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PAPER

Extended phenylene based microporous organic polymers with selective carbon dioxide adsorption[†]

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Two microporous conjugated polymers with extended phenylene backbones have been synthesized through Suzuki cross-coupling reactions. The structure and the pores of the polymers have been controlled by the use of *para-* and *meta-*structure directing 1,3,5-triphenyl tribromide monomers. Gas sorption studies revealed an unprecedented CO₂ selectivity over N₂ for these conjugated polymer networks. The networks have furthermore been tested as hydrogen storage materials and showed significant hydrogen uptake at high pressures.

1. Introduction

The design of porous materials that selectively capture CO_2 from power plant flue gas is of paramount importance for stabilizing the atmospheric CO_2 levels. Although various metal–organic frameworks (MOFs) are being studied to address this challenge, the search for new cheap, robust, air-stable and readily available porous materials is essential for the environment friendly selective sorption.¹ In contrast to the various MOFs and organic molecular porous materials² reported for selective CO_2 capture, organic microporous polymers with selective adsorption characteristics are seldom explored.^{2,3} Herein we report for the first time, the selective sorption of CO_2 over N_2 in conjugated microporous polymers, based on extended *p*- and *m*-phenylenes, having high stability and tunable pore size.

Microporous organic polymers with an amorphous two or three dimensional network are a new class of porous macromolecules with high chemical and thermal stability, low density, predictable structure and tunable functionality.⁴ Moreover, it has been shown that the crystalline order in the framework is not a prerequisite for controlling the pore distribution and surface area of organic frameworks.⁵ Hence various organic reactions have been exploited to synthesize microporous polymers such as hypercross-linked polymers (HCPs),⁶ polymers of intrinsic microporosity (PIM),⁷ conjugated microporous polymers (CMPs)⁸ and covalent triazine frameworks (CTFs).⁹ Among various microporous polymers, the CMPs introduced by Cooper et al.,⁸ exhibit unique properties like energy transfer and catalysis due to their integrated π -conjugated functionality.^{8i,j} Sonogashira-Hagihara and Suzuki cross-coupling reactions of various structurally different monomers have been used extensively to synthesize different poly(arylene ethynylene) and poly(phenylene) based CMPs with excellent adsorption characteristics. More recently, microporous poly(phenylene) networks containing extended phenylenes were synthesized through ethynyl trimerization of acetylene bis-functionalized biphenyl monomers, which exhibit hydrogen sorption characteristics.¹⁰ In this report, we have used triphenylbenzene derivatives with para- and metasubstituted tribromide substitutions as structure directing monomers in the Suzuki cross-coupling synthesis of poly(phenylene)s (p-**PPF** and *m*-**PPF**) with extended π -conjugated backbones in the scaffold (Scheme 1). The para- and meta- pre-organization of the bromo functional groups would direct the growth of polymer chains in different directions to result in extended poly(phenylene) porous network with different pore sizes.11

2. Experimental section

Physical measurements

SEM measurements were performed on a Leica-S440I by keeping the samples on copper substrate followed by heating at



Scheme 1 Molecular structures of microporous polyphenylenes.

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150 °C under vacuum and measurements were done with an accelerating voltage of 10 kV. Electronic emission spectra were recorded on Perkin Elmer Ls 55 Luminescence Spectrometer. Fluorescence spectra of solid powders were recorded in frontface geometry with 325 nm and 350 nm excitation wavelengths. Solid state ¹³C NMR CPTOSS measurements were performed on a Bruker Avance 400 (400 MHz) spectrometer with a MAS rate of 5 kHz. Infrared (IR) spectra were recorded on small amount of the samples embedded in KBr pellets using a Bruker FT-IR spectrometer. Thermogravimetric analysis (TGA) was carried out (Metler Toledo) in nitrogen atmosphere (flow rate 50 mL min⁻¹) in the temperature range 30–600 °C (heating rate 5 °C min⁻¹). CHNS analyses were carried out using a Thermo Scientific Flash 2000 Elemental Analyzer. Powder XRD pattern of the compounds were recorded in a Bruker D8 Discover (40 kV, 30 Ma) instrument using Cu K α radiation ($2\theta = 0.8-60^{\circ}$).

Adsorption measurements

N₂, H₂ and CO₂ adsorption studies of *p*-PPF and *m*-PPF (150 mg), which were degassed at 150 °C for a period of 18 hours under high vacuum (10⁻¹ Pa), were carried out using a QUAN-TACHROME QUADRASORB-SI analyzer at 77 K (for N2 and H₂) and at 195 K (for CO₂). The adsorbates were charged into the sample tube, and then the change of the pressure was monitored. The degree of adsorption was determined by the decrease of the pressure at the equilibrium state. All operations were computer-controlled and automatic. High-pressure H₂ and CO₂ sorption measurements at 77 K and 273 K were carried out on a fully computer controlled volumetric BELSORP-HP, BEL JAPAN high pressure instrument. The H₂ and CO₂ gases used for the high pressure measurements are scientific/research grade with 99.999% purity. Dead volume of the sample cell was measured with helium gas of 99.999% purity. Non-ideal corrections for H₂ and CO₂ gases were made by applying virial coefficients at respective measurement temperatures.

Energy minimization

The monomers and the first generations of *p*-**PPF** and *m*-**PPF** were optimized using the Gaussian-09 suite of programs.^{11,12} The optimization was carried out within Density Functional Theory (DFT) using the B3LYP¹³ hybrid exchange-correlation functional and 6-31G basis set. The optimised geometries were visualised using Visual Molecular Dynamics (VMD).¹⁴

Synthesis

The *para-* and *meta-*directing monomeric 1,3,5-triphenyl tribromide derivatives (**3** and **4**, respectively) were synthesized by the trimerisation reaction of the corresponding bromo acetophenones (**1** and **2**) in the presence of silicon tetrachloride (see Scheme 2). Suzuki coupling of these tribromide monomers with benzene-1,4-diboronic acid gave the corresponding poly(phenylene)s in quantitative yield. In a typical synthetic procedure, a mixture of corresponding tribromo derivative (**3** or **4**) (0.46 mmol) and 1,4-benzene diboronic acid (0.92 mmol) in DMF (20 mL) was degassed by four freeze–pump–thaw cycles. 2 M K₂CO₃ in water (4 mL) and tetrakis(triphenylphosphine)-palladium(0) (70 mg, 60.6 µmol) were added to this mixtures, which was followed by another degassing step. Subsequently, the resultant mixture was purged with Ar and stirred at 150 °C in a Schlenk flask for 36 h. After cooling to room temperature the mixture was poured into water and filtered. The resulting precipitate containing the polymeric product was then washed with methanol, dichloromethane and then dried in vacuum. The polymer was further purified by continuous soxhlet extractions with water, methanol, dichloromethane and tetrahydrofuran for 12 h each.¹¹ The structure and morphology of the resulting polymers were well characterized by a variety of techniques (*vide infra*).¹¹

3. Results and discussion

Structural characterization

The molecular structures of polymers with repeating phenylene linkages have been characterized with solid-state ¹³C-CP TOSS NMR, FT-IR and optical spectroscopic techniques. Solid-state NMR of p-PPF showed three peaks at 126.2, 130.3, and 138.8 ppm corresponding to the two types of un-substituted and substituted phenyl carbon atoms, respectively (Fig. 1a). On the other hand the *m*-phenylene polymer (*m*-PPF) showed only two broad peaks at 145.4 and 131.6 ppm, which can be assigned to the substituted and un-substituted phenyl carbon atoms, respectively (Fig. 1b). The structures with the phenylene linkages are also evident from the FT-IR measurements, which showed signals corresponding to aromatic C=C stretch (1600 cm⁻¹), C= C vibrational modes of the substituted phenyl rings (1390 and 1480 cm⁻¹) and aromatic C–H stretch (3030–3060 cm⁻¹). In addition, IR signals corresponding to trace amounts of the end functional B(OH)₂ or OH groups (3300 cm⁻¹) and C-Br (1005 cm⁻¹) are also observed (Fig. 1c).¹¹ p-PPF showed excitation and emission maxima at 361 nm and 411 nm, respectively which is consistent with the reported values of poly(p-phenylene) π -conjugated chains, reiterating the presence of poly(phenylene) backbones.11,15 However, the absorption and emission spectra of m-PPF showed blue shifted maxima at 325 nm and 382 nm, respectively which could be attributed to its lower effective conjugation length compared to *p*-PPF and is consistent with the poly(m-phenylene) backbones reported in the literature (Fig. 1d).^{11,16} Powder XRD measurements of both polymers showed very broad low intensity peaks (d values of 0.49 nm and 0.24 nm for *p*-PPF and 0.46 nm and 0.24 nm for *m*-PPF) indicating their amorphous nature.¹¹ Since the energy minimized conformation of the monomeric units of *p*-PPF and *m*-PPF shows non-planar geometries (Fig. 2), the polymeric structures resulting from these structure directing monomers can be envisaged to extend into a three-dimensional topology rather than two-dimensional planar structures. The model presented in Fig. 2 is a schematic of the frameworks, based on the energy minimized conformations of the monomers and first generation oligomers.¹¹ Furthermore, the more twisted geometry of meta-directing monomer compared to its para-analogue would give a more densed three dimensional architecture for *m*-PPF compared to p-PPF.

Morphology and thermal stability

After having characterized the molecular structure, we further investigated the morphology and thermal stability of the PPF



Scheme 2 Synthetic schemes for the synthesis of *p*-PPF and *m*-PPF.

polymers. Scanning Electron Microscopy (SEM) of the samples showed porous networks formed by the inter-linking of spherical particles having diameter ranging from 50-100 nm (Fig. 3a and b). Detailed analysis of the images from *p*-PPF and *m*-PPF did not show any significant difference in the size of the particles.

Thermogravimetric analysis (TGA) showed that *p*-PPF is stable up to 250 °C and that maximum weight loss occurs at temperatures in the range of 250–600 °C (60%) (Fig. 3c). The initial weight loss up to 150 °C can be attributed to the trapped solvent in the porous network. On the other hand, *m*-PPF showed



Fig. 1 Solid state ¹³C-CP TOSS NMR of (a) *p*-PPF and (b) *m*-PPF (* indicates the spinning side bands). (c) FT-IR spectra of *p*-PPF and *m*-PPF. (d) Emission spectra of *p*-PPF and *m*-PPF.



Fig. 2 Energy minimized geometry of basic structure directing units and the schematics of the expected three-dimensional polymeric structure of (a) *p*-**PPF** and (b) *m*-**PPF**.

stability up to 300 °C and only 10% weight loss is observed at the initial stages due to trapped solvents. However, above 300 °C a sharp weight loss (\sim 70%) occurred up to 600 °C (Fig. 3c). The





We have carried out N₂ (77 K) and CO₂ (195 K) adsorption experiments to evaluate the permanent porosity of the desolvated microporous polymers, *p*-PPF and *m*-PPF. CO₂ (kinetic diameter; 3.3 Å) sorption measurements show typical type-I profile with steep uptake at low pressure regions, suggesting the microporous nature of both the polymers (Fig. 4). Remarkably on the other hand, N₂ (3.6 Å) was hardly adsorbed by both the polymers as evident from the type-II profile indicating only surface adsorption. The uptake value of CO₂ was 103 mL g⁻¹ and 78 mL g⁻¹ for *para*- and *meta*- polymers, respectively. The selectivity for CO₂ adsorption by both *p*-PPF and *m*-PPF was further evident from the various adsorption measurements performed at similar conditions (195 K), which showed only type-II profiles for N₂ and Ar gases.¹¹

The Langmuir surface areas calculated from the CO₂ sorption are found to be 370 m² g⁻¹ and 276 m² g⁻¹ for *p*-PPF and *m*-PPF, respectively. The corresponding Brunauer–Emmet–Teller (BET) surface areas are 269 m² g⁻¹ and 229 m² g⁻¹, respectively. The total pore volumes of *p*-PPF and *m*-PPF, estimated from the amount of CO₂ adsorbed at $P/P_0 \approx 0.85$ are about 0.20 cm³ g⁻¹ and 0.15 cm³ g⁻¹, respectively. The differential pore volume distributions as a function of pore diameter calculated using the Horváth–Kawazoe method suggest that the pores are in the microporous regions (~5 Å) for both CMPs which is in



Fig. 3 SEM images of: (a) *p*-PPF and (b) *m*-PPF. (c) TGA curves of *p*-PPF and *m*-PPF.



Fig. 4 Sorption isotherms for: (a) *p*-**PPF** and (b) *m*-**PPF** (empty circles show adsorption, filled circles show desorption, P_0 is the saturated vapor pressure of the respective adsorbates).

agreement with *d*-values calculated from powder XRDdata.^{8,10,11} Although the pore sizes of the polymers are in good agreement with the calculated *d*-values from PXRD data (see above), elucidation of an exact molecular picture of these networks is very difficult. The small surface area of *p*-PPF, despite the possibility to have uniform pores due to the structural pre-organization of monomers, could be attributed to the interpenetration of the polymeric networks instead of crystalline eclipsed stacking (Fig. 2). On the other hand, the smaller pore size and pore volume of *m*-PPF compared to the *p*-PPF system from the meta-conformation of the polymer, which would give a more dense network, as evident from the schematics shown in Fig. 2.

Since the pore size distribution of the polymeric networks is above the kinetic diameters of the gases investigated, the contribution of a "molecular sieving effect" towards the observed CO₂ selectivity is unlikely.¹¹ On the other hand the small pore aperture of the polymeric networks might contribute a diffusion barrier for gas adsorption. In this case the pore surface with large aromatic π -clouds and the polar end functional groups would interact more effectively with CO₂ having a large quadruple moment (-1.4×10^{-39} C m²) compared to N₂, providing extra potential energy for adsorption which can overcome the diffusion barrier. Similar selectivity for CO₂ has been observed for MOFs with highly polar pore surfaces.¹⁷ The CO₂ adsorption process was completely reversible and could be repeated many times with similar uptake. The hysteretic sorption profiles for



Fig. 5 High pressure sorption isotherms of (a) *p*-**PPF** and (b) *m*-**PPF** for H_2 at 77 K, (c) for CO₂ of *p*-**PPF** and *m*-**PPF** at 273 K (empty circles show adsorption and filled circles show desorption).

both the polymers suggest strong interaction of the CO_2 molecules with the pore surface. To the best of our knowledge, no other microporous conjugated organic polymers with such high selectivity of CO_2 adsorption over N_2 or Ar have been reported.

High pressure CO₂ and H₂ adsorption

The excellent stability with permanent porosity of p-**PPF** and m-**PPF** established by the selective CO₂ adsorption characteristics inspired us to study the high pressure gas storage properties, in particular hydrogen and carbon dioxide, which are related to

energy and environmental issues. Hydrogen storage capacities of *p*-PPF and *m*-PPF were measured at 77 K using the BELSORP-HP apparatus up to 45 bar. As demonstrated in Fig. 5a and b, *p*-PPF and *m*-PPF exhibit saturation amount of hydrogen uptake of about 67 mL g⁻¹ and 56 mL g⁻¹, respectively. The steep uptake at low pressure regions in both polymers indicates strong interaction of the H₂ with the pore surfaces of the polymers. CO₂ storage capacities of the polymers at 273 K up to 30 bar are about 58 mL g⁻¹ and 41 mL g⁻¹, respectively (Fig. 5c). The H₂ and CO₂ storage capacity of these polymers are comparable to a MOF having a similar surface area.¹⁸

4. Conclusions

In conclusion, we have synthesized and characterized two conjugated poly(phenylene) based microporous polymers, p-PPF and *m*-PPF, using Suzuki coupling reactions of *para*- and meta-structure directing monomers, respectively. Characterization of these polymers suggested the presence of three-dimensional amorphous networks. Remarkably, sorption measurements of both the polymers revealed very high selectivity for CO₂ adsorption over N₂ or Ar. This selective CO₂ capture was hitherto unknown for the family of CMPs and is comparable with the similar reports with various MOFs and molecular porous solids. Furthermore, both p- and m-PPF exhibited hydrogen sorption at high pressures. These stable CMPs could find applications as reusable CO₂ adsorbates and in stabilizing atmospheric CO2 levels.

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