

Click-based porous inorganic-organic hybrid materials (PHMs) containing cyclophosphazene units and its application in Carbon dioxide capture

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EXPERIMENTAL SECTION

Materials: All chemicals used in this study were of analytical reagent grade and used without further purification. Phosphonitrilic chloridotrimer (PNC) (99%, Sigma Adrich), propargylamine (98%, Alfa Aeser), triethylamine (Rankem), p-xylene dibromide (97%, Alfa Aeser), sodium azide (Spectrochem), cupric sulphate pentahydrate (Leonid), L-ascorbic acid (Leonid), N,N-dimethylformamide (DMF) (Fisher Scientific).

Synthesis of compound I

Compound-I was synthesized by adding a solution of 1 g PNC in 2 ml THF to a solution of 1 ml of propargylamine and 1.6 ml triethyl amine in 10 ml THF. After addition, the reaction mixture was stirred for 4 h at RT. The resulting solution was then filtered and the solvent was stripped off from the filtrate to obtain a crude material. The crude product obtained was extracted using chloroform and water. The organic layer was isolated and dried over anhydrous Na₂SO₄, and then chloroform was removed under reduced pressure to obtain the desired product as orange yellow solid. (Yield: 85-90%) ¹H NMR (CDCl₃, 300MHz): δ 2.18 (6H, NH), δ 2.9 (6H, CH), δ 3.69 (12H, CH₂) (Figure S1a). ³¹P NMR (CDCl₃, 300MHz): δ 17.91 (Figure S1b). FT-IR (KBr, cm⁻¹): 3410, 3371, 3299 (ν N-H), 3200 (νN-H, νC-H), 1406, 1353, 1186, 1085, (ν P-N_{ring}), 978, 905, 856, 628 (Figure S2).

Synthesis of compound II

Compound-II was synthesized by adding 1.9 g of NaN₃ to a solution of 2 g p-xylene dibromide in 40 ml acetone and the reaction mixture was stirred for 12 h at RT. It was filtered and solvent was stripped off from the filtrate to obtain desirable liquid product (Yield: 90%). FT-IR (KBr, cm⁻¹): 3340, 3030, 2930, 2875 (ν C-H), 2100 (azide stretch), 1515, 1450, 1345 (δ C-H) (Figure S3).

Synthesis of PHM-1

In a typical synthesis, to a solution of 1 mmol compound I and 3 mmol compound II dissolved in 40 ml DMF, a solution of freshly prepared $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (10 mol%) and sodium ascorbate (20 mol%) in 4 ml of water was added. The solution was stirred at 40 °C for 12 h. The compound was obtained as brown powder and dried under vacuum. ^1H NMR (DMSO): δ 8.5-7.9 (triazole-H), δ 7.3-7.1 (Ar-H), δ 5.7(CH₂-NH), 5.3 (CH₂-Ar), 4.3 (CH₂-N₃) δ 3.9 (NH). ^{31}P NMR (DMSO): δ -0.02. FT-IR (KBr, cm^{-1}): 3420 (ν N-H), 2925, 2855 (ν C-H), 1640 (ν triazole ring), 1452 (δ C-H), 1330, 1138, 1060, 965, 520 (ν P-N_{ring}).

Characterization:

NMR was recorded on Bruker DPX-300 NMR spectrometer. The FT-IR spectra were obtained with the Perkin-Elmer C91158 infrared spectrophotometer in wavelength range of 400 to 4000 cm^{-1} using KBr pellet. The microstructural analysis of the PHM-1 was carried out using the FE-SEM MIRA3 TESCAN at the energy of 10 kV. Before analysis, the material was coated with gold by a standard sputtering technique for 60 sec. TEM analysis was done using TECNAIG²S, for which sample was prepared by dispersing powder in ethanol followed by placing a drop on a carbon coated copper grid. The XRD pattern was recorded on a Bruker D8 FOCUS X-ray diffractometer using Cu K α radiations ($\lambda=0.15404$ nm) with a scanning speed of 2°/minute and measured in the range of 10 to 80° in 2 θ scale. UV-visible spectrum was recorded on Shimadzu UV-1800 in DMSO at the concentration of 10⁻⁴M. TG/DTG analysis was performed on EXSTAR TG/DTA 6300 in which the temperature was raised from 25 to 700 °C at heating rate of 10°C/min under nitrogen. The sample weight was continuously recorded as a function of temperature and time. N₂ sorption isotherm was recorded at 77 K using Autosorb-iQ (Quantachrome Instruments). PHM-1 was degassed at 120 °C for 6 h prior to analysis. Specific surface area was calculated by applying BET model within pressure range of P/P₀ 0.05-0.35. The pore size distribution was calculated by DFT method. The pore volume was calculated from the uptake at a relative pressure of 0.99 $\text{cm}^3 \cdot \text{g}^{-1}$. CO₂ sorption isotherm was recorded at 273 and 298 K using Autosorb-iQ (Quantachrome Instruments).

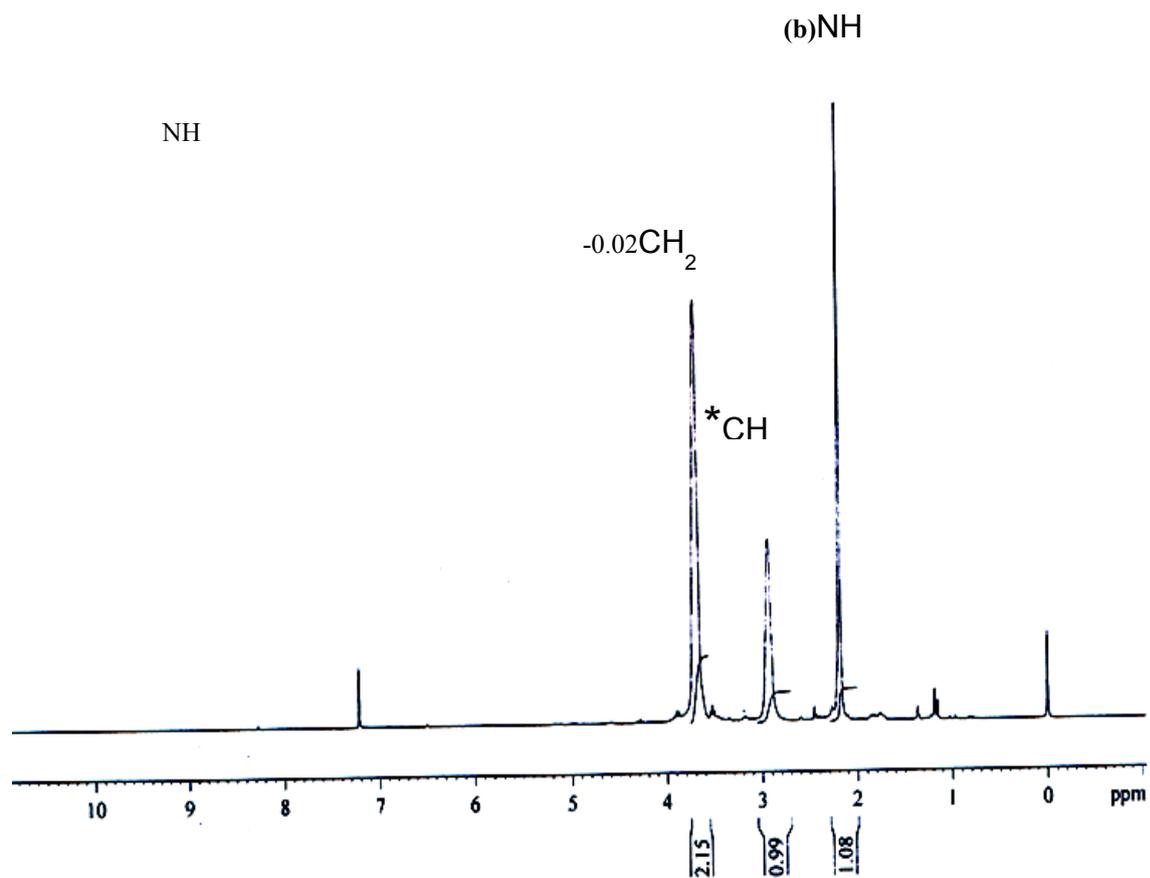


Figure S1a. ¹H NMR of Compound I.

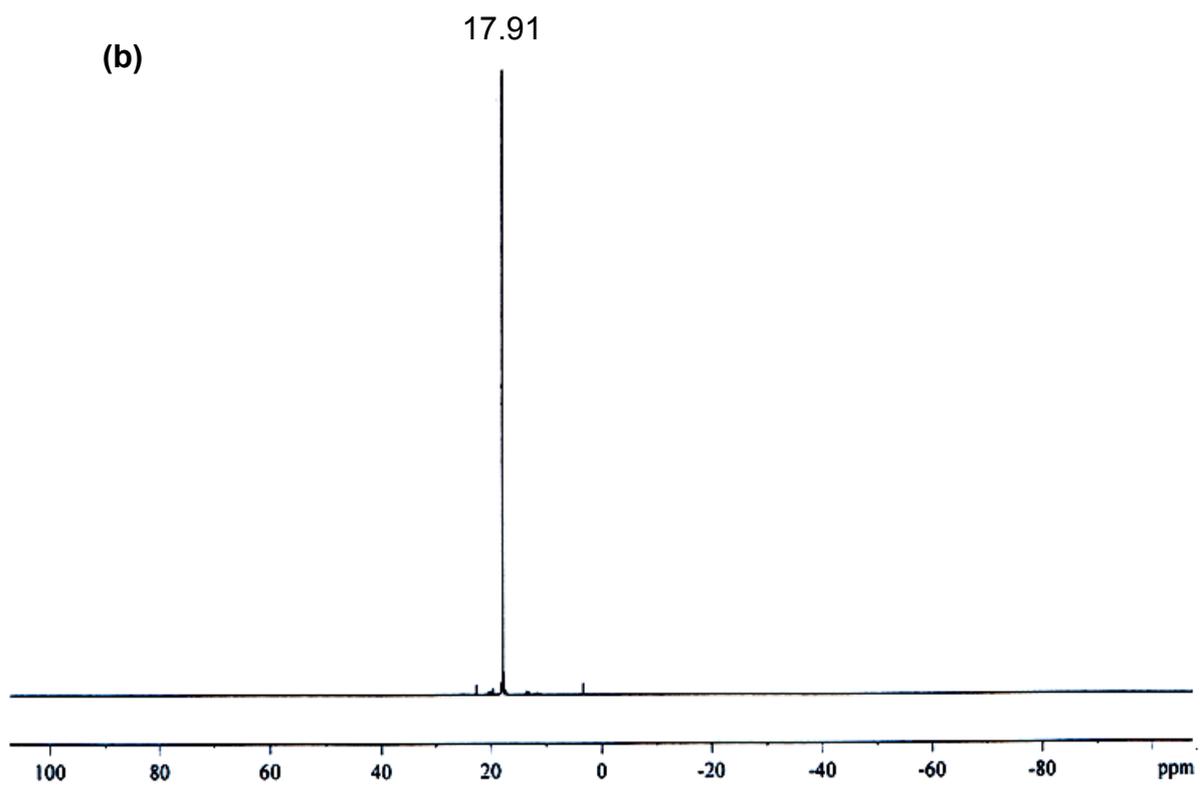


Figure S1b. ^{31}P NMR of Compound I.

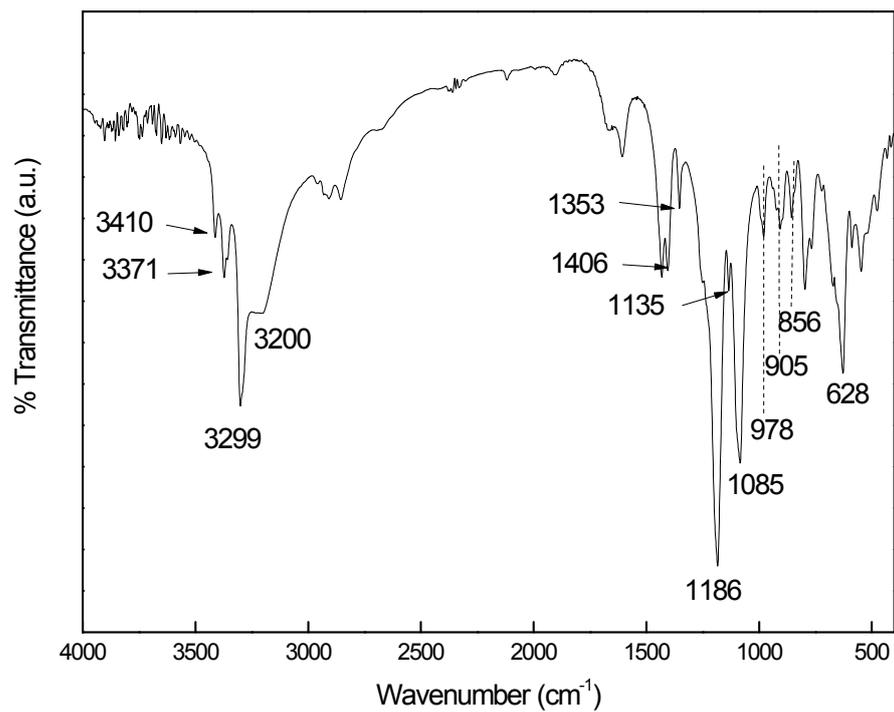


Figure S2. FT-IR of Compound I.

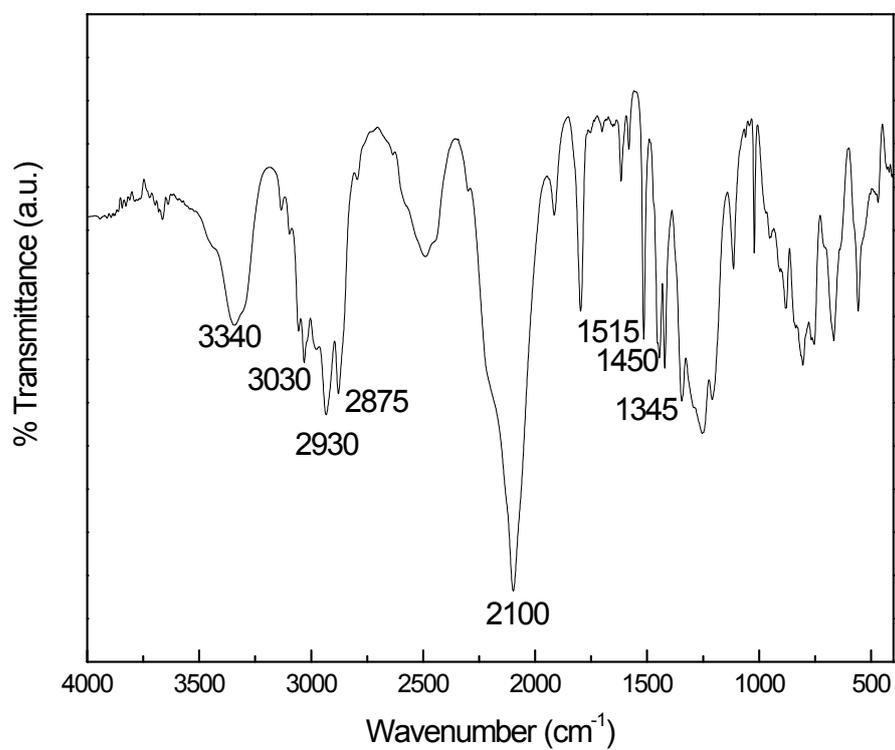


Figure S3. FT-IR of Compound II.

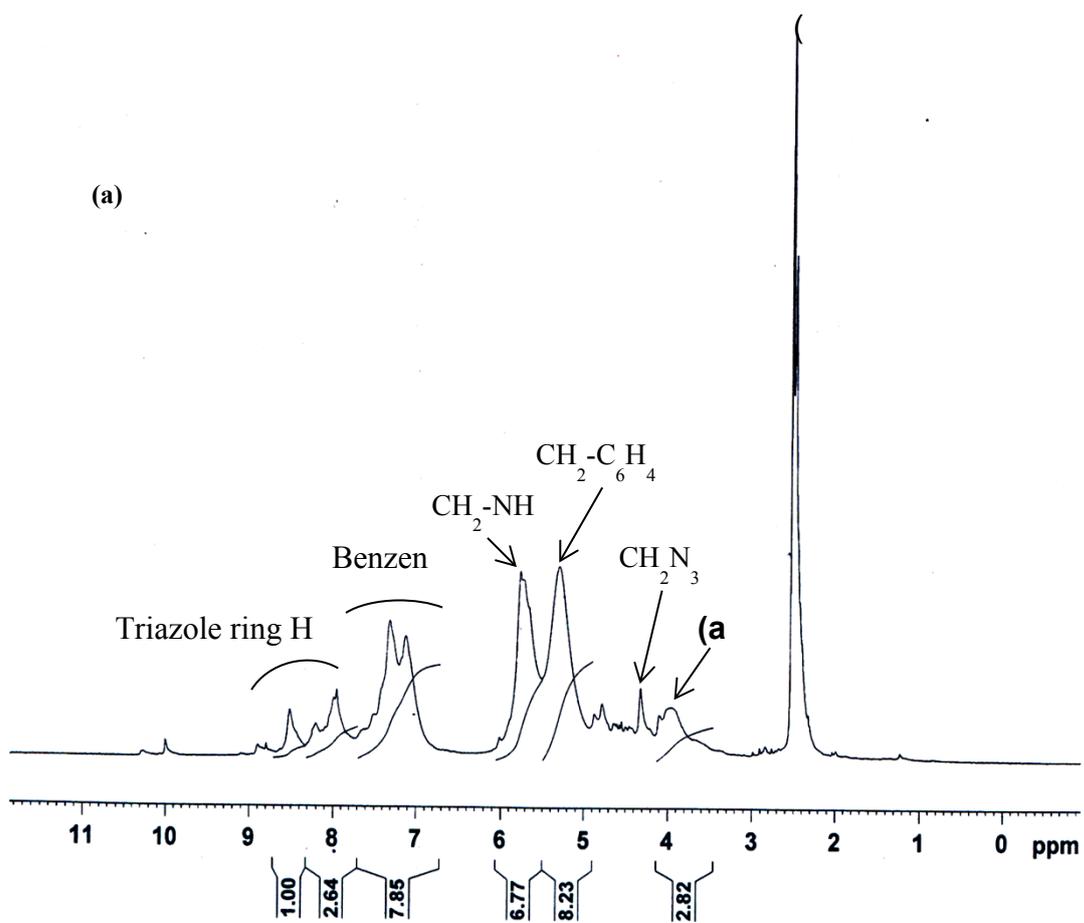


Figure S4a. ^1H NMR of PHM-1.

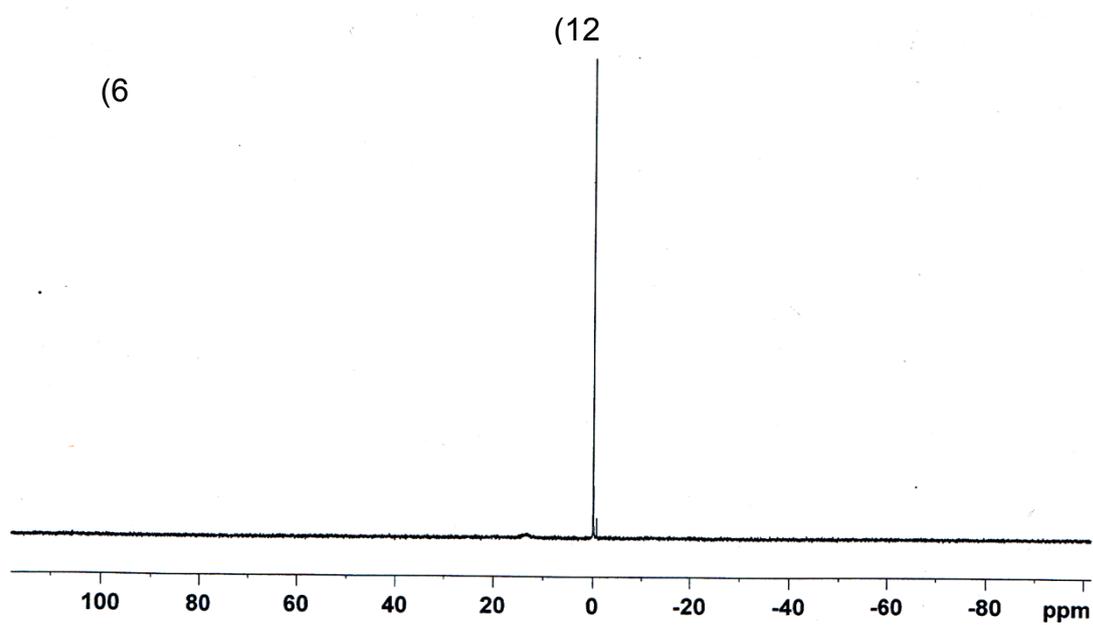


Figure S4b. ^{31}P NMR of PHM-1.

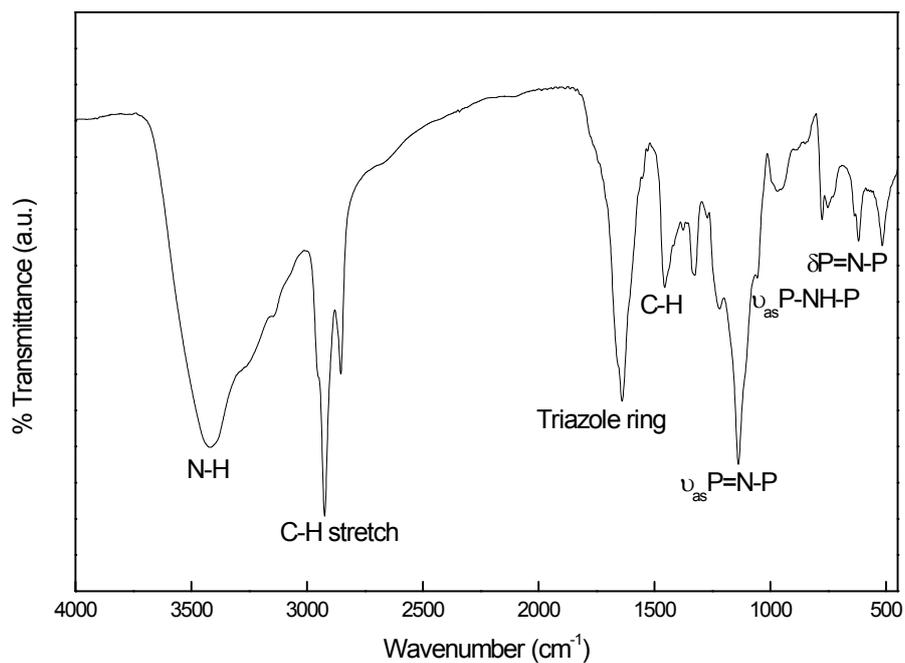


Figure S5. FT-IR spectrum of PHM-1.

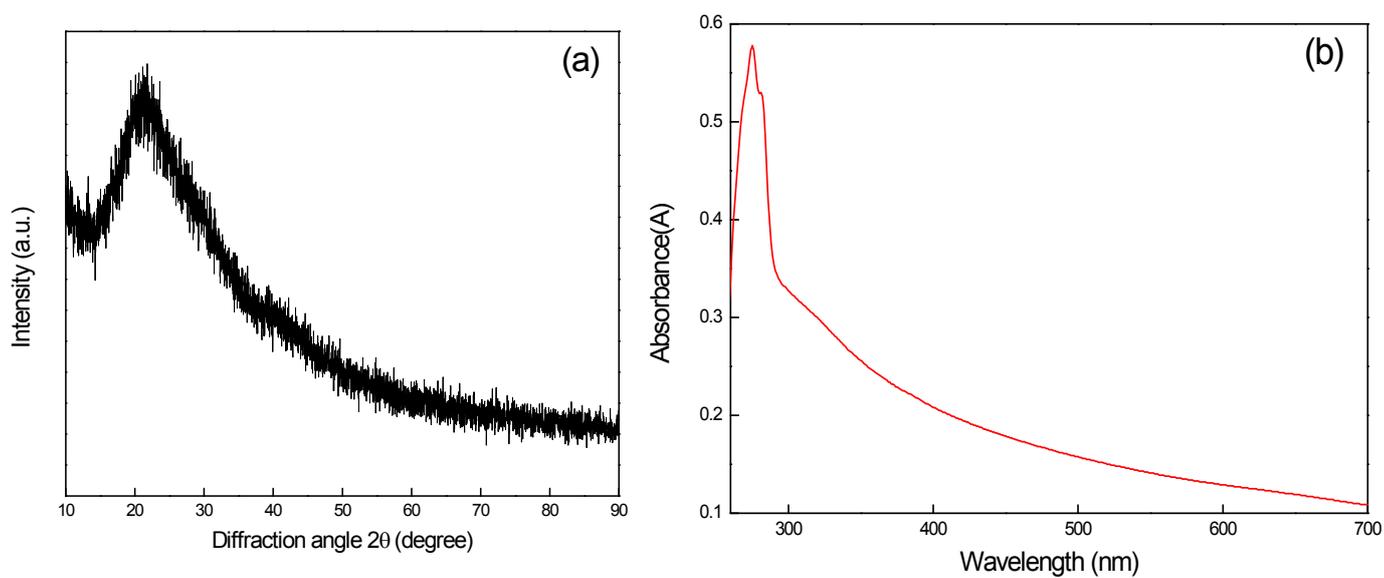


Figure S6. (a) XRD pattern and (b) UV-vis spectrum of PHM-1.

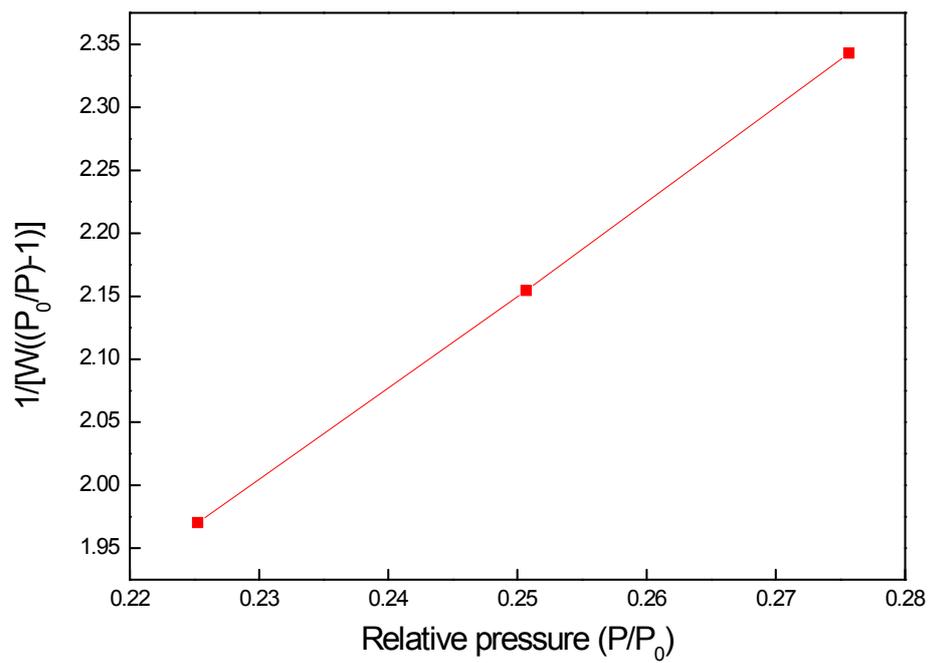


Figure S7. Multi-Point BET plot of PHM-1.