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Porphyrin based porous organic polymers: novel synthetic strategy and exceptionally high CO_2 adsorption capacity†

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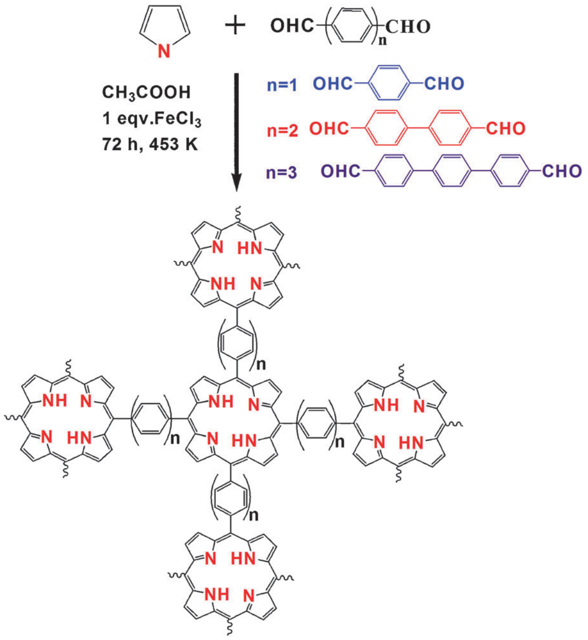
Iron containing porous organic polymers (Fe-POPs) have been synthesized by a facile one-pot bottom-up approach to porphyrin chemistry by an extended aromatic substitution reaction between pyrrole and aromatic dialdehydes in the presence of small amount of Fe(III). The Fe-POPs possess very high BET surface area, large micropores and showed excellent CO_2 capture ($\sim$19 wt%) at 273 K/1 bar.

Advancement of society largely depends on usage of petroleum products and burning of fossil fuels, which emit CO_2, one of the major greenhouse gases responsible for global warming. With the advancement of the society, the carbon level in the atmosphere is increasing and the situation is turning worse day by day. Hence, novel strategies for developing highly efficient materials for CO_2 sequestration or separation from flue gases are very demanding and have a direct environmental impact *via* greenhouse gas remediation. Geologic sequestration, *i.e.* injecting the captured CO_2 stream into a targeted underground geologic component, has been proposed as a feasible way to control the carbon level in the atmosphere.[1] However, due to several drawbacks of this system, alternative methods *i.e.* chemisorption on solid oxide surfaces or physical adsorption on porous solids like silicates, activated carbons,[2] *etc.* have attracted increasing attention recently. However, only very high surface area MOFs,[3] ZIFs,[4] COFs,[5] porous BCN,[6] amorphous supramolecules like cucurbit[7]uril[7] have shown significant CO_2 adsorption at atmospheric pressure. Unlike framework materials, organic polymers belong to such group of materials where wide scope of utility could be manifested by varying the functionality through judicial choice of organic functional monomers. Pure organic polymers like hypercrosslinked polymers or polymers with intrinsic microporosity (HCPs/PIMs),[8] porous aromatic frameworks (PAFs),[9] and related porous polymeric frameworks[10] have been designed starting from a variety of building blocks. But only few of them showed outstanding CO_2 adsorption capacity. Thus, designing a new class of high surface area organic polymers and exploring their potential application in CO_2 capture from the atmosphere is a big challenge today.

Porphyrin based organic polymers are very exciting in this context due to the presence of basic pyrrole containing macrocyclic cavity, which facilitates strong interaction with Lewis acid CO_2. Pre-synthesized metallo-porphyrin monomers have been used for designing porous organic polymers (POPs) either *via* a C–C cross coupling reaction using expensive Pd-catalyst or condensation with tetra(4-aminophenyl) methane.[11] But none of the process is simple and the synthesized materials capture high amount of CO_2. Our design and synthesis strategy for POPs involved a bottom up approach that produces the building block porphyrinic molecules as the basic component *in situ*. This unique methodology using an extended aromatic substitution reaction of pyrrole with several di-aldehydes (Scheme 1, n = 1,2,3) to construct a porous porphyrinic network is very simple and produces a highly porous network.

The synthesis involved simple one-pot aromatic electrophilic substitution on pyrrole with several aromatic di-aldehydes containing *para* –CHO groups for extended cross-linking from the macrocyclic porphyrin repeating units (Scheme 1) through a



Scheme 1 Formation of molecular building blocks of Fe-POPs.

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hydrothermal reaction in the presence of very small amount of $FeCl_3$ at 453 K for 3 days. Reactions were accomplished by treatment of freshly distilled pyrrole with terephthaldehyde (POP-1), biphenyl-dicarboxaldehyde (POP-2) and *p*-terphenyl-dicarboxaldehyde (POP-3) in glacial acetic acid medium in a high pressure Teflon lined autoclave. Under acidic synthesis conditions, aromatic aldehyde first gets activated through protonation, this is followed by electrophilic aromatic substitution at the activated carbon atoms of the pyrrole ring and then condensation to yield macrocyclic porphyrin building blocks with free –CHO groups. This undergoes further condensation with pyrrole and di-aldehydes to form dark brownish extended porous organic polymeric network structures. The product yields vary from 44%–21% based on the starting pyrrole and aldehyde amounts. Fe-POPs are stable on exposure to boiling water and conc. HCl, suggesting highly cross-linked and robust structures.

Powder XRD analysis of these Fe-POPs revealed no strong diffraction peaks, implying that the microporous polymers are composed of an amorphous network (Fig. S1, ESI†). It is pertinent to mention that using pre-synthesized metalloporphyrin[11] building blocks for POP formation also resulted in materials without any definite XRD pattern (except predesigned metalloporphyrin building blocks used for the synthesis of COFs[12]) suggesting the irreversibility of the reaction or nearby completion of polymerization and formation of a purely amorphous highly cross-linked polymer. In our synthetic approach the cross-linking points of these POPs are the porphyrin ring formation involving the reaction of four pyrroles and four aldehyde molecules followed by an extended aromatic substitution reaction. Under acidic pH in the presence of an Fe(III) oxidant, the only other possibility is the polymerization of pyrrole to give polypyrrole or oligopyrrole, terminal substituted dipyrromethane or macrocycle containing 5 or more pyrrole moieties. However, absence of any broad peak at *ca.* 24.0 degrees of 2θ (characteristic peak of amorphous polypyrrole polymer)[13] rules out the possibility of the polymerization of pyrrole in Fe-POPs under the synthesis conditions. Further, the surface areas of the resulting Fe-POPs are 750–875 $m^2\ g^{-1}$ (see below) whereas the maximum attainable surface area of polypyrrole or other oligopyrroles (under identical synthesis conditions in the absence of the dialdehyde) is 60.0 $m^2\ g^{-1}$ only. This also rules out the possibility of impurity phases and suggested that porphyrin building blocks are randomly oriented.

FE-SEM revealed that Fe-POP-1 is composed of uniform nanospheres (Fig. S2a, ESI†) of dimension *ca.* 50–100 nm which are self-assembled to form uniform large spherical particle of *ca.* 350–700 nm. Such hierarchical morphological feature is quite unique and interesting particularly for applications in adsorption and catalysis. Fe-POP-2 and Fe-POP-3 also show similar morphology (Fig. S2b–c, ESI†). TGA (Fig. S3a–c, ESI†) analysis of all three samples revealed high thermal stability, up to 523 K. The FT-IR spectra of all the materials (Fig. S4, ESI†) suggest the absence of C=O groups (1720–1740 cm^{-1}) of the aldehyde confirming the formation of polymeric networks. Other bands corresponding to phenyl and pyrrole moieties (Supporting information) confirmed the direct incorporation of the pyrrole moiety and formation of microporous porphyrin networks. Further, these Fe-POPs exhibit a new vibration band at 1001 cm^{-1} attributed to the strong coordination of Fe(III) with porphyrin units. Existence of Fe is also evident from AAS analysis, which suggests the presence of 0.00267 mmol of Fe/g of Fe-POP-1, which is much lower than one Fe atom/porphyrin unit. This result suggested that many of the porphyrin units are Fe-free and can interact with Lewis acid, CO_2. The solid state ^{13}C CP-MAS NMR spectrum of Fe-POPs showed four resonances between 110.0 to 153.5 PPM depending upon the aldehyde (Fig. S5a–b, ESI†). In Fe-POP-3, peaks at 126.3 and 136.2 PPM correspond to phenyl carbon atoms and those at 119 and 153.5 PPM to porphyrin macrocycles.[11b] These ^{13}C MAS NMR spectra showed no signal corresponding to free aldehyde or pyrrole, confirming the complete polymerization of pyrrole and di-aldehydes. Moreover, UV-vis DRS (Fig. S6, ESI†) and PL emission bands (Fig. S7, ESI†) also suggested the presence of porphyrin moieties in these Fe-POPs.

Porous properties of these POPs have been established from the N_2 sorption analysis at 77 K. Prior to nitrogen adsorption measurement, the polymers were rigorously washed by Soxhlet extractions with water, ethanol, dry THF, acetone and dichloromethane, respectively, and then dried under vacuum at 393 K for 3 h. As evidenced from Fig. 1, N_2 sorption isotherms for Fe-POPs show type I isotherm, typical for microporous solids, where a steep gas uptake at low relative pressure and their mostly flat extrapolation in the intermediate sections of P/P_0 are observed. While changing from phenyl linker to biphenyl and then to *p*-terphenyl BET surface areas of POP-1, 2 and 3 varied from 875 to 855 and 750 $m^2 g^{-1}$ respectively (Table S1, ESI†). Pore size distributions (Fig. S8, ESI†) indicated peak pore diameters of 1.1, 1.04 and 0.75/1.75/2.6 nm for Fe-POP-1, 2 and 3 materials, respectively. Existence of super micropores/mesopores in Fe-POP-3 could be attributed to the large *p*-terphenyl linker between the repeating porphyrin units. Thus from ^{13}C solid state NMR and surface area analysis we can conclude that complete condensation of pyrrole with di-aldehydes in the formation of porphyrin networks occurred instead of formation of linear or branched polypyrroles.[14] Again $FeCl_3$ has also played a pivotal role in the formation and *in situ* build-up of the nucleus porphyrin cavity resulting in highly porous extended network material with random arrangement of pores. In the absence of $FeCl_3$ a very dirty

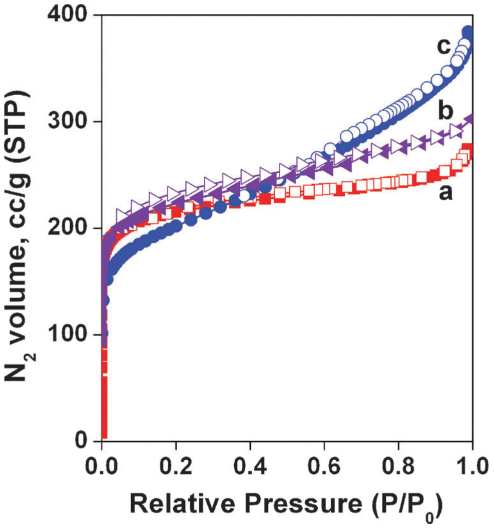

Fig. 1 Nitrogen sorption isotherms for different Fe-POPs: Fe-POP-1 (a), Fe-POP-2 (b) and Fe-POP-3 (c).

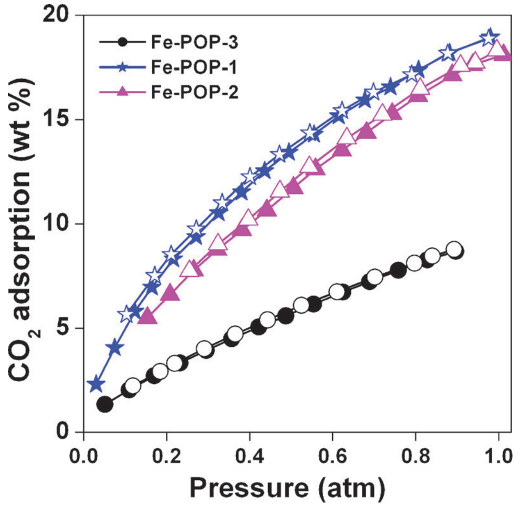

Fig. 2 Gravimetric CO_2 uptake for Fe-POPs at 273 K.

reaction with almost purely non-porous polymers was obtained.

In Fig. 2 we have plotted the CO_2 adsorption isotherms at 273 K for three microporous porphyrin networks. The total gravimetric uptake of POP-1 was 19.0 wt% and that for POP-2 and POP-3 were 18.6 and 9.0 wt%, respectively, at only 1 atm. pressure. These curves are gradually increasing, suggesting further high adsorption capacity for CO_2 at elevated pressure. Among several CO_2 adsorbing materials that have been reported so far, ZIFs synthesized by Furukawa and Yaghi,[4] MOF by Rosi *et al.*,[15] and Zhou *et al.*[16] and BCN graphene by Rao *et al.*[6] are quite interesting due to their very high absorption capacity and crystallinity in their framework structure. Although our Fe-POPs possess relatively low surface areas and amorphous framework structures compared to the above-mentioned materials, they showed exceptionally high uptake for CO_2. Among the porous organic network materials known till date the highest CO_2 uptake observed was for porous benzimidazole-linked polymer (BILP-1).[17] The CO_2 uptake observed in our Fe-POP-1 is 4.30 mmol g^{-1} (19 wt%). To the best of our knowledge this is the highest CO_2 uptake under these conditions (273 K, 1 bar pressure) for any porous organic network material. This higher CO_2 adsorption capacity could be attributed to strong van der Waals force (chemisorption) between (acidic) CO_2 and POPs surface, due to the existence of basic porphyrin subunits in the polymeric network.[15] It is interesting to note that for all the Fe-POP samples adsorption isotherms are reversible in nature. Thus, Fe-POPs can absorb large amount of CO_2 on exposure to atmosphere and can release the equivalent amount of CO_2 from its cavity while releasing the pressure.

In conclusion, we have designed a series of novel porphyrin based porous organic polymers through a simple one-pot bottom up approach involving extended aromatic substitution on pyrrole with aromatic di-aldehydes. These materials possess high surface areas and exhibited outstanding adsorption capacity for CO_2. A simple and affordable synthetic approach described herein for designing Fe-POPs may thus contribute significantly in wide-scale applications in environmental research.

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