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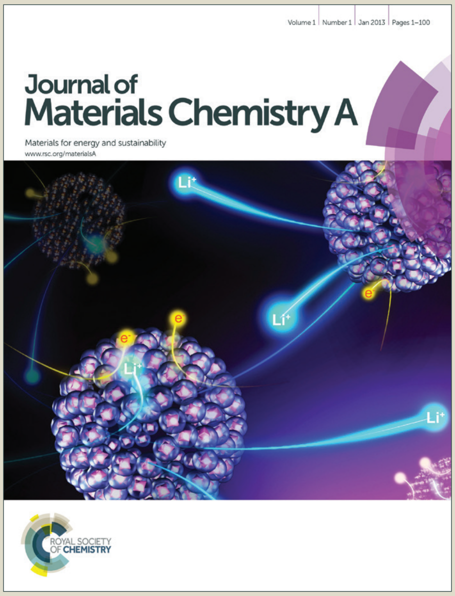

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Cationic Microporous Polymer Networks by Polymerisation of Weakly Coordinating Cation with CO_2-storage Ability

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Microporous organic polymer networks with weakly coordinating cations in their backbone have been synthesized by metal catalyzed C-C bond forming reactions. A functionalized tetraphenyl phosphonium ion was synthesized and successfully used as tecton in a co-polymerisation with tetrakis(4-bromophenyl) methane using nickel catalyzed Yamamoto coupling and with triethynylbenzene in a palladium catalyzed Songashira-Hagihara reaction. The microporous materials showed an apparent BET surface area of 1455 m^2/g and 540 m^2/g, respectively. The Yamamoto product provide a CO_2 uptake of 2.49 mmol/g at 273 K and 1 bar. After ion exchange with chloride CO_2 uptake is further increased to 2.85 mmol/g.

Introduction

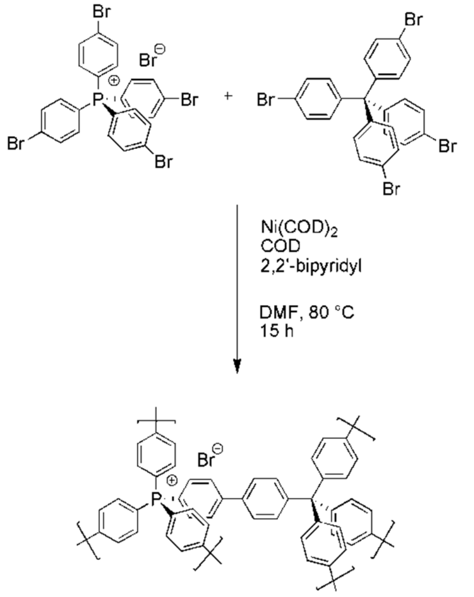
Microporous polymer networks are of increasing interest regarding their potential applications e.g. in the areas of separation, catalysis and gas storage.[1-7] Several classes of these materials, which are built by polymerization of rigid, two or three dimensional organic tectons have been described such as polymers of intrinsic microporosity (PIMs),[8] covalent organic frameworks (COFs, CTFs)[9-11] and conjugated microporous polymers (CMPs).[12, 13] Depending on the functional groups of the tecton different polymerization reactions have been described to build such networks, such as oxidative polymerizations,[5, 14] polycondensations[15] and trimerizations[16, 17] as well as Sonogashira,[12, 18, 19] Suzuki[20, 21] or Yamamoto[22, 23] metal-catalyzed C-C coupling reactions.

Some microporous polymer networks show exceptionally high surface areas which allow the storage of high amounts of gases such as hydrogen or carbon dioxide.[19, 24, 25] For example tectons based on tetraphenylmethane subunits exhibit BET surface areas of up to 5640 m²/g.[23] Related tetrahedral tectons were reported, using silicon or germanium as central atom to connect the four phenyl rings.[26-31] Beside group 14 elements, the exchange of the central carbon with elements from group 13 or 15 should yield negatively or positively charged tectons. The first group reporting a charged microporous polymer network based on such quaternary tectons were Zhang *et. al*,[32] who used the positively charged phosphorus analogue of tetraphenylmethane, *i.e.* tetraphenylphosphonium cations with halides as counter ions. By polymerizing this tecton *via* Yamamoto C-C coupling reaction a polymer was obtained that contained a mixture of phosphonium and phosphine moieties within the polymer resulting from partial decomposition of the phosphonium tecton during polymerization. Recently we reported the use of tetrakis(4-bromo, 2,3,5,6-tetrafluorophenyl)borate as a tecton to generate a microporous anionic borate network (ABN) by Sonogashira-Hagihara coupling with 1,3,5-triethynylbenzene as comonomer.[33] The counter cations, located within the pore channels, are highly accessible and can be easily exchanged, comparable to the extra framework cations found in zeolites. Ion exchange followed by the introduction of a ligand yielded an immobilized charged organometallic complex which can be used as a catalyst in the aerobic oxidation of alkenes.

Results and Discussion

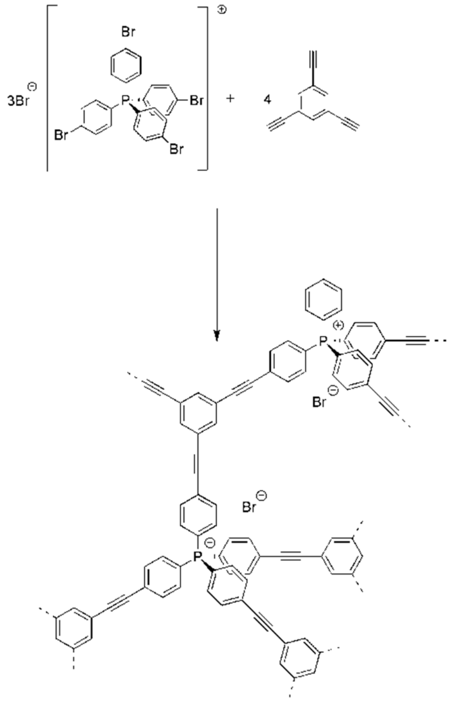
Here, we present the synthesis of two charged co-polymer networks containing a positively charged tetrahedral monomer, *i.e.* tetraphenylphosphonium and a neutral co-monomer. The first polymer network is in principle the cationic counterpart of the previously reported anionic microporous polymer network (ABN). Instead of the negatively charged tetrakis (4-bromo, 2,3,5,6-tetrafluorophenyl)borate, the positively charged tetrakis(4-bromophenyl)phosphonium bromide was used as a monomer in a Sonogashira-Hagihara coupling with 1,3,5-triethynylbenzene. The second polymer network is generated by a Yamamoto coupling of the tetrakis(4-bromophenyl)phosphonium bromide with tetraphenylmethane. As the direct coupling of tetrakis(4-bromophenyl)phosphonium bromide yields to substantial decomposition of the monomer as reported by Zhang[32] we envisioned that the use of a mixture of charged and non-charged monomers might help to stabilize the charges within the network in the same way as for zeolites. Löwenstein's rule for zeolites states that it is impossible to build in two aluminum atoms side by side in a tetrahedral composite. Even though this rule cannot simply be applied to organic networks, it inspired us to dilute the charged tectons with neutral ones to prevent the decomposition which was observed by Zhang *et. al*.[34] and also by our own experiment. Note that also for the negatively charged borate tectons, we observed partial decomposition when a direct coupling was attempted, while the addition of a neutral co-monomer yielded pure borate networks.[34]

The synthesis of a phosphonium monomer containing polymerizable bromine groups was undertaken by firstly reacting 1,4-dibromobenzene and phosphorus trichloride to yield tris(4-bromophenyl)phosphine. A fourth bromophenyl group was introduced *via* palladium catalyzed coupling reaction to obtain tetrakis(4-bromophenyl)phosphonium bromide (see Supporting Information). This tetrahedral monomer was then able to participate in a nickel catalyzed Yamamoto reaction together with the neutral co-monomer tetra(4-bromophenyl)methane to produce an insoluble yellow network in 97 % yield (Scheme 1). The resulting cationic tetraphenylphosphonium-tetraphenylmethane bromide network (CPN-1-Br) is solely composed of phosphorous in the form of cationic phosphonium. Infrared spectra of the resulting polymer network clearly indicates the disappearance of the characteristic arylbromide bond at 1065 cm^{-1} (Figure S1). Together with the high yield this points to the successful inclusion of both monomers into the co-network.



Scheme 1. Synthesis of the CPN-1-Br.

A second charged phosphonium microporous polymer network (CPN-2-Br) was formed by the palladium catalyzed Sonogashira-Hagihara cross-coupling of tetrakis(4-bromophenyl)phosphonium bromide with 1,3,5-triethynylbenzene using optimized reaction conditions used previous for the synthesis of the anionic charged network[33] (Scheme 2). Again high yields of ~100 % and the disappearance of the characteristic arylbromide bond at 1065 cm^{-1} (Figure S1) point to the inclusion of both monomers.



Scheme 2. Synthesis of CPN-2-Br.

The chemical identities of both materials were further confirmed by ^{13}C- and ^{31}P solid state NMR. For the Yamamoto linked network CPN-1-Br, signals at δ = 143, 138, 129, 125 and 63 ppm in the ^{13}C {^{1}H} MAS NMR indicate the presence of five different carbon environments (Figure 1a). The signal at 63 ppm can be assigned to the central quaternary C-atom connected to four phenyl groups. The intense signal at 125 ppm can be assigned to the C_{Ar}-H of the tetraphenylphosphonium unit and the signal at 129 ppm can be assigned to the C_{Ar}-H of the tetraphenylmethane unit. The signal at 137 ppm corresponds to C_{Ar}-C_{Ar}-atoms as well as the carbons connected to phosphonium, while the aromatic carbons adjacent to the central carbons in the tetraphenylmethane unit exhibits a chemical shift of 143 ppm.

Figure 2a shows the ^{13}C {^{1}H} MAS NMR of CPN-2-Br. The resonance at 89 ppm can be assigned to the acetylene groups and the signal at 122 ppm to the aromatic carbons of both monomers next to the triple bond. The intense signals at 126 ppm and 129 ppm can be assigned to the C_{Ar}-H of the tetraphenylphosphonium unit as well as of the 1,3,5-triethynylbenzene. The signal of the C_{Ar}-P-Atoms is observed as a shoulder of the broad signal in the area between 133 ppm to 143 ppm. Notably, the ^{31}P-NMR spectra of both materials (Figure 1b and Figure 2b) show just one intense signal at 24 and 25 ppm with a comparable shift to that seen for the monomer, tetrakis(4-bromophenyl)phosphonium bromide. No resonance due the cleaved corresponding phosphine can be observed in contrast to the network previously reported by Zhang *et al*.[32] We conclude therefore that the additional non-charged monomers were able to stabilize the charged phosphonium units in the polymer network.

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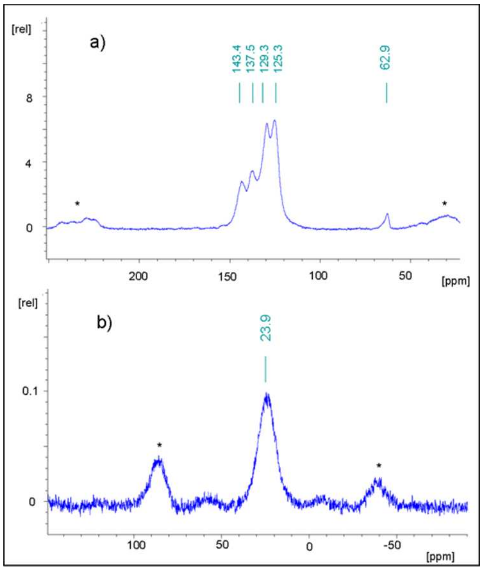

Figure 1. a) ^{13}C-NMR and b) ^{31}P-NMR spectra of CPN-1-Br.

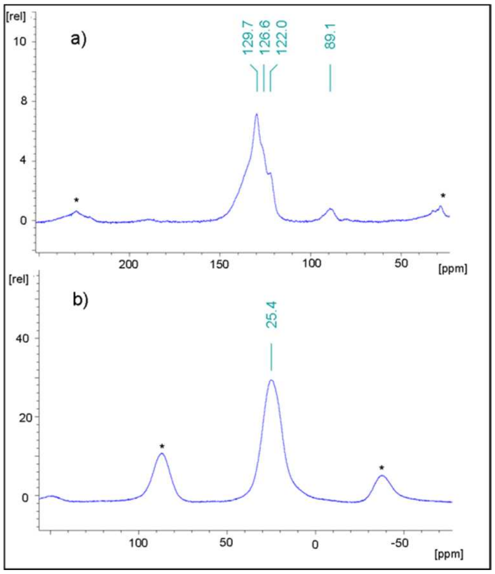

Figure 2. a) ^{13}C-ssNMR and b) ^{31}P-ssNMR of CPN-Br.

The networks were also characterized by nitrogen gas adsorption/desorption at 77 K. The Yamamoto network CPN-1-Br showed a Type I isotherm with a significant amount of gas adsorbed at low pressures followed by a large adsorption at higher pressures attributed to gas condensing into the voids between the polymer particles (Figure 3). As often observed for the relatively soft polymer networks, the desorption branch does not close on the adsorption at low pressures.[34] An apparent BET surface area of 1455 m^2/g was calculated for the network over a relative pressure range of 0.01-0.15 P/P$_0$ (see Figure S2). The total pore volume was calculated to be 1.0 cm^3/g. The Sonogashira network CPN-2-Br shows a lower BET surface area of 540 m^2/g compared to CPN-1-Br. A pore volume of 0.33 cm^3/g was calculated for CPN-Br.

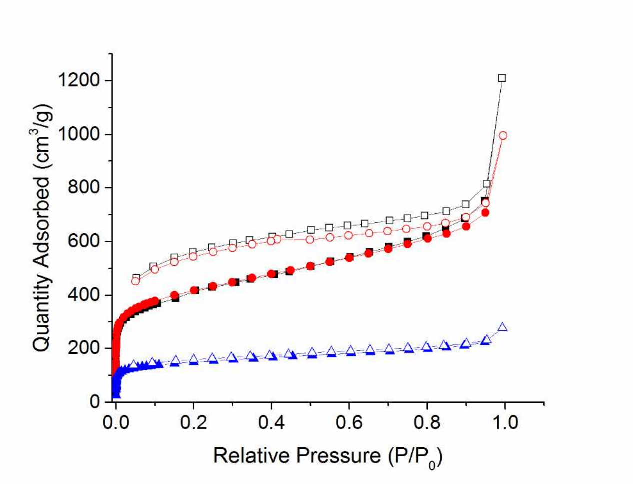

Figure 3. Nitrogen adsorption (closed)/desorption (open) isotherms at 77 K for CPN-1-Br (black squares), CPN-1-Cl (red circles) and CPN-2-Br (blue triangles)

As previously shown for borate networks[33] the counter ions can be exchanged after synthesis. Here, the as synthesized bromine ions can be simply and completely exchanged by chloride ions (CPN-1-Cl), by stirring the CPN-1-Br in saturated sodium chloride solution and methanol. After ion exchange the BET surface area slightly increased to 1504 m^2/g with a pore volume of 1.0 cm^3/g. Pore size distributions were calculated for the networks and showed the largest pores for CPN-1-Br and CPN-1-Cl to be centered around 16 Å (see Figure S5) similar to that for PPN-6.[35] CPN-2-Br had a smaller pore size (7 Å)

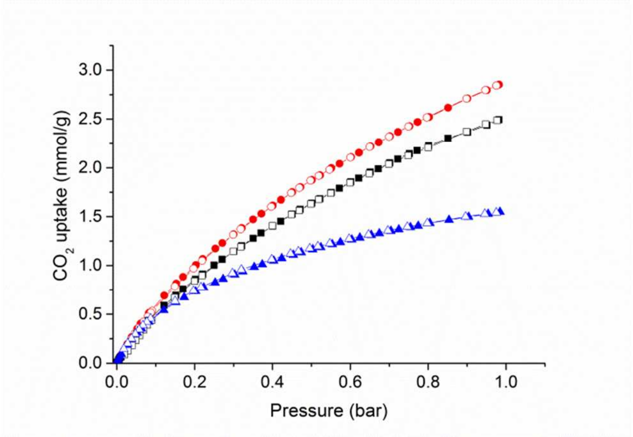

Figure 4. Carbon dioxide adsorption (closed)/desorption (open) isotherms for CPN-1-Br (black squares), CPN-1-Cl (red circles) and CPN-2-Br (blue triangles) measured at 273 K.

The CO_2 uptakes for the networks were measured at 273 (Figure 4) and 195 K (Figure S8 and S9) up to a pressure of 1 bar. It was assumed that for CO_2 with its quadrupole moment, the introduction of network charges might have a considerable influence on the adsorption capacity. Furthermore, it was interesting to investigate if ion exchange within such networks influences the sorption characteristics, *e.g*. due to different size or Lewis acidity of the respective counter anions. CPN-1-Br showed an uptake at 273 K of 2.49 mmol/g while the network after anion exchange, CPN-1-Cl, showed an increased CO_2 uptake of

2.85 mmol/g at 273 K and 1 bar. In comparison to the non-charged network (PAF-1/PPN-6) the CO_2 uptake is increased by around 40 % despite a much lower surface area (1504 m^2/g *vs* 5600 m^2/g).[25] This increased uptake can thus be attributed to the charges within the network. The Sonogashira network (CPN-2-Br) showed a lower uptake than the Yamamoto networks (1.55 mmol/g) in line with its lower surface area. Using the two adsorption isotherms at 195 and 273 K the isosteric heats of adsorption were calculated using Clausius-Claperon equation (Figure S10). The heat of adsorption of CPN-1-Br at zero coverage was calculated to be 31.0 kJ/mol placing it amongst the highest reported microporous polymer networks and almost double the non-charged PAF-1/PPN-6 analogue (15.6-17 kJ/mol).[23, 35] This value is similar to the acid containing PPN-6-SO_3H[35] and CMP-1-COOH[36] networks, although lower than the amine functionalized PPN-6 series (such as PPN-6-DETA).[37] The chloride exchanged network, showed a similar heat of adsorption while the Sonogashira network (CPN-2-Br) was slightly lower at 28.2 kJ/mol at zero coverage rising to 31.8 kJ/mol at a coverage of 7 cm^3/g.

Conclusion

In conclusion, we have successfully synthesized two different charged microporous organic polymer networks CPN-1-Br and CPN-2-Br using tetrakis(4-bromophenyl)phosphonium bromide as a tecton. The tecton was stabilized by an analogous methane monomer which coupled trough a Yamamoto reaction with the tecton to form the CPMN-Br. The polymer network CPN-Br was obtained through a Sonogashira-Hagihara coupling with 1,3,5-triethynylbenzene. In this case 1,3,5-triethynylbenzene is the neutral, uncharged stabilizing factor, which ensures the intactness of the tetrahedral phosphorus building unit during the reaction. Nitrogen sorption revealed a high surface area that, together with the charged nature of the polymer, ensured very good CO_2 uptakes for the CPN-1-Br and CPN-1-Cl in comparison to non-charged network (PAF-1/PPN-6).

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Notes and references

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† Footnotes should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/b000000x/

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