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Microporous Polymers

An Anionic Microporous Polymer Network Prepared by the Polymerization of Weakly Coordinating Anions**

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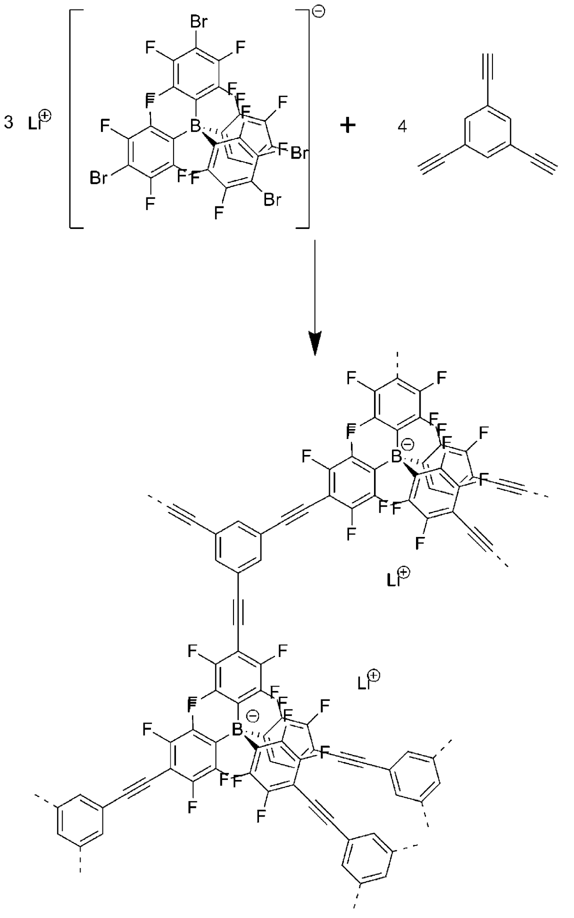
Salts and complexes of weakly coordinating anions (WCAs) have found promising applications as catalysts and superacids, and for the preparation of highly active organometallic compounds.[1] Tetrakis(pentafluorophenyl)borate is such a WCA which has been frequently described and applied,[2] for example recently as a building block in dendrimers.[3] The structurally related, but uncharged, tetraphenylmethane is a suitable tecton for the generation of microporous polymer networks;[4] when it is functionalized with polymerizable groups, the resulting networks sometimes display extraordinarily high surface areas.[5] Furthermore it has been shown that the central carbon atom can be replaced by other elements such as silicon to form element–organic frameworks.[6]

In this context a functionalized tetraphenylborate anion should be suitable for the formation of microporous polymer networks. This type of material—microporous anionic borate networks (ABNs)—would combine the field of WCAs with the field of microporous polymer networks. In this material it can be assumed that due to the microporous architecture the countercation would be mobile and fully accessible even in the solid state, comparable to the extra-framework cations in inorganic zeolites. As the nonfluorinated tetraphenylborate anion shows limited chemical and photochemical stability, we used a more common fluorinated compound with a suitable functional group for polymerization, namely lithium tetrakis(4-bromo-2,3,5,6-tetrafluorophenyl)borate (Li[B(C_6F_4Br)$_4$]), as the tecton in this work (for the synthetic protocol and analysis of this tecton, see Figures S1–S5 in the Supporting Information).

Recently bromo-functionalized tetraphenylphosphonium has been reported as a tecton, which in principle would yield the cationic counterpart to our proposed anionic networks. Yamamoto coupling[7] was applied to couple these tectons, yielding a mixture of phosphonium and phosphine moieties within the polymer.[8] Likewise all our attempts to directly couple Li[B(C_6F_4Br)$_4$] by Yamamoto coupling failed; we obtained networks with variable amounts of borate and borane moieties in low yields. Therefore we copolymerized Li[B(C_6F_4Br)$_4$] with 1,3,5-triethynylbenzene using Sonogashira coupling (Scheme 1).



Scheme 1. Synthesis of Li-ABN.

The Sonogashira coupling was introduced by Cooper et al. to prepare conjugated microporous polymers.[9] After optimizing the reaction conditions (see the Supporting Information) we were able to generate a network (Li-ABN), which contained boron solely in the form of anionic borate. The chemical identity of the material was proven by ^{13}C, ^{11}B, and ^{7}Li NMR spectroscopy. The ^{13}C NMR signals of Li-ABN (Figure 1a) can be assigned to the predicted structure of the network. Notably, the ^{11}B NMR spectrum of Li-ABN (Figure 1b) shows just one intensive signal with a chemical shift comparable to that of monomeric Li[B(C_6F_4Br)$_4$] in the solid state (Figure S4).

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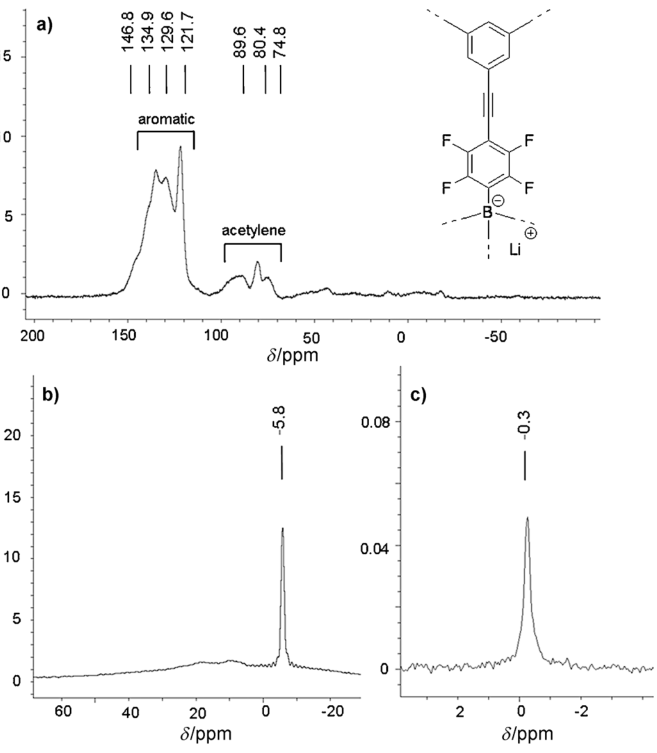


Figure 1. a) ^{13}C, b) ^{11}B, and c) ^{7}Li NMR spectra of Li-ABN.

Therefore it can be concluded that all the boron atoms in Li-ABN are present as borates and no B–C cleavage has occurred to form the corresponding borane. Indeed, no signal at 59 ppm can be identified which would be characteristic for triphenylborane.[10] Also the solid-state ^{7}Li NMR spectrum of Li-ABN (Figure 1c) shows just one signal for the lithium cation and its chemical shift is analogous to that observed in the monomer (Figure S5).

The network Li-ABN shows a high permanent surface area of 890 m^2 g^{-1} and a pore volume of 0.61 cm^3 g^{-1} as can be derived from the nitrogen physisorption isotherm (Figure 2). To verify the suitability of Li[B(C$_6$F$_4$Br)$_4$] for the generation of microporous networks, its uncharged counterpart, tetrakis(4-bromophenyl)methane, was similarly used as a tecton in a Sonogashira coupling with 1,3,5-triethynylbenzene (Figures S6 and S7). The uncharged network showed a comparable surface area of 761 m^2 g^{-1} and pore volume of 0.54 cm^3 g^{-1}, which proves that anionic and uncharged tectons are interchangeable in these porous architectures. Considering that the molecular weight of the anionic repeating unit is much higher than that of the uncharged repeating unit, it can be concluded that Li[B(C$_6$F$_4$Br)$_4$] is a highly suitable tecton for the generation of high-surface-area networks. It should be noted, however, that homocoupling of 1,3,5-triethynylbenzene can also occur under these reaction conditions.[11] This side reaction might lead to an increased amount of 1,3,5-triethynylbenzene in the resulting network.

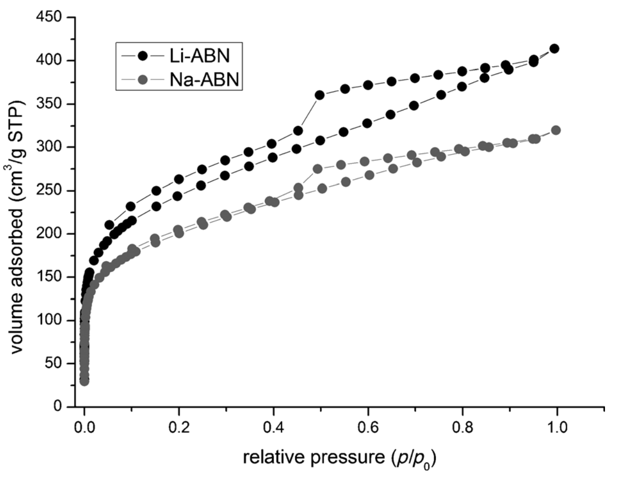


Figure 2. N$_2$ physisorption isotherms at 77 K for Li-ABN and Na-ABN.

The microporous anionic organic networks reported herein have some chemical similarities to inorganic zeolites. While in the latter, Si is exchanged by Al to create charged networks with extra-framework cations (which are crucial for the functionality and applications of zeolites as both ion exchangers and catalysts), in our system replacement of C by B yields the charged network. To further demonstrate this resemblance, ion-exchange experiments were carried out.

Li ions were rapidly and completely exchanged by sodium ions in the networks when Li-ABN was stirred in saturated sodium chloride solution for 5 h. Complete ion exchange could be confirmed as an intense signal appeared in the ^{23}Na NMR spectrum (Figure 3a) of the product, while no signal could be detected by ^{7}Li NMR spectroscopy (Figure 3b). After ion exchange a slightly reduced surface area of 731 m^2 g^{-1} and pore volume of 0.48 cm^3 g^{-1} was observed from the nitrogen physisorption isotherms (Figure 2), which can be explained by the higher molecular mass and larger size of the sodium ions compared to lithium ions

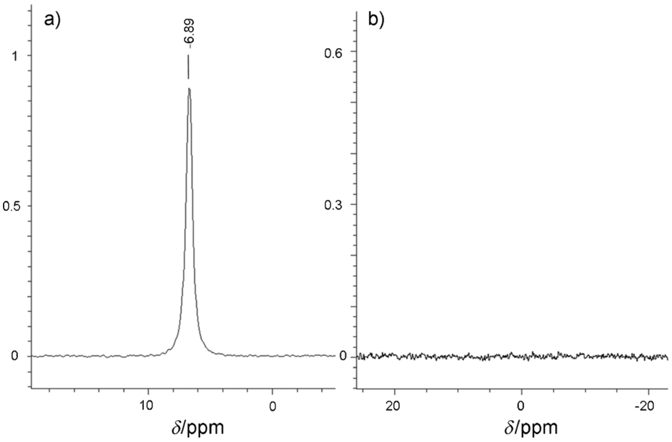
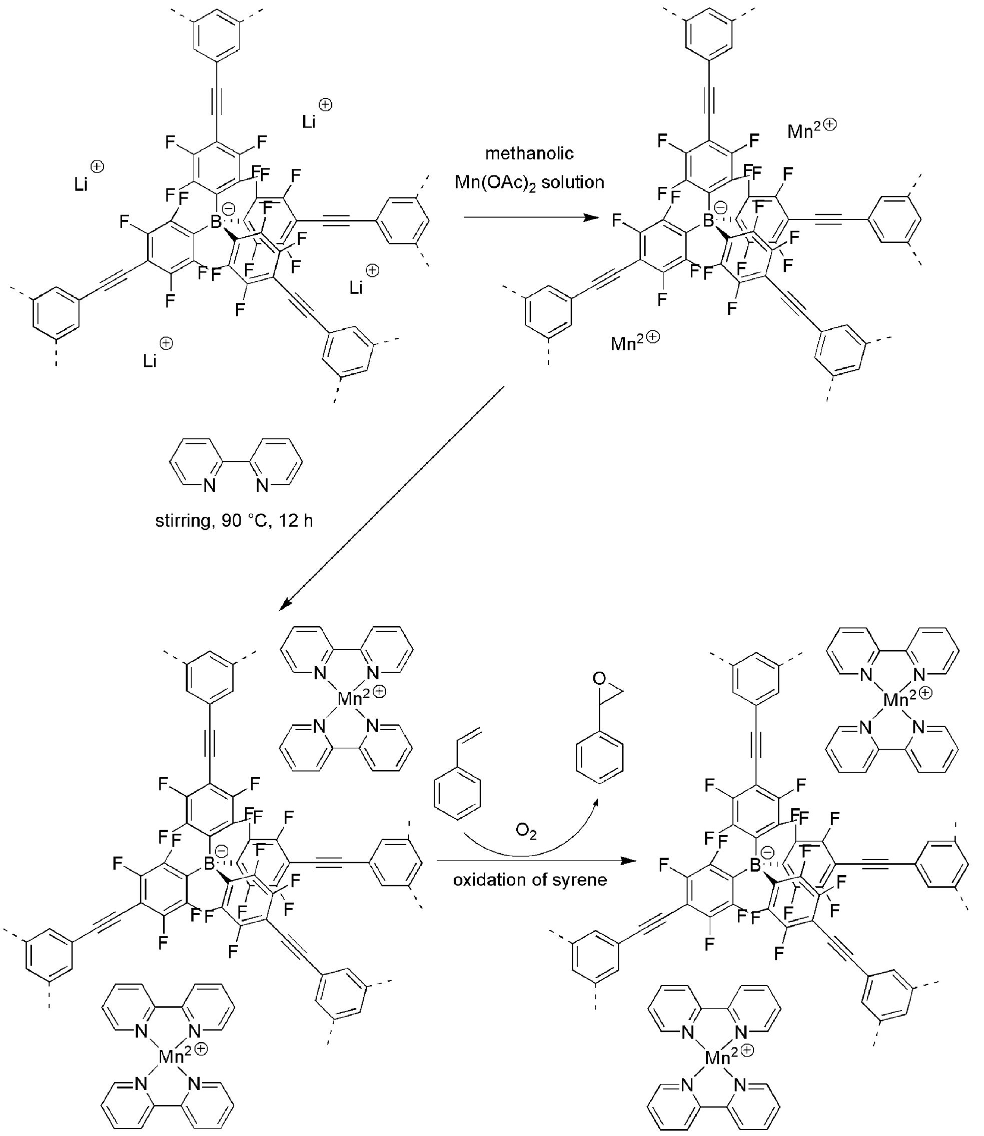


Figure 3. NMR spectra of Na-ABN prepared by ion exchange from Li-ABN: a) ^{23}Na and b) ^{7}Li.

Ion exchange in Li-ABN can in principle be carried out with a range of cations. Therefore we aimed to test the material for another application, also motivated by zeolite research. In zeolites, it has been shown that ion exchange can be used to incorporate catalytically active transition-metal ions in the framework. When an organic ligand is added it is even possible to assemble metal–organic complexes in the zeolite cages. This approach is known as “ship-in-the bottle” synthesis and yields immobilized molecular catalysts.[12] Such transition-metal complexes immobilized in zeolites have received special attention as inorganic mimics of enzymes.[13]

Manganese(II) bipyridine complexes ([Mn(bpy)$_2$]X) can be used as catalysts for the oxidation of alkenes and alkanes,[14] but their catalytic activity is limited by self-oxidation and dimerization through the formation of μ-oxo bridges.[15] For this reason in a pioneering work on the immobilization of metal–organic complexes in zeolites, a [Mn(bpy)$_2$]$^{2+}$ complex was chosen and indeed its immobilization led to improved catalytic stability and recyclability.[16]

We used a similar procedure for the immobilization of [Mn(bpy)$_2$]$^{2+}$ in ABN. The “ship-in-a-bottle” strategy was used, even though the soft and amorphous network might not be suitable for the immobilization of the complex solely by steric confinement, as is possible in the rigid cages found in zeolites. However, it could be assumed that a cationically charged complex must stay inside the network just because of the anionic charge of the ABN. The open network structure of the ABN with a mean pore diameter of roughly 15 Å provides enough space for [Mn(bpy)$_2$]$^{2+}$) and it can be assumed that substrates as well as products can diffuse in and out of the pores without much restriction.



Scheme 2. Immobilization of [Mn(bpy)$_2$]$^{2+}$ in an ABN and its catalysis of styrene oxidation.

The first step in immobilizing [Mn(bpy)$_2$]$^{2+}$ in ABN (Scheme 2) was the exchange of lithium for manganese ions by stirring Li-ABN in manganese(II) acetate solution (for experimental details see the Supporting Information). Two lithium ions should be replaced by one manganese ion to achieve charge balance. For the resulting Mn-ABN no lithium can be detected by ^{7}Li NMR analysis. The surface area is reduced to 499 m^{2}g^{-1} and the pore volume to 0.50 m^{3}g^{-1}. To form the immobilized complex, Mn-ABN was stirred at 90 °C in pure bpy (m.p. 70 °C) and subsequently washed with dichloromethane to remove excess ligand. The surface area and pore volume were further reduced to 398 m^{2}g^{-1} and 0.33 m^{3}g^{-1}, respectively (Figure S8). Another indication of the successful immobilization of [Mn(bpy)$_2$]$^{2+}$ in the ABN is the appearance of two weak absorption bands at 300 nm and 251 nm in the UV/Vis spectrum not seen in Li-ABN (Figure S9), which can be attributed to π–π* transition of the pyridine rings of the ligand.[16d]

The exchange of lithium ions by manganese ions was also monitored by EPR spectroscopy. The spectrum (see Figure S10) is dominated by a strong, unstructured signal with $g = 2.00$, which can be attributed to stable radicals in the polymer network, which is not surprising for extended delocalized organic materials.[17] The spectrum also exhibits the typical six-line hyperfine pattern characteristic for Mn^{2+} centers with close to isotropic g and A tensors.

The immobilized [Mn(bpy)$_2$]$^{2+}$ units in ABN were also examined (see Figure S11). The spectrum shows in principle the same pattern, but in addition to the normal allowed transitions, more pronounced forbidden transitions also appear, possibly generated by chemical change in the manganese environment. Between every pair of the six allowed transitions is an additional, partly resolved pair of forbidden transitions with lower intensity.[18] As expected, the possible superhyperfine pattern (nine lines) due to the coordination of the four nitrogen donor atoms of the bipyridine ligands is not resolved, but it might easily be superimposed by the relatively broad lines of the six allowed transitions. The intensity of the signals in all cases is in good agreement with the assumed Mn^{2+} concentration in the extended network.

The oxidation of styrene with $[Mn(bpy)_2]^{2+}$-ABN as the catalyst was carried out at 80 °C in acetonitrile using dioxygen with a slightly higher oxygen flow rate than that reported.[19] Within one hour complete conversion was observed, with selectivity for the formation of styrene oxide of 65 %. Notably, this selectivity increased to 81 % in the two subsequent runs (Table 1). These conversions and selectivities are much higher than for the reaction without catalyst as well as for the experiments in which Mn-ABN and even pure $[Mn(bpy)_2]^{2+}$ are used as catalysts (Table 1). However, the latter can be explained by the limited solubility of the pure complex in acetonitrile, which thus inhibits comparison to homogeneous catalysis. The $[Mn(bpy)_2]^{2+}$-ABN catalyst is recyclable and stable during the first three runs, while kinetic studies show a small deceleration in the third run (Figure S12). After removal of the network by hot filtration, the conversion of styrene is slowed down to the level of the blank reaction, proving the immobilization of the metal complex in the network.

Table 1: Results of the catalytic oxidation of styrene.

Catalyst	Styrene conversion [%]	Product selectivity [%][a]		
		So	Bza	other
$[Mn(bpy)_2]^{2+}$-ABN:				
1st run	100	65	8	27
2nd run	99	81	9	10
3rd run	98	81	9	10
$[Mn(bpy)_2]^{2+}$	84	76	14	10
Mn-ABN	77	75	17	8
blank	39	71	24	5

[a] So: styrene oxide; Bza: benzaldehyde; styrene (1.14 mL, 10 mmol), CH_3CN (10 mL), isobutyraldehyde (2.28 mL, 25 mmol), catalyst (50 mg), O_2 flow rate: 200 mL min^{-1}, $T = 80$ °C, $t = 1$ h.

In conclusion, a microporous polymer network was prepared from a weakly coordinating, anionic tecton. Sonogashira coupling of a brominated tetraphenylborate with 1,3,5-triethynylbenzene yielded a microporous covalent network with high surface area. As in inorganic zeolites, the exchange of framework atoms ($Si \rightarrow Al$ vs. $C \rightarrow B$) results in an anionic charge in the network which is balanced by extra-framework cations. The latter cations can be easily exchanged, here shown by the complete exchange of Li^+ by Na^+ ions.

The resulting material consists of immobilized, weakly coordinating tetraphenylborate ions. Thus we envision these materials can be used for a wide variety of applications, for example, as ion exchangers, ion conductors, and solid superacids. We examined the anionic polymer network as a solid counterion for a catalytically active cationic species, here $[Mn(bpy)_2]^{2+}$, which was immobilized using a "ship-in-the-bottle" approach. The resulting network is a promising catalyst for the aerobic oxidation of alkenes. We envisage that with this type of immobilized catalyst, chemical reactions could be influenced by tuning the nature of the anionic network, which should be possible using different types of co-monomers. Furthermore, pore volume and pore size within this network can be tailored by simple ion exchange, such that these values can be adjusted for the adsorption and separation of gaseous compounds.

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