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

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Porous inorganic-organic hybrid material (PHM) has been synthesized by click chemistry with cyclophosphazene in the framework. The PHM-1 is x-ray amorphous and has high specific surface area of 453 $m^2.g^{-1}$ with pore size distribution of 3.7 nm. It shows reversible CO_2 uptake of 1.83 $mmol.g^{-1}$ at 273 K.

Porous inorganic-organic hybrid materials (PHMs) are one of the promising materials owing to their large surface area, low density, high thermal, mechanical and hydrothermal stability, ease of synthesis, and ready functionality.[1a-f] Continuous and tremendous efforts have been made recently for the development of PHMs with interesting structure and properties, however, there is an utmost need for the synthesis and design of the PHMs with tailor made functionalities to improve the properties and hence, applications. Incorporation of various inorganic moieties is regarded as one of the most efficient way to have PHMs rigid frameworks with better stability and the organic moieties play a pivotal role in the functionalities of the resulting PHMs.[1f]

Capturing carbon dioxide (CO_2) in an economical ways from the flue gas is considered one of the technological solution for global warming.[2a-b] With the alarming increase in the CO_2 content in the environment which reaches as high as 401.30 ppm in June 2014, there is an urgent need for getting the right adsorbent.[2c] Traditionally, amine solutions were used for the CO_2 sorption, however, the method is not cost effective as substantial amount of energy is wasted to regenerate the sorbents.[3a] Recently, several solid adsorbents have been researched, which includes, activated carbon, MOFs, COFs, ZIFs, zeolites, mesoporous silica, porous electron-rich covalent organonitridic frameworks (PECONFs) and so on.[3b-h] Each material has their own advantages and disadvantages. The activated carbons have low

selectivity and capture capacity. Higher heat of adsorption of zeolites makes desorption process more energy intensive and they are also sensitive to moisture. MOFs, COFs and ZIFs are air and moisture sensitive. Although many MOFs shows higher CO_2 capture capacity but they are chemically and thermally not very stable. Having an isosteric heat of adsorption in between pure physisorption and chemisortion with a good thermal and hydrothermal stability of the adsorbent and reversible adsorption and desorption cycles make the materials ideal for the CO_2 capture applications.

The click chemistry first reported by Sharpless and co-workers in 2001, is the reaction between organic azides and terminal alkyes.[4a] The click reaction in general carried out under mild reaction condition with wide group tolerance, high yield, excellent modularity and most importantly regioselective.[4a] The 1,4-disubstituted 1,2,3-triazolyl in the product can act as a stable linkage between two organic, inorganic or biomolecules.[4a-f] Recently, a large varieties of materials were synthesized by click chemistry that includes conjugated polymers,[4b] porous polymers,[4c-d] and inorganic organic hybrid materials.[4e-f] However, only few reports are available on PHMs by this click chemistry. All the reports on PHMs are restricted to the post-synthesis functionalization of the porous framework surface using click chemistry.[1f,5a] The post-synthesis functionalization of the surface has several disadvantages. There is always a challenge for the reacting molecule to functionalize, surface coverage, competition between the medium and the molecule to enter the pores, etc.[5b-c] To the best of our knowledge no report is available on the single-step synthesis of PHMs by click chemistry. Here, for the first time we report a single-step synthesis of a high surface area PHM.

The cyclophosphazene was chosen as the inorganic moiety because of its paddle-wheel structure[6] and hence, could provide a rigid

framework with permanent porosity. There are reports on the synthesis of hybrid polymeric materials using polyphophazene (linear chain) and azides by click reactions, however, in these cases, porous structures were not observed.[4e-f] Permanent porosity is always a challenge as nature tends to minimize the pore volume and surface area because of the higher surface energy of the porous materials. The phosphonitrilic chloride trimer (PNC) was used as the cyclophophazene source as it reacts readily with the organic amine. The organic amine, propargylamine, with terminal alkyne linkage reacted with the PNC to form the compound-I, Hexakis(propargylamino)cyclotriphosphazene, by adopting a method employed by Bickley *et al.*[7a] Similarly, the compound-II, 1, 4-bis(azidomethyl)benzene, was synthesized by following the work of *Wan et al.*[7b] (*pl. see SI for detailed synthesis of compounds I and II*). Further, compound-I with a terminal alkyne and the compound-II with the azide group were reacted by click chemistry to form the product as shown in Scheme-1. The nitrogen atoms in the framework with the lone pair of electrons act as Lewis base and can interact with the Lewis acidic gas CO_2 and hence, the interaction could be exploited for the CO_2 capture applications.

For the synthesis of the PHM-1, 1 mmol of compound-I and 3 mmol of compound-II were dissolved in 40 ml N,N dimethylformamide (DMF). To this solution, freshly prepared solution of $CuSO_4.5H_2O$ (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.
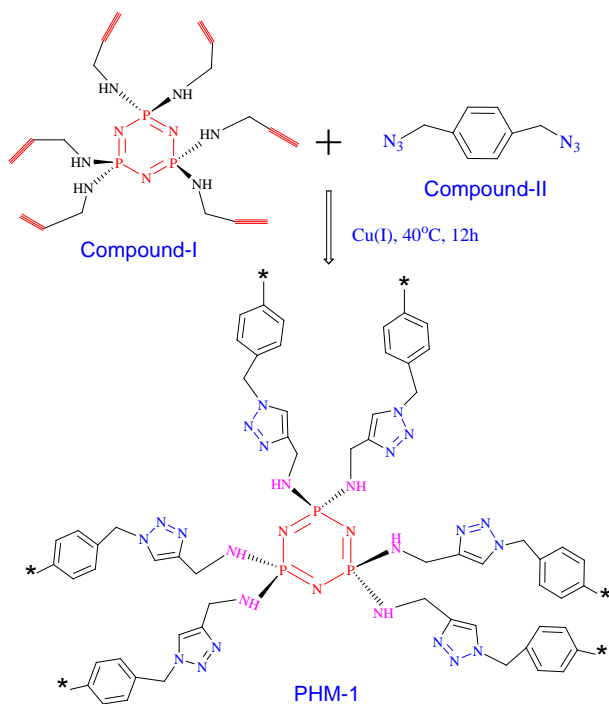
Scheme 1. Reaction scheme for the synthesis of PHM-1.

To investigate the structure of the PHM-1, the ^1H NMR (*Figure S4a*) and ^{31}P NMR (*Figure S4b*) were studied. Broad signal in the ^1H spectrum at a chemical shift of 8.5-7.9 ppm can be assigned to triazole ring proton.[4e] The chemical shift for aromatic proton was observed at 7.3-7.1 ppm.[8a] Sharp signals appearing at 5.7-5.3 ppm can be assigned to methylene proton[8a] and a broad signal around 3.9 ppm is due to NH

proton.[4e] The chemical shift observed at 4.3 ppm is due to end $-CH_2$ group attached to $-N_3$.[7a] A singlet in the ^{31}P NMR spectra as shown in *Figure S4b* at -0.02 ppm indicates that all the phosphorus are in magnetically equivalent environment and hence, confirms the reaction was complete under the experimental condition.[3h,8b]

In order to investigate the structure in more detail, PHM-1 was further studied by FT-IR spectroscopy (*Figure S5*). The spectrum shows a broad band around 3420 cm^{-1} due to N-H stretching vibration[3h] and a sharp band at around 1640 cm^{-1} due to triazole ring stretching.[9a] Disappearance of band at around 2100 cm^{-1} suggests complete azide-alkyne coupling.[9a] Sharp bands around 2925 to 2855 cm^{-1} and at 1452 cm^{-1} are attributed to C-H stretching and bending vibrations, respectively.[9b] Bands at ~1330 and 1138 cm^{-1} are due to •$_{as}$(P=N–P) vibrations. Bands at around 1060 and 965 cm^{-1} can be attributed to •$_{as}$(P–NH–P) vibrations and a sharp band at 520 cm^{-1} can be assigned to •(P=N–P) vibrations.[3h]

The microstructure of PHM-1 was investigated by the FESEM and TEM (*Figure 1*). The granular particles with irregular shape and sizes were intergrown forming a porous structure as manifested by SEM and TEM. The SAED pattern as shown in the inset of *Figure 1b* indicates that the PHM-1 has an amorphous structure. This amorphous structure was further confirmed from the XRD pattern as shown in *Figure S6a*. The PHM-1 absorbs visible light as studied by UV-vis spectrum in *Figure S6b*. Two absorption bands centered at 275 and 285 nm were observed and were attributed to the phenyl ring bonded to triazole ring, and triazole ring, respectively.[10]
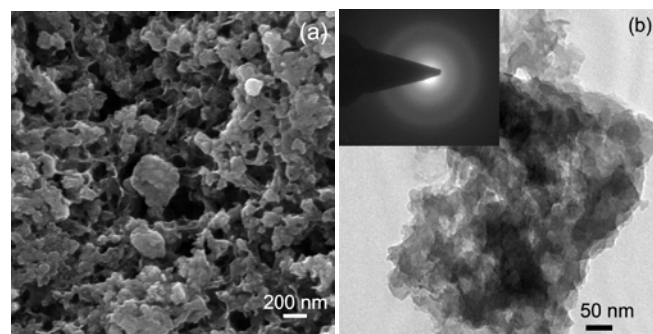

Figure 1. (a) FE-SEM and (b) TEM images of PHM-1.

Thermal stability of PHM-1 was investigated by TGA and DTG thermograms (*Figure 2*). The PHM-1 shows a total mass loss of 51 wt% on heating up to 700 °C in nitrogen. The mass loss occurs in three steps which can clearly be seen in the DTG thermogram. The first step mass loss of 10 wt% at ~ 100 °C can be attributed to desorption of trapped moisture. This is common in porous materials with high surface area.[11] The second step mass loss of 5 wt% on heating up to 280 °C can be attributed to desorption of trapped solvent DMF. Although the specimen was washed several times with ethanol and water, still we could observe a little amount of DMF in the sample. This is possibly due to the trapping of solvent in some of the closed micropores. Such phenomenon was also observed earlier.[3h] The PHM-1 is stable up to a temperature of 280 °C. The third step mass loss of around 30 wt% on heating up to 450 °C could be attributed to framework condensation. On further heating there is carbonization and polymerization of the P-N framework.[8b]
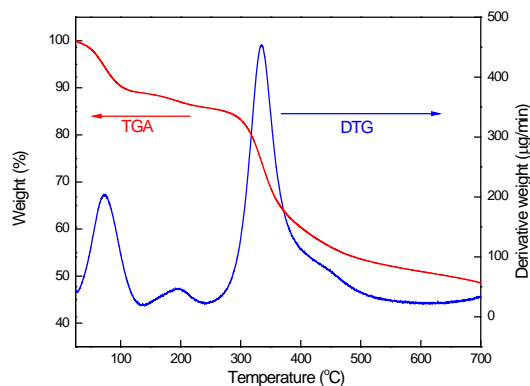
Figure 2. TGA and DTG thermogram of PHM-1 measured in nitrogen atmosphere with a heating rate of 10 °C min^{-1}.

Porous nature of PHM-1 was evaluated by nitrogen sorption measurement at 77 K (*Figure 3a*). A rapid uptake at low pressure indicates the presence of micropores in PHM-1. In addition to that a sharp uptake at P/P_0 of 0.8 with a hysteresis further indicates the presence of mesopores. Thus, the PHM-1 has a hierarchical pore structure with the presence of micropores and mesopores. The pore size distribution (PSD) calculated by density functional theory (DFT) as shown in the inset of Figure 3a further confirms the presence of both micro and mesoporosity. However, the majority of the pores are in mesopore region with the PSD centered at 3.7 nm. The PHM-1 has a specific surface area of 453 m^2.g^{-1} and 620 m^2.g^{-1} calculated by the BET and Langmuir equations, respectively. The total pore volume calculated at $P/P_0 = 0.99$ was 1.05 cm^3.g^{-1}.
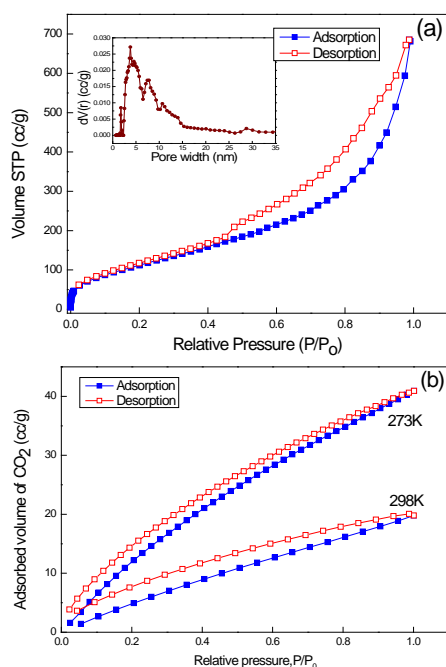

Figure 3. (a) N$_2$ sorption isotherm and pore size distribution (inset) measured at 77 K and (b) CO$_2$ sorption isotherm of PHM-1 measured at 273 and 298 K.

High surface area, pore volume and presence of nitrogen with lone pair of electron in the framework prompted us to study CO$_2$ sorption properties of the specimen. *Figure 3b* shows CO$_2$ sorption isotherm measured at 273 and 298 K. The PHM-1 has a CO$_2$ uptakes capacity of 1.83 mmol and 0.88 mmol at 273 and 298 K, respectively. The isotherms measured at 273 and 298 K are almost reversible in nature. This indicates that the interaction between the PHM-1 and CO$_2$ was physisorption in nature. Furthermore, the isosteric heat of adsorption of 26 kJ.mol^{-1} at the onset calculated by using the Clausius-Clapeyron equation confirms the observation.

In summary, a porous inorganic-organic hybrid material having cyclophosphazene in the framework was reported for the first time by facile single step click chemistry. The material designated as PHM-1 has high BET and Langmuir surface area of 453m^2.g^{-1} and 620 m^2.g^{-1}, respectively. It captures 1.83 mmol.g^{-1} of CO$_2$ at 273 K. The cyclophosphazene, with a paddle-wheel structure,[6] in the framework plays an important role for the formation of the porous structure as non-porous materials were obtained if linear chain polyphosphazenes were used in similar click reaction as reported earlier.[4e,4f] The method reported here can be extended for the synthesis of many more PHMs for various applications.

Notes and references

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