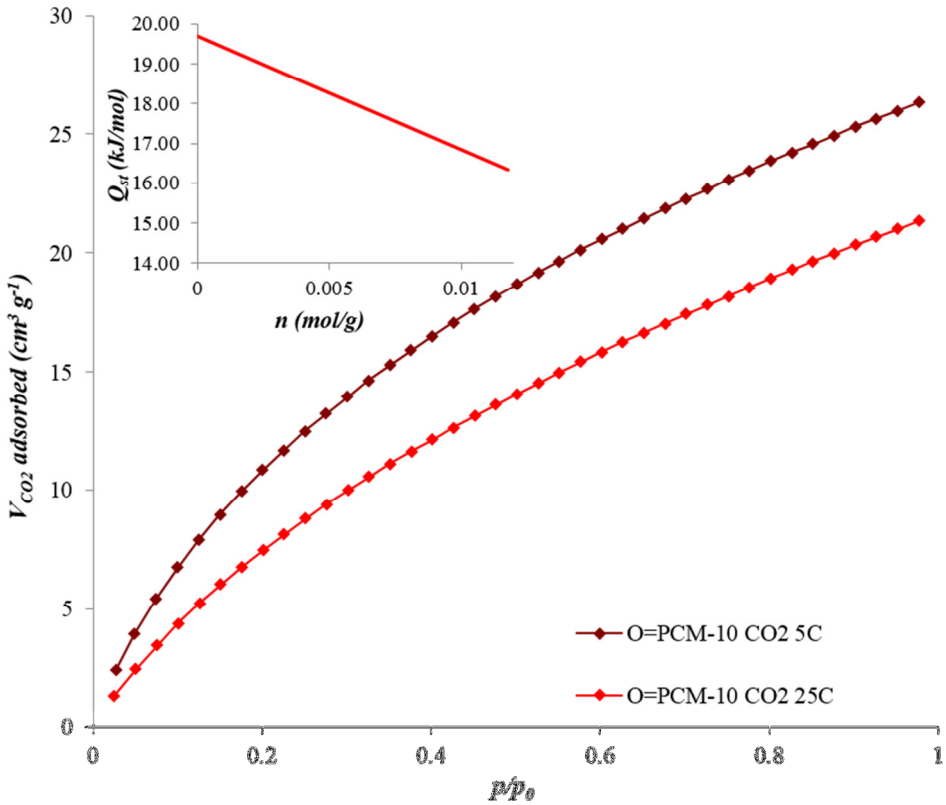



**Figure S3C.** 278 K and 298 K adsorption isotherms and $Q_{st}$ plots for O=PCM-10.

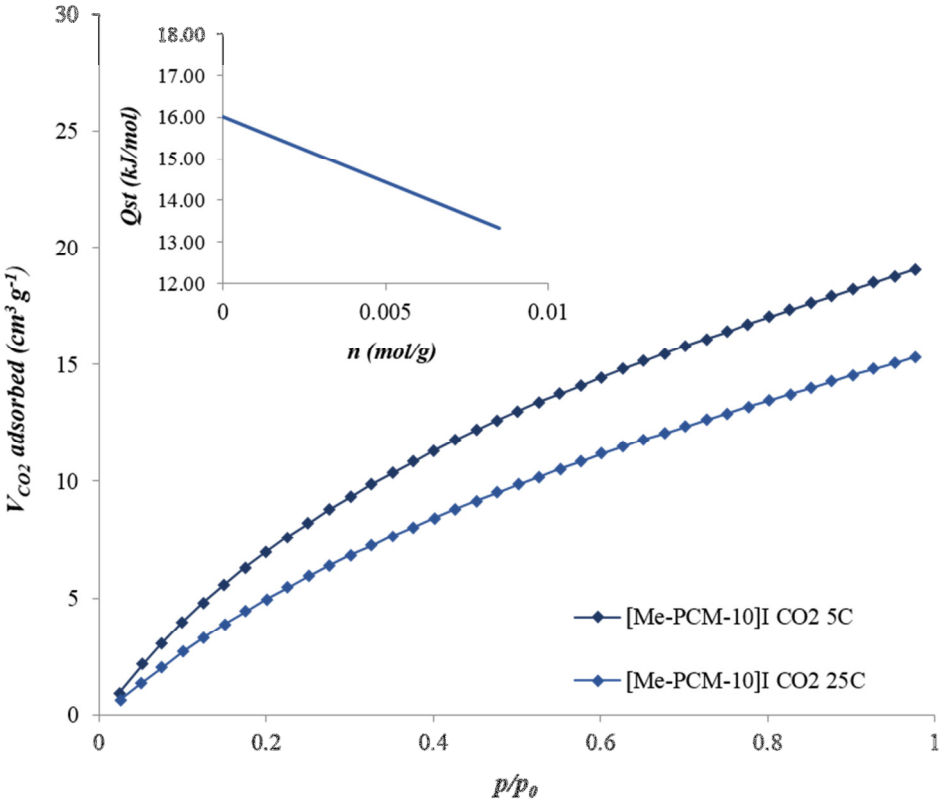



**Figure S3D.** 278 K and 298 K adsorption isotherms and $Q_{st}$ plots for [Me–PCM-10]I.

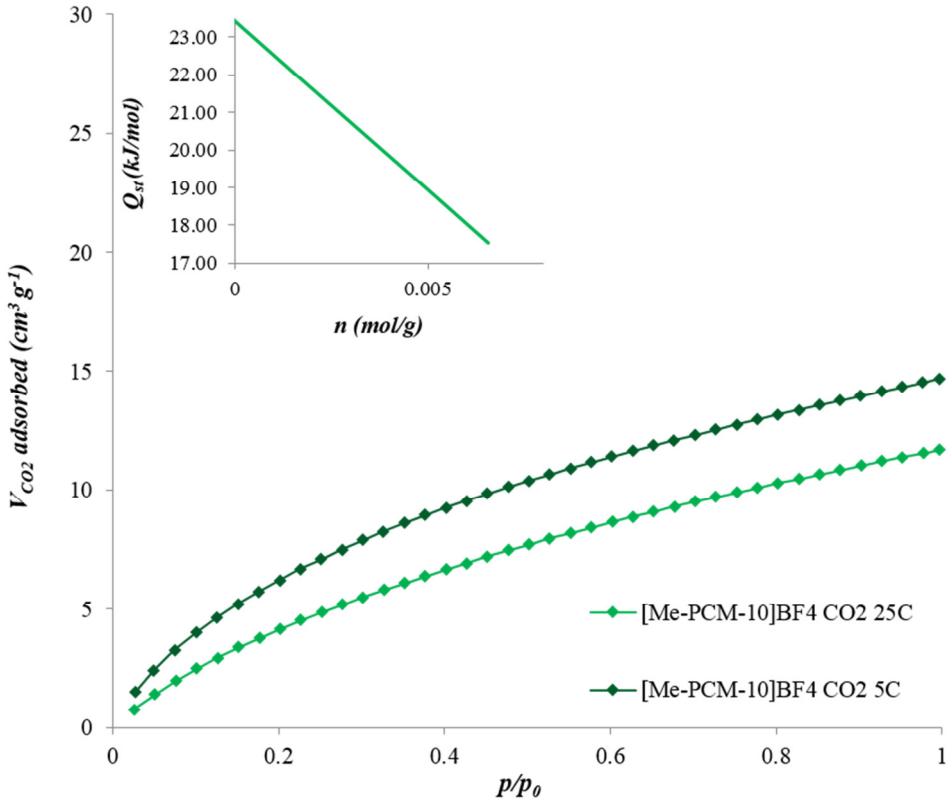



**Figure S3E.** 278 K and 298 K adsorption isotherms and $Q_{st}$ plots for [Me–PCM-10]$BF_4$.

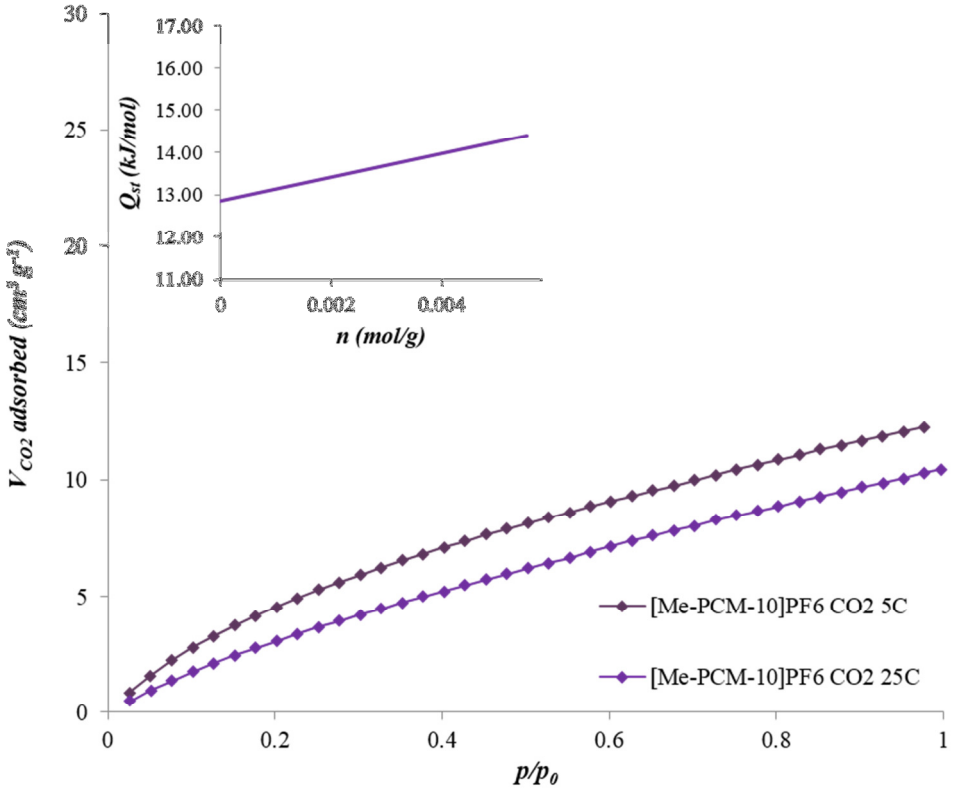



**Figure S3F.** 278 K and 298 K adsorption isotherms and $Q_{st}$ plots for [Me–PCM-10]$PF_6$.

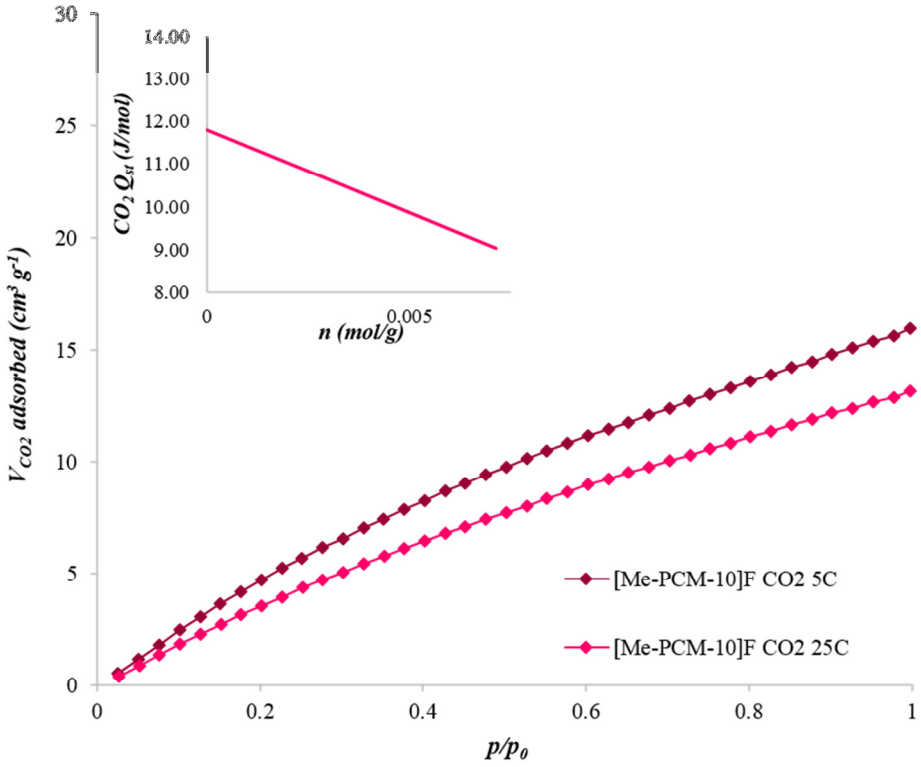



**Figure S3G.** 278 K and 298 K adsorption isotherms and $Q_{st}$ plots for [Me–PCM-10]F.

**Thermogravimetric Analysis**

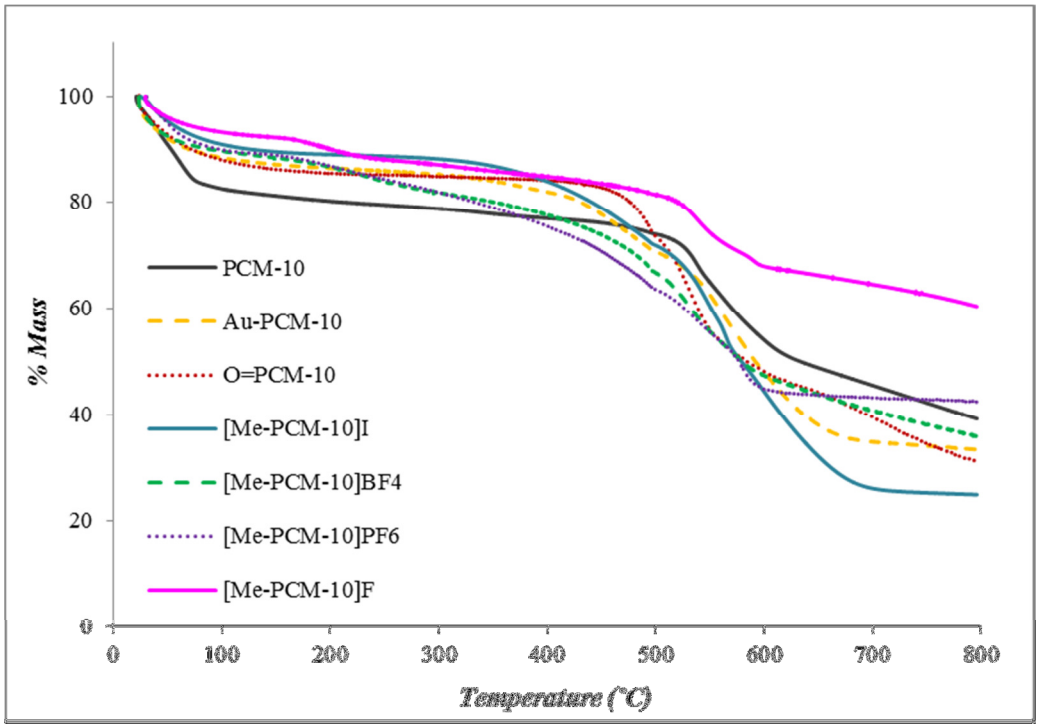



**Figure S4A**: TGA of as synthesized PCM-10 and all PSM composite materials.

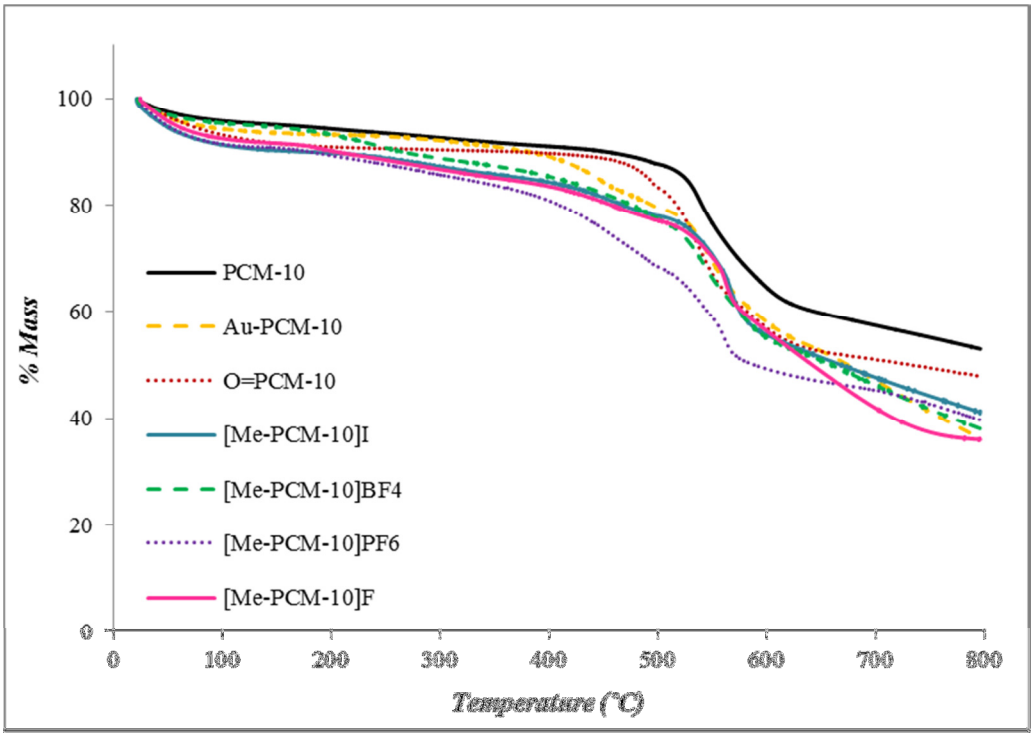



**Figure S4B**: TGA of PCM-10 and all PSM composite materials activated at 120 ˚C under vacuum for 12h.

**Comparisons of $H_2$ uptake at 77 and 87 K**

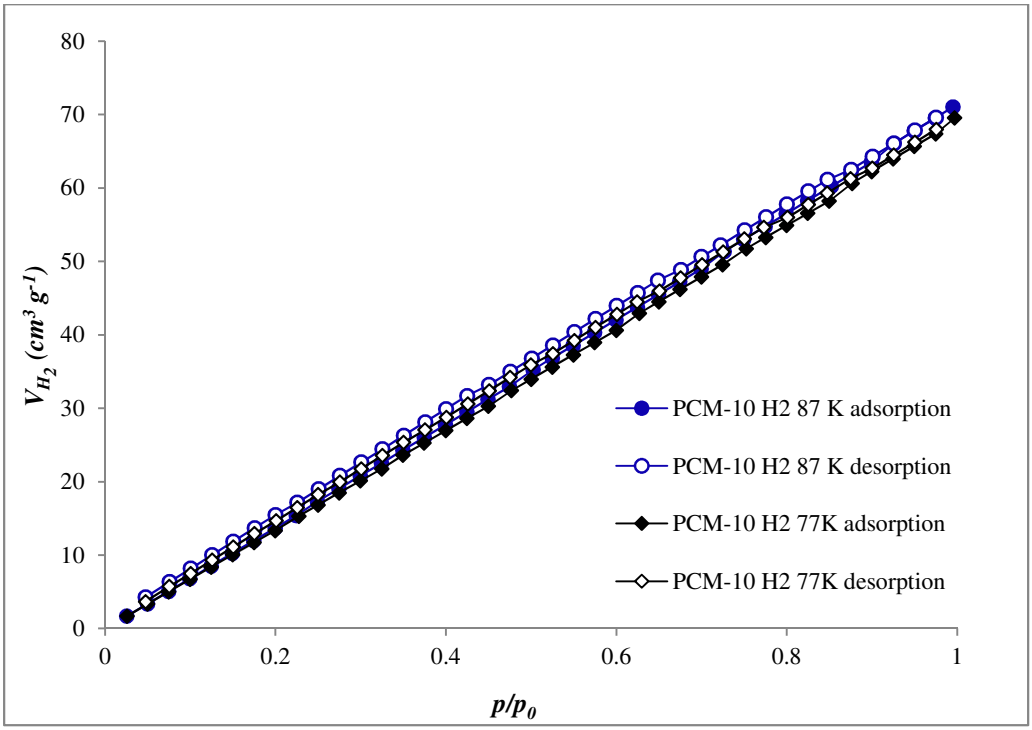



**Figure S5A:** PCM-10 $H_2$ uptake at 77 and 87 K.

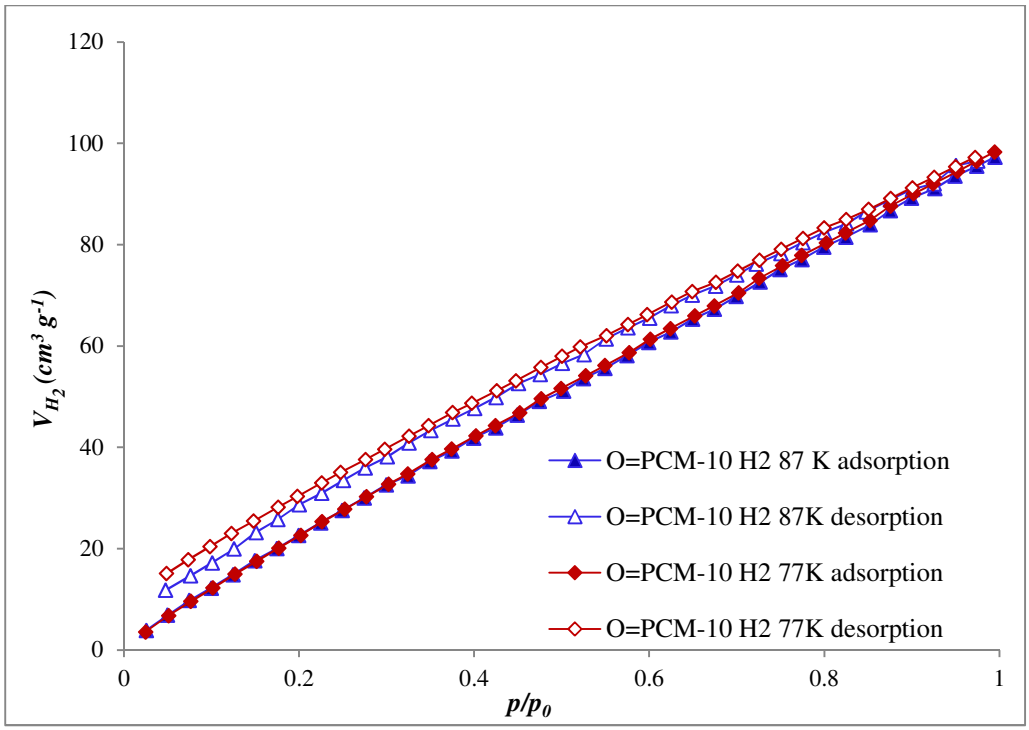



**Figure S5B:** O=PCM-10 $H_2$ uptake at 77 and 87 K.

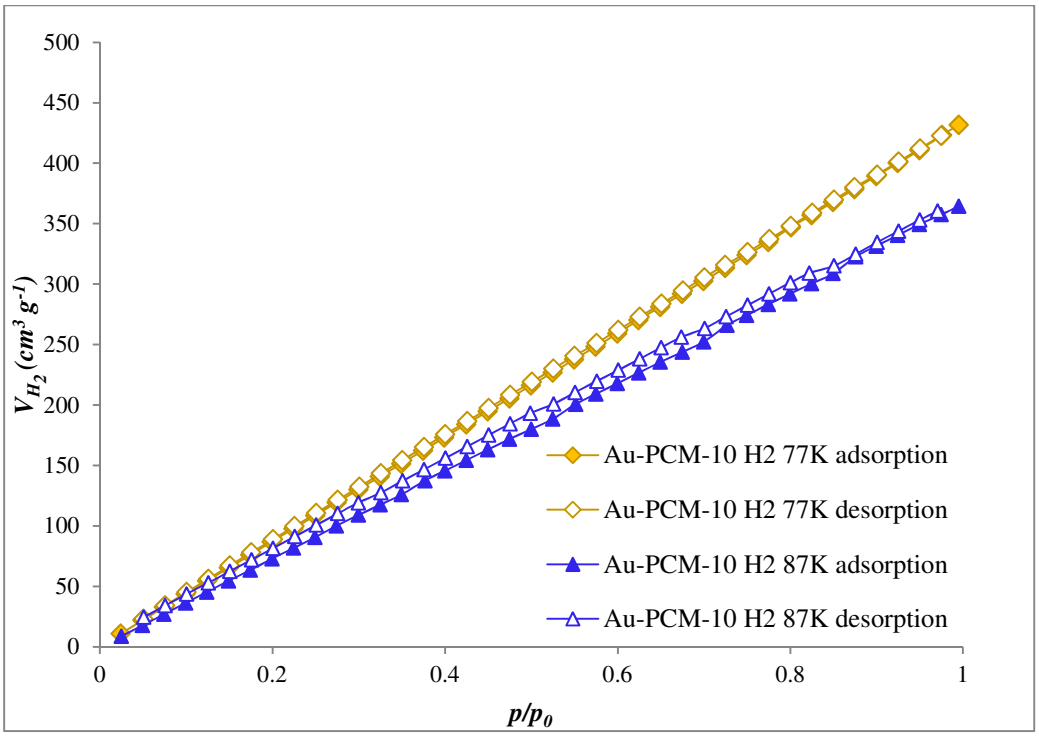
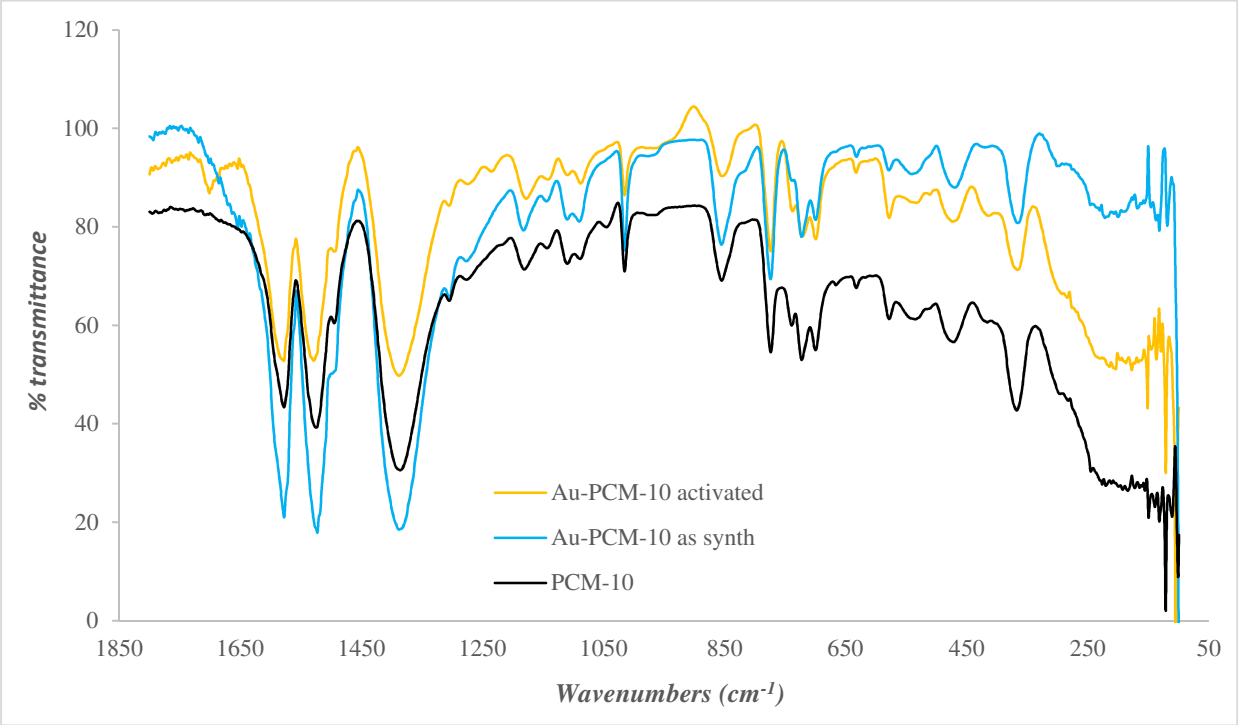



**Figure S5C:** ClAu–PCM-10 $H_2$ uptake at 77 and 87 K.

**FT-IR spectral comparisons**



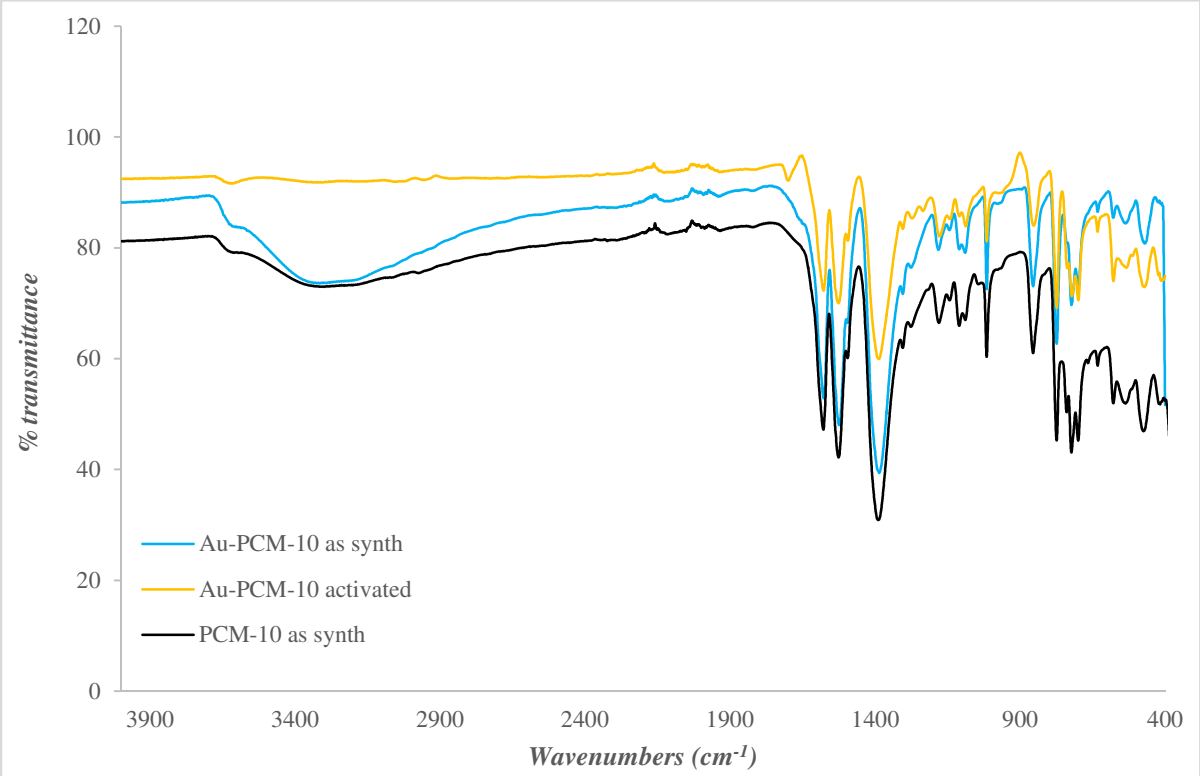




**Figure S6A**: FIR (top) and IR (bottom) spectra of ClAu—PCM-10 as synthesized and activates *versus* as synthesized PCM-10.

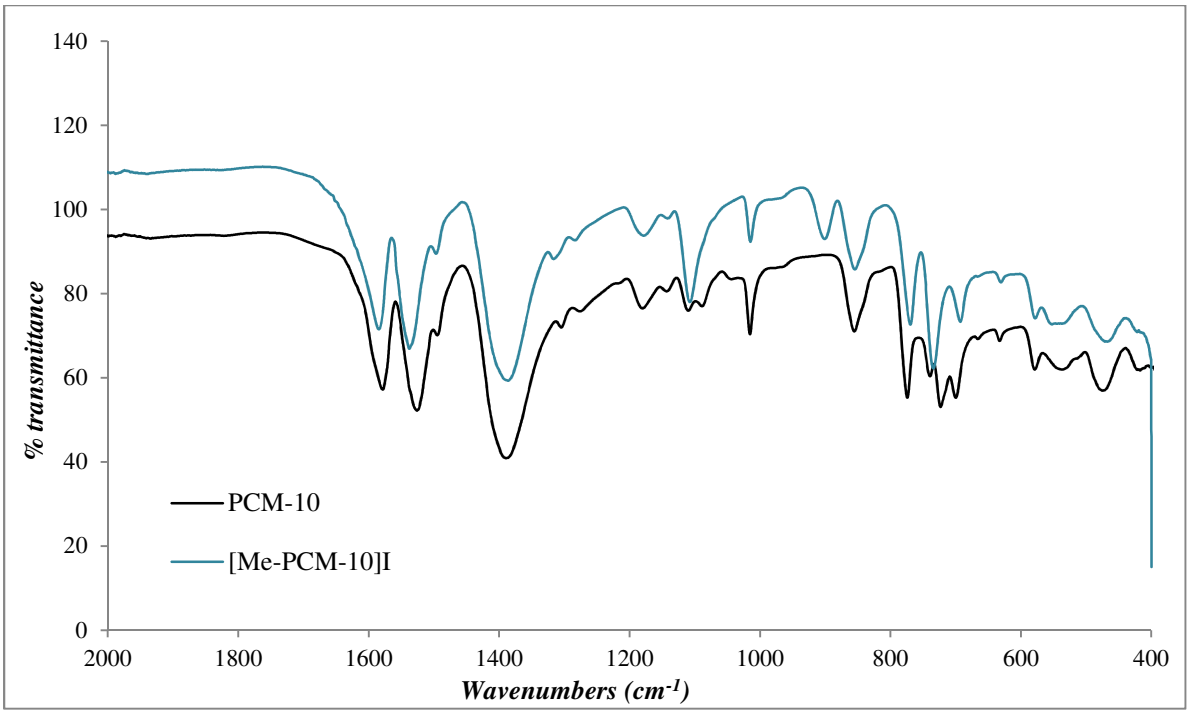



**Figure S6B**: IR of [Me–PCM-10]I *versus* PCM-10

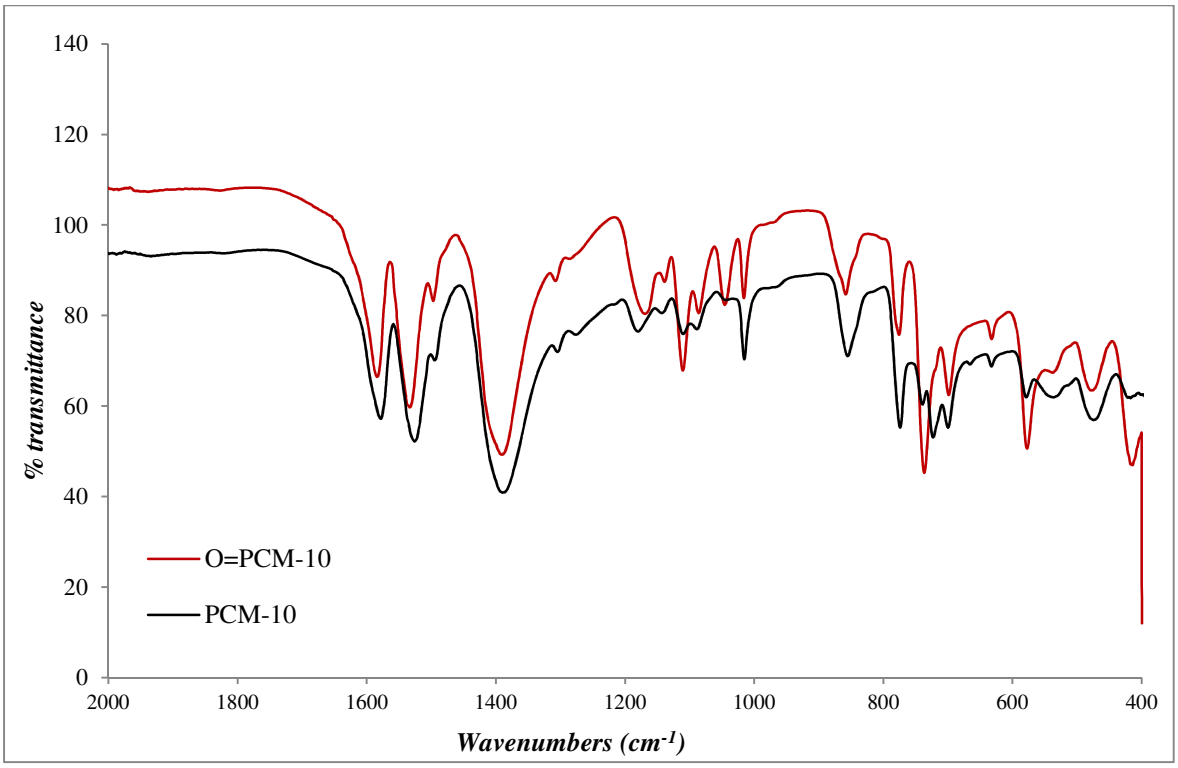



**Figure S6C**: IR of O=PCM-10 versus PCM-10.

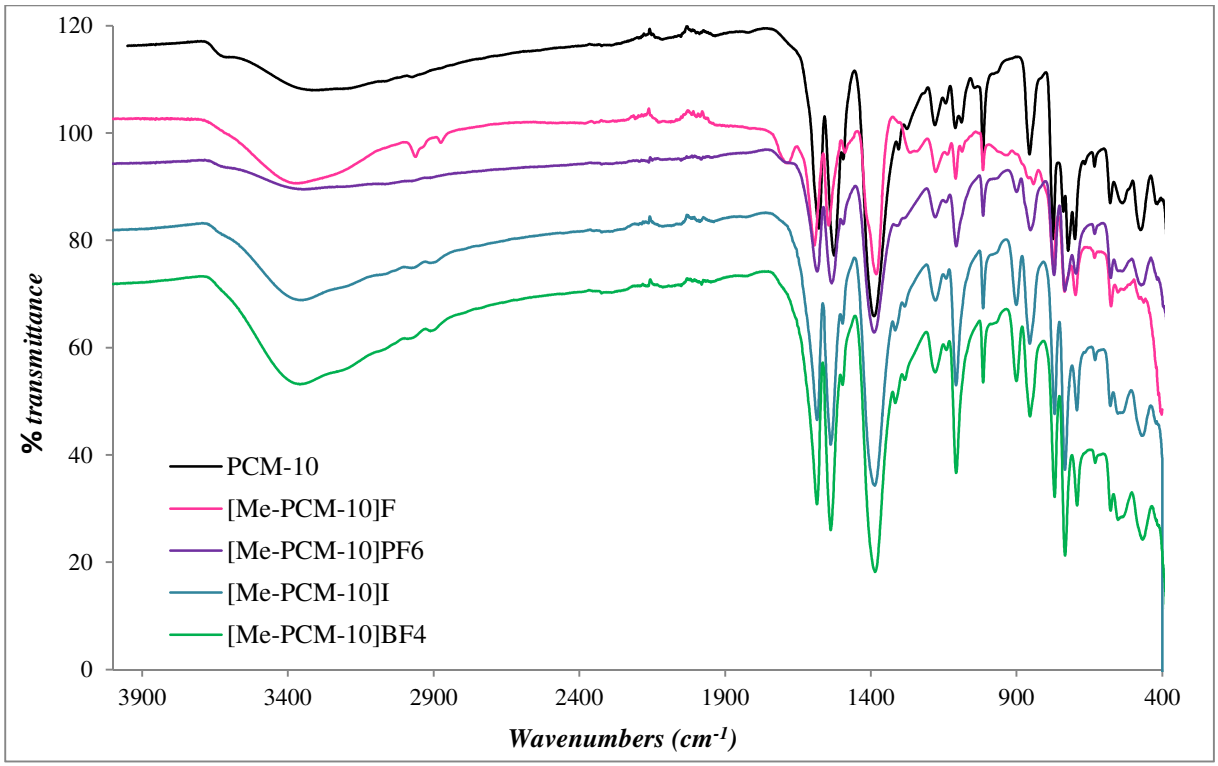



**Figure S6D**: Methyl phosphonium materials IR absorption plots.

**Table S1.** Comparison of $CO_2$ adsorption at 196 K and 1.0 atm in PCM-10 and the PSM-derived materials.

| Material | Formula weight (g/mol) | $CO_2$ weight % (196K) | mol $CO_2$ / mol P |
|---|---|---|---|
| PCM-10 | 938.84 | 13.77 | 1.47 |
| Au-PCM-10 | 1403.68 | 10.41 | 1.66 |
| O=PCM-10 | 970.84 | 14.00 | 1.54 |
| [Me-PCM-10] I | 1222.72 | 9.10 | 1.26 |
| [Me-PCM-10] $BF_4$ | 1142.52 | 15.12 | 1.96 |
| [Me-PCM-10] $PF_6$ | 1258.84 | 7.69 | 1.10 |
| [Me-PCM-10] F | 1006.91 | 6.30 | 0.73 |

**Table S2.** Elemental analysis for F and I to obtain estimated values for PSM completeness (I determined by furnace decomposition and titration; F determined by ISE spectroscopy; Midwest Microlabs).

| Material | P:F (molar ratio) | | % modification |
|---|---|---|---|
| | Theory | Found | |
| [Me–PCM-10]$BF_4$ | 1:4 | 1:1.99 | 50 |
| [Me–PCM-10]$PF_6$ | 1:3 | 1:0.5 | 17 |
| [Me–PCM-10]F | 1:1 | 1:2.4 | > 100 |
| | | | |
| **Material** | **P:I (molar ratio)** | | **% modification** |
| | **Theory** | **Found** | |
| [Me–PCM-10]I | 1:1 | 1:1.2 | > 100 |