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A polymer analogous reaction was carried out to generate a porous polymeric network with *N*-heterocyclic carbenes (NHC) in the polymer backbone. Using a stepwise approach, first a polyimine network is formed by polymerization of the tetrafunctional amine tetrakis(4-aminophenyl)methane. This polyimine network is converted in the second step into polyimidazolium chloride and finally to a polyNHC network. Furthermore a porous Cu(II)-coordinated polyNHC network can be generated. Supercritical drying generates polymer networks with high permanent surface areas and porosities which can be applied for different catalytic reactions. The catalytic properties were demonstrated for example in the activation of CO_2 or in the deoxygenation of sulfoxides to the corresponding sulfides.

1 Introduction

N-Heterocyclic carbenes (NHCs)[1,2] have attracted tremendous interest in recent years. Especially due to their exceptional sigma donor properties, NHCs are very useful ligands for transition metal complexes and are also promising organo-catalysts.[3–5] To enable the recyclability of such complexes various studies have focused on the immobilization of NHC based catalysts.[6–10] For example, NHCs have been polymerized into dendrimers or attached on preformed solid supports[11] and recyclable, self-supported organocatalysts based on poly(NHC)s have been recently reported.[12–14] Besides the easier recyclability, immobilization of NHCs can have another advantage as NHCs are sensitive to air and moisture[15] when no bulky substituents are attached.[16] However, also the incorporation of NHCs into a polymer backbone has been reported to increase their stability.[17]

Recent studies showed that functionalized NHCs can also be applied as maintaining part of metal organic frameworks (MOFs)[18] or in polymer networks with intrinsic microporosity (PIMs).[19,20] The latter materials are prepared from rigid and contorted molecules, often called knots or tectons which are polymerized either directly or using linear linkers.[21] A large variety of functional groups and polymerization schemes have been described to enable the synthesis of such extended polymer networks with high permanent porosity.[21–30] Functionalized tetraphenylmethanes have been frequently used as tectons, yielding porous polymer networks with sometimes exceptionally high surface areas[19,31,32] For example, the reaction of tetrakis(4-aminophenyl)methane with terephthaldehyde resulted in the formation of a three-dimensional polyimine network with permanent microporosity. Noteworthy, even a periodic covalent organic framework is formed from this approach.[33] In this work a new synthesis route to form porous polymer networks based on imidazolium or NHC linkers with tetraphenylmethane knots is introduced (Fig. 1). In the first step, tetrakis(4-aminophenyl)methane (TAM) is allowed to react with glyoxal forming a polyimine network (PImin). The PImin network is subsequently transformed into a polyimidazolium chloride salt (PImCl) using chloromethyl ethyl ether for the ring closure. This ionic compound reacts with sodium tertbutanolate and copper acetate immediately to form a Cu(II)-coordinated NHC (PCu–NHC). Thus the formation of the NHC-based networks is carried out in a polymer analogous reaction rather than using a preformed NHC monomer.

2 Experimental section

Materials

Tetrakis(4-aminophenyl)methane was synthesized according to the previous reports.[33,34] Chloro-methyl ethyl ether, glyoxal (40 wt%), sodium *tert*-butanolate, copper(II) acetate, and epichlorohydrin were purchased from Sigma-Aldrich. 1,1,1,3,3,3-Hexafluoro-2-propanol (HFIP) was received from Alfa Aesar. Dry ice was prepared from bottled CO_2 (99.995%, Air

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† Electronic supplementary information (ESI) available: C, H, N elemental composition of the polymer networks. Fig. S1 and S2 according to "figure captions". See DOI: 10.1039/c2py20947k
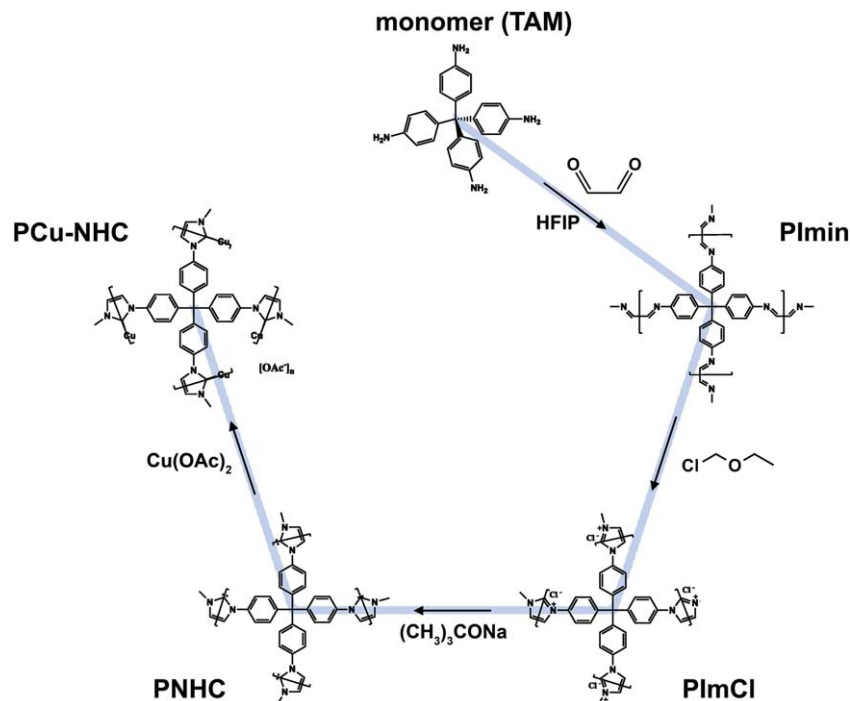
Fig. 1 Synthetic route towards polyimine, polyimidazolium chloride and NHC based networks starting from tetrakis(4-aminophenyl)methane.

Liquide), which was used as feed-gas in catalytical testing as well.

Polyoxymethylene, dry methanol (100%), toluene (98%), *n*-hexane (99%) and ethyl acetate (99%) were purchased from Sigma-Aldrich. Ethanol (99%) was purchased from Acros Organics and acetone (99%) was purchased from Fluka.

Chemicals for the catalytical testing were purchased from Sigma-Aldrich as follows: diphenylsulfoxide (96%), butylsulfoxide (96%), bis-p-chlorophenylsulfoxide (97%), methyl-(methylthio)methylsulfoxide (98%), tetramethylen sulfoxide (96%), phenyl-vinyl-sulfoxide (95%), *p*-tolyl sulfoxide (98%), and PhSiH$_3$ (97%).

Methods

Nitrogen sorption experiments and micropore analyses were performed at 77 K using a QUADROSORB SI, from Quantachrome Instruments equipped with an automated surface area and a pore analyzer. BET surface areas were determined over a 0.05–0.25 p/p_0 range.

Before analysis, samples were degassed at 120 °C for 20 h. Samples used for N$_2$ sorption measurements were rinsed in acetone and kept in the wetted state until critical point drying to prevent the pore channel collapse due to surface tension. The surface area was calculated from the multipoint BET plot and the pore volume was determined by NLDFT.

^{13}C{^{1}H} CP/MAS NMR spectra were recorded on a Bruker Avance 400 spectrometer using a 4 mm double resonance HX MAS probe operating at a ^{13}C-frequency of 100.57 MHz. The CP spectra were recorded with a cross polarization time of 2 ms and composite pulse 1H decoupling was applied during the

acquisition. The electron paramagnetic resonance experiments were performed on a solid sample. The spectra were recorded in the X-band (=9.5 GHz) on a Bruker Elexsys E 500 spectrometer at room temperature. The simulation of the spectrum was carried out with the program package WINEPR.[35]

Thermogravimetric analysis (TGA) under a nitrogen atmosphere at 10 K min^{-1} was performed on a Perkin Elmer STA 6000.

Scanning electron microscopy (SEM) was used to investigate the NHC-based network and its educts using a Philips XL 20 SEM at an accelerating voltage of 10 kV. Prior to SEM imaging, the samples were mounted on aluminium sample holders (Ø: 12 mm) with self-adhesive carbon pads followed by gold sputter coating in an argon atmosphere at 1.0×10^{-2} mbar using a Balzers SCD050 sputter coater. SEM images were recorded as Tiff-files. The Feret diameter of PImCl was measured using ImageJ on representative SEM images at 100 000× by a statistical analysis of 102 pores.

Copper species in the PCu–NHC were detected by inductively coupled plasma (ICP) on a Horiba ultima 2 spectrometer.

Quantitative analysis was conducted by GC-MS, for which an Agilent Technologies 7890A GC system running with a HP-5MS capillary column and an Agilent Technologies 5975C mass selective detector was used with a known amount of toluene as an external standard. Elemental analysis (C, N, H) was performed on a Vario Micro setup.

Synthesis

(a) **Synthesis of the polyimine (PImin).** Initial tests with varied amounts of the two monomers and the solvent were

carried out until homogenous and complete gelation of the mixtures was observed, thus finally yielding the procedure described in the following. Tetrakis(4-aminophenyl)methane (1.4 g, 3.68 mmol) was dissolved in 5 mL (47.49 mmol) of 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), resulting in a clear, red solution to which 40 wt% glyoxal (1 mL, 19.64 mmol) was added. Immediately the colour of the mixture changed from red to dark brown-red and the mixture was directly transferred to a PTFE vessel after 15 s. Approximately 20 s later a gel formed spontaneously.

The HFIP-based gel inside the polytetrafluoroethylene (PTFE) vessel was transferred to a stainless steel autoclave (Berghof, Germany) with a heating jacket. The autoclave was completely filled with dry ice (approximately 300 g) and was closed pressure tight. The autoclave was heated to 65 °C internal temperature resulting in a pressure of approximately 180 bar. The temperature and pressure were kept constant for 5 h, subjecting the gel to supercritical carbon dioxide. Subsequently, the pressure was reduced *via* a double valve system to ambient pressure in 60 s. This process removes the solvent by dilution, while conventional supercritical drying is performed under a constant flow, which gives an increased efficacy of solvent removal. The PTFE vessel with the supercritical dried specimen was transferred to a desiccator filled with dry poly(oxymethylene) and was fumigated for 8 h followed by vacuum heating (1 mbar, 80 °C) for 5 hours (yield: 1.51 g, 97%).

(b)   Synthesis of imidazolium chloride polymer (PImCl). To 1 g of the imine polymer an excess of chloromethyl ethyl ether (1 mL, 0.01 mol) was added under a nitrogen atmosphere. During addition the suspension changed its colour from yellow to dark brown. After 48 hours the resulting product was washed with acetone. Samples were supercritical point dried according to the procedure described for the polyimine (yield: 1.19 g, 97%).

(c)   Synthesis of NHC polymer (PNHC). 1.1 g of the PImCl polymer was added to a solution of 0.2 g (2.08 mmol) of sodium *tert*-butanolate in 5 mL of dry methanol. The resulting mixture was stirred for 24 hours and the crude product was washed with 5 mL of ethanol and two times with 5 mL of acetone. The resulting powder was supercritical point dried according to the procedure described for polyimine (yield: 0.93 g, 98%).

(d)   Synthesis of the copper coordinated NHC polymer (PCu–NHC). The polyimidazolium chloride network (0.5 g) was treated with an excess of 0.09 g (0.936 mmol) sodium *tert*-butanolate and an excess of copper(II) acetate (0.2 g, 1.10 mmol) in 5 mL of dry methanol. The mixture was stirred for 48 hours and the obtained product was washed with dried 5 mL of ethanol and 5 mL of acetone. Samples were supercritical point dried according to the procedure described for polyimine (yield: 0.53 g, 96%).

Catalytical testing

(a)   CO$_2$ cycloaddition. The reactor setup consisted of a 100 mL stainless steel Berghof BR-100 high pressure reactor with simple heating and stirring using a laboratory heating plate with a heater block. The reactor was fitted with a PTFE insert, a pressure indicator, a temperature probe submersion tube to measure the internal reactor temperature, a pressure relief valve and a metal rupture disc to safely limit the maximum pressure. In a typical reaction, 100 mg of catalyst and 18 mmol of epichlorohydrin were charged in a 100 mL PTFE insert. The reactor was sealed and flushed 5 times at room temperature with CO$_2$ to remove the air from the vessel. The pressure was adjusted to 6.9 bar and the reactor was heated to 130 °C. After 4 hours of reaction time, the reactor was cooled down to room temperature and the pressure was released. The collected sample was centrifuged, filtered and analysed by GC-MS with toluene as the internal standard (RT = 1.45 min).

(b)   Deoxygenation of sulfoxides. A centrifuge tube was charged with PCu–NHC (5 mol%), *p*-tolyl sulfoxide (1 mmol) and PhSiH$_3$ (1 mmol). According to the addition of toluene (3.0 mL) the mixture was stirred in an oil bath at 100 °C for 24 h. After the completion of the reaction, the catalyst was separated by centrifugation and the solution was diluted with dichloromethane and an aliquot was taken for GC-analysis (30 m Rxi-5 ms column, 40–300 °C). The solvent was removed and the residue was purified by column chromatography.

Di(*p*-methylphenyl)sulfide: R_f = 0.79 (*n*-hexane : ethyl acetate 1 : 5); ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.06–7.22 ppm (m, 8H), 2.30 (s, 6H, CH$_3$); ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 137.1, 132.8, 131.3, 130.1, 21.3 ppm; MS (ESI) *m/z* = 214 (100, M+), 199 (34), 184 (20), 105 (18), 91 (33), 65 (19).

Diphenylsulfide: R_f = 0.75 (*n*-hexane : ethyl acetate 1 : 5); ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.26–7.47 ppm (m, 10H); ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 135.8, 131.0, 129.2, 127.0 ppm; MS (ESI) *m/z* = 186 (100, M+), 152 (11), 92 (19), 77 (27), 65 (20), 51 (43).

Dibutylsulfide: ^{1}H NMR (CDCl$_3$, 100 MHz) δ = 2.28 (t, 4H, J = 7.20 Hz, S(CH$_2$CH$_2$CH$_2$CH$_3$)$_2$), 1.14–1,49 (m, 8H, S(CH$_2$CH$_2$CH$_2$CH$_3$)$_2$), 0.75 ppm (t, 6H, J = 7.20 Hz, CH$_3$); ^{13}C NMR (CDCl$_3$, 50 MHz) δ = 32.1, 32.0, 22.3, 13.8 ppm; MS (ESI) *m/z* = 146 (40, M+), 103 (15), 90 (31), 61 (97), 56 (100).

Di(*p*-chlorophenyl)sulfide: R_f = 0.67 (*n*-hexane : ethyl acetate 1 : 10); ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 7.23–7.33 ppm (m, 8H); ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 133.9, 133.4, 132.3, 129.4 ppm; MS (ESI) *m/z* = 254 (M+, not detected), 219 (33), 184 (100), 139 (11), 108 (29), 91 (18), 75 (24).

2,4-Dithiapentane: MS (ESI) *m/z* = 110 (14, M+), 108 (99), 61 (100).

Tetrahydrothiophene: ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 2.42–2.55 (m, 4H), 1.36–1.48 ppm (m, 4H); ^{13}C NMR (CDCl$_3$, 50 MHz): δ = 32.1, 32.0 ppm; MS (ESI) *m/z* = 87 (13, M+), 59(49), 43 (100).

3   Results and discussion

The present study describes a novel synthetic route towards the synthesis of NHC-containing porous organic networks. In a first step tetrakis(4-aminophenyl)methane was polymerized with glyoxal to form an imine polymer. A key element of this synthesis was to identify a suitable solvent for the monomer and the initial products of the growing polymer network, which should additionally exhibit acidic properties and strong hydrogen bonding capability to enable high degrees of polymerization. It was frequently suggested that high conversion

during the polymerization reaction is crucial to allow high permanent porosities within the resulting polymer network.[36] Hexafluoro-2-propanol (HFIP) combines all the required properties. Furthermore in contrast to the usually used solvents like DMF or DMSO, HFIP exhibits a much lower boiling point. Another essential processing step is the removal of organic solvents from the polymer network. In this regard, a well-developed method is the supercritical drying with CO_2, especially for the removal of certain organic solvents (e.g. acetone and ethanol). Furthermore porous polymer foams or aerogels can be obtained via supercritical drying.[37,38] Therefore, prior to any analytical measurement, supercritical drying with carbon dioxide was performed to remove organic solvents and generate porosity. High porosities were for example reported for supercritical dried conducting polymers showing specific surface areas of 170–370 m^2 g^{-1}.[39]

The successful formation of the imine network was followed by solid state NMR measurements. The $^{13}C\{^1H\}$ CP/MAS NMR spectrum (Fig. 2) of the polyimine network showed resonances (142 ppm, 131 ppm, 115 ppm, 60 ppm), which can be assigned to the tetraphenylmethane knot (δ = 146 ppm, 136 ppm, 131 ppm, 64 ppm).[31] The C=N carbon of the imine functionality can be assigned to the signal in the range of 150–160 ppm.[40]

In a second step the polyimine network was transformed into the imidazolium chloride using chloromethyl ethyl ether for providing a C1 unit for the ring-closure. The $^{13}C\{^1H\}$ CP/MAS NMR spectrum of PImCl shows again the expected signals of the tetraphenylmethane knot, however no resonances for the imine

carbons can be observed, while a new broad signal appeared at 122–128 ppm, which can be assigned to the C4 and C5 carbons in the imidazolium-ring. The resonances for the C2 carbon in imidazolium salts are in the range of 130–140 ppm, thus exactly in the range of the TAM moiety and therefore cannot be clearly identified in these spectra (see ESI, Fig. S1(b)† PImCl).[41] Deprotonation of PImCl should yield the free PNHC based network, which was carried out using sodium tert-butanolate. For the resulting NHC network again the signals of the tetraphenylmethane knot were observed. However, no clear proof of the formation of the pure NHC can be given at this point as the signals of the carbon within the NHC ring can be assigned again at 126 ppm, while the carbene carbon within this ring should show a significant shift towards the lower field. Even so a relatively weak additional peak can be observed at a low field, i.e. 228 ppm; this is not much more pronounced than for the PImCl network (see ESI, Fig. S1(b)† PNHC). It should be however noted that absorbed water and gas molecules might aggravate the designation of the highly active carbene carbon in the NHC.

The formation of the PCu–NHC was conducted by the reaction of the PImCl network with sodium tert-butanolate and afterwards with copper(II) acetate. The successful incorporation of Cu into the network was proven via ICP measurements, showing an amount of 2.9 wt%, which indicates a Cu coordination to nearly every second NHC unit.

Elemental analysis shows the expected elemental composition for all the networks (Table S1†), even though PImCl and PNHC show a slightly lesser amount of carbon and nitrogen than theoretically predicted, which however has been frequently observed for highly condensed, aromatic networks. In contrast, the amount of carbon and nitrogen measured for the PCuNHC exhibited slightly increased values to the calculated, completely Cu-coordinated NHC-network, which again shows that not every NHC unit is coordinated with copper.

SEM measurements reveal a foam-like structure for the polyimine network (Fig. 3a), while each subsequent processing step yields more compact structures. PImCl (Fig. 3b) shows a particulate structure at lower magnifications while at higher magnifications macro/mesopores with an average pore
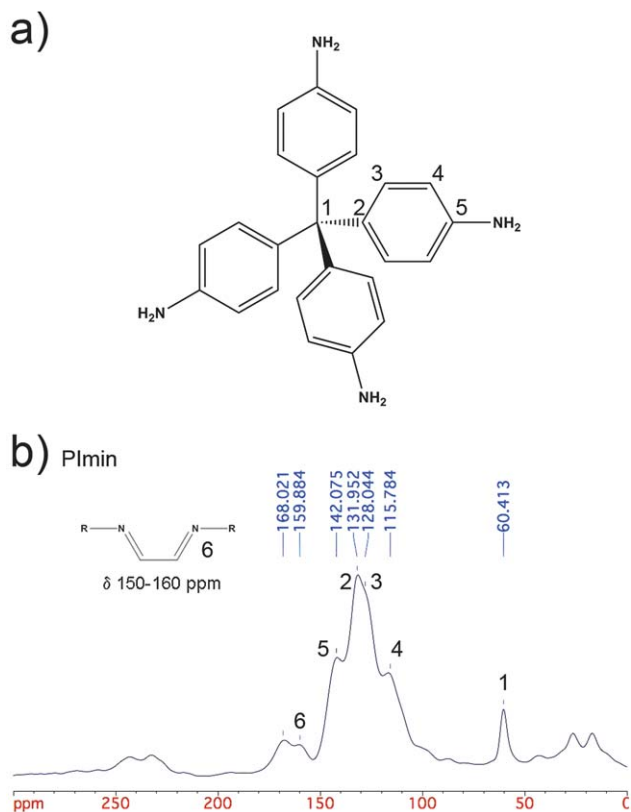

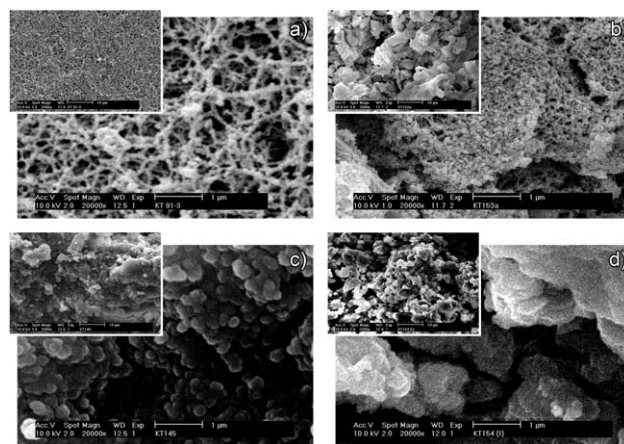**Fig. 2** PImin structure (a) and the related $^{13}C\{^1H\}$ CP/MAS NMR spectrum (b).

Fig. 3 SEM images of (a) PImin, (b) PImCl, (c) PNHC and (d) PCu–NHC.

diameter of ~50 nm are observed. For PNHC and PCu–NHC no larger pores can be seen.

After supercritical drying the imine network features a high surface area of 608 $m^2 g^{-1}$ and a pore volume of 1.2 $cm^3 g^{-1}$ as determined by N_2 sorption measurements at 77 K using a QUADROSORB SI from Quantachrome Instruments equipped with an automated surface area and a pore analyzer. The apparent BET surface areas were determined by applying the Brunauer–Emmett–Teller (BET) method in the relative pressure range of 0.05–0.25. Pore volumes were derived from the adsorption branches of the isotherms using the non-local density functional theory (NL-DFT) pore model for carbon with slit/cylindrical pore geometry. Prior to analysis, samples were degassed at 120 °C for 20 h.

With each reaction step the accessible surface area is continuously reduced (Fig. 4, Table 1).

In principle this can be expected for this polymer analogous reaction as in every reaction step, besides the reaction of the imidazolium salt to the NHC network, the molecular weight of the repeating unit is increased, naturally influencing the apparent gravimetric surface area and pore volume. Furthermore, any additional reaction step, by applying again solvents and elevated temperature, allows the networks conformational changes to finally pack more efficiently. On the other hand, the formation of imidazolium and NHC rings stiffens the overall polymer network, which can yield lower flexibility and thus work against the dense packing of the polymer network. In principle these effects can be distinguished by comparing the surface area derived from the supercritical drying, *i.e.* mainly the external or macropore surface area, with the surface area derived from micropores, *i.e.* the intrinsic microporosity. Another explanation for the continuously reduced surface area might be dynamic reorientation processes, which could result in the opening or closing of the imine bonds. Nevertheless, we have no indication from our solid-state NMR data hinting at this effect. A comparison of these values is shown in Table 1. A lower contribution of micropores to the surface area of PImCl and PNHC can be observed from the nitrogen sorption measurements and thus it can be reasoned that the surface area of the polymers is mainly generated from the supercritical drying process.

EPR spectroscopy was carried out to confirm the coordination of Cu to the NHC in PCu–NHC. Fig. 5 shows the X-band EPR spectrum of a solid sample of PCu–NHC recorded at 295 K together with a simulation using the experimental parameters.

The spectrum is of axial symmetry. In the parallel part, the hyperfine structure of the interaction of the unpaired electron with the nuclear spin of the copper center (Cu d^9: $S = 1/2$; ^{63}Cu: $I = 3/2$ and ^{65}Cu: $I = 3/2$) is partly resolved and some parameters can be determined ($g_\parallel$, $g_\perp$, $A_\parallel$, $A_\perp$ can only be estimated, see below). The perpendicular part is not resolved yet. Due to the relatively broad lines, no super hyperfine structure of possible donor atoms (*e.g.* ^{14}N: $I = 1$) can be detected, which proves the expected coordination sphere. The partly resolved
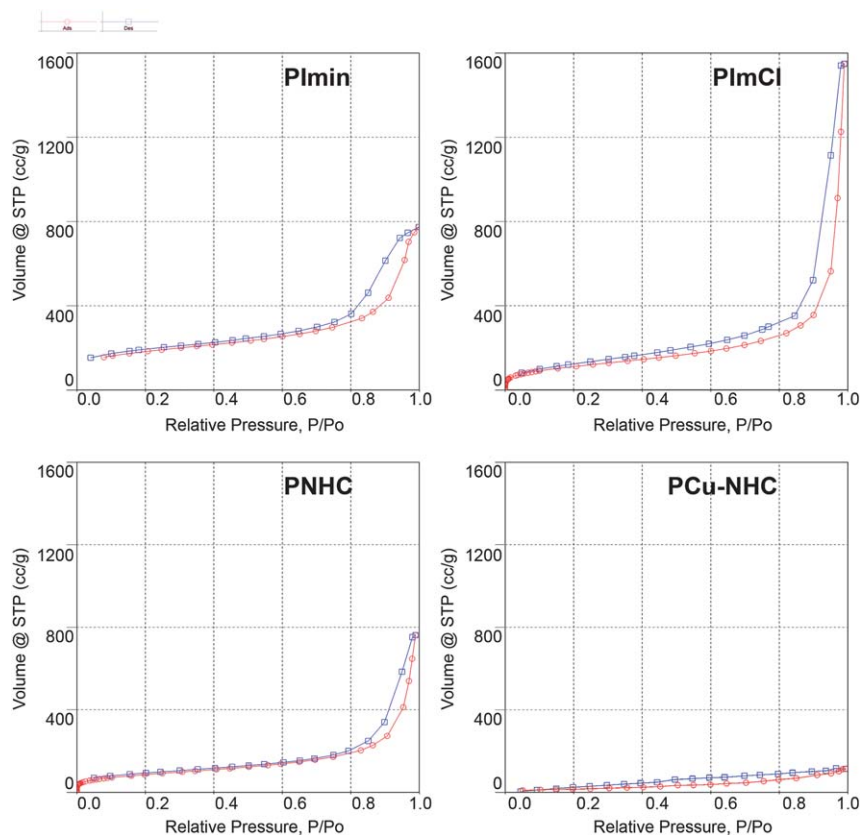

Fig. 4 N_2 sorption isotherms of PImin, PImCl, NHC-TAM and PCu–NHC network.

Table 1 Surface area and pore volume data of polymerized networks determined by nitrogen sorption measurements at 77 K

Entry	Network	S_{BET}^{a} (m² g⁻¹)	V_{total}^{b} (cm³ g⁻¹)	$S_{BET,micro}^{c}$ (m² g⁻¹)	V_{micro}^{d} (cm³ g⁻¹)
(i)	PImin	608	1.20	240	0.124
(ii)	PImCl	409	2.40	30	0.007
(iii)	PNHC	311	1.18	44	0.017
(iv)	PCu–NHC	62	0.18	0	0

^{a} Apparent BET surface area determined in the 0.05–0.25 p/p_0 range. ^{b} Total pore volume determined by NL-DFT. ^{c} Cumulative surface area for pores sizes below 2 nm as determined by NL-DFT. ^{d} Cumulative pore volume for pores sizes below 2 nm as determined by NL-DFT.
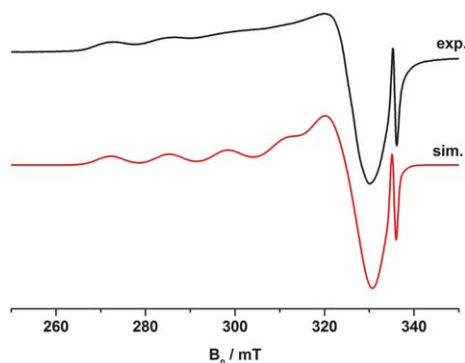
Fig. 5 X-band EPR spectrum of a solid sample of PCu–NHC recorded at 295 K together with a simulation using the experimental parameters.

EPR pattern of the polymer copper sample indicates that the copper centres are well dispersed in the polymer. The resulting experimental parameters of the Cu-tensor main axes are: $g_{\parallel} = 2.302^{\pm0.005}$, $g_{\perp} = 2.060^{\pm0.005}$ and the coupling constants $A_{\parallel} = 140^{\pm3} \times 10^{-4}$ cm⁻¹, $A_{\perp} \sim 30^{\pm5} \times 10^{-4}$ cm⁻¹. The parameters are characteristic for square planar Cu(ɪɪ) compounds and no copper dimers are present in the sample. In the spectrum an

additional, not structured signal appears at ~335 mT ($g = 2.001 \pm 0.002$) which can be attributed to traces of an organic radical, not surprising for such an extended system with several aromatic units. This radical may be easily generated during the synthesis.

Imidazol-2-ylidenes are the most often studied and applied NHCs in homogeneous catalysis. The incorporation of NHCs into highly porous networks enables the immobilization of these compounds, which can be further used as ligands or organocatalysts. Consequently, initial investigation was performed to elucidate the catalytic performance of the described materials. Interestingly, NHCs can activate CO_2 and form imidazolium carboxylates, which allow further reactions with various organic compounds.[42–44] In this regard, NHCs proved to be effective catalysts for the reaction of CO_2 with epoxides to produce cyclic carbonates.[45–49] Furthermore, imidazolium compounds have been frequently used to activate CO_2.[20,50] Our current research deals with imidazolium based ionic liquids immobilized on silica surfaces which are used for the conversion of CO_2 to synthesis cyclic carbonates with high catalytic activity and selectivity.[51]

Accordingly the networks PImCl and PNHC were tested for such transformations, namely the synthesis of chloropropene carbonate derived from epichlorohydrin and CO_2 via GC-MS. Representative chromatograms obtained after the cycloaddition of CO_2 over PImCl with epichlorohydrin (see ESI, Fig. S2(a)† PImCl) and PNHC (see ESI, Fig. S2(b)† PNHC). The respective retention times were: toluene RT = 1.45 min, chloropropene carbonate RT = 2.90 min, no starting epoxide can be detected RT = 1.30 min.

PImCl shows high conversion and selectivity for this reaction. At an elevated temperature and pressure 100% conversion of the epichlorhydrin was achieved within 4 h, accompanied by selectivity towards the cyclic carbonate of 85.5 wt%. The activation of PImCl by deprotonation to form PNHC even increases the selectivity to the desired product. The stability of the catalyst could also be proven as further recycling steps showed no decrease in activity (Table 2).

Table 2 Results of catalytic experiments with the networks PNHC (104 mg), PImCl (103 mg), epichlorohydrin (18 mmol), CO_2 (6.9 bar)

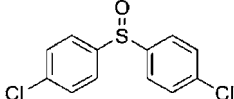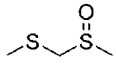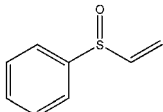| Catalyst	Cycle no.	Conversion (%)	Yield (%)
PImCl	—	100.0	85.5
PNHC	1	100.0	94.3
PNHC	2	100.0	95.4
PNHC	3	100.0	95.2
PNHC	4	100.0	94.5
PNHC	5	98.9	92.0
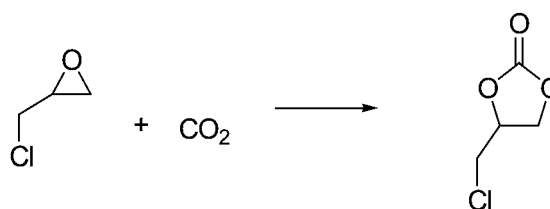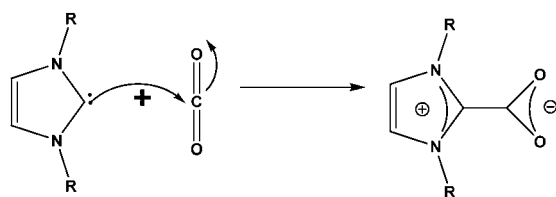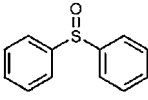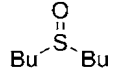
Table 3 Results for the deoxygenation of *p*-tolyl sulfoxide with phenylsilane and PCu–NHC as pre-catalyst

Cycle no.	Conversion (%)	Yield (%)
1	>99	>99
2	>99	>99
3	>99	>99
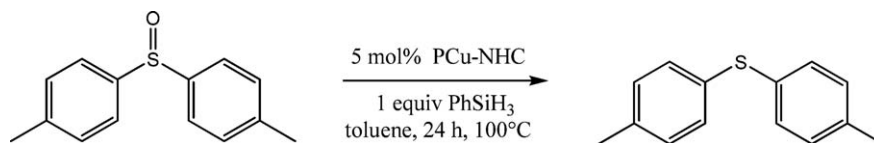
Table 4 Scope and limitations of the Cu-coordinated network (PCu–NHC) in the reduction of sulfoxides [PCu–NHC (5 mol%) and PhSiH₃ (1.0 mmol), sulfoxides (1.0 mmol), toluene (2.0 mL) at 100 °C for 24 h]

Catalysis	Substrate (mg)	Selectivity (%)	Conversion/Yield (%)
1	Diphenylsulfoxide 202.27	>99	48
2	Butylsulfoxide 162.30	>99	>99
3	Bischlorophenylsulfoxide 272.17	>99	88
4	Methyl(methylthio)methylsulfoxide 124.22	>99	92
5	Tetramethylensulfoxide 104.17	>99	>99
6	Phenyl-vinyl-sulfoxide 152.21	>99	11

In addition, the potential of the Cu-coordinated network (PCu–NHC) was explored in the deoxygenation of organic sulfoxides to produce the corresponding sulfides.[52–54] Recently, the copper-catalyzed deoxygenation of sulfoxides applying hydrosilanes as reductant has been demonstrated.[55,56] As pre-catalysts Cu(acac)₂ has been proven to obtain the desired products in excellent yields and selectivities.[55] However, the application of copper salts as pre-catalysts allows not for an easy separation and in consequence not for a recycling of the catalyst. In this regard the utilization of the Cu-coordinated network (PCu–NHC) can be a recyclable alternative. In accordance to a recently reported protocol *p*-tolyl sulfoxide and phenylsilane were reacted in the presence of catalytic amounts of the Cu-coordinated network (PCu–NHC). After 24 hours at 100 °C an excellent performance was observed, with a yield and a selectivity of >99% (Table 3). In contrast, in the absence of the catalyst no product formation was observed. Noteworthy, during the reaction the material was insoluble in the reaction media, hence after the reaction was complete the mixture was cooled to room temperature and the material was filtered and washed with toluene. After drying in a vacuum the material was subjected again to catalysis revealing excellent yields and selectivities.

Once suitable reaction conditions were established, the scope and limitations of the heterogeneous copper-catalyzed deoxygenation of various sulfoxides, including aromatic and aliphatic sulfoxides, using phenylsilane as reducing reagent were examined (Table 4). Excellent yields (>99%) were achieved in the deoxygenation of substituted dialkyl sulfoxides after 24 h at 100 °C (Table 4, entries 2, 4 and 5), whereas diaryl sulfides were accessed in good to moderate yields (Table 4, entries 1 and 3). The low yield for the reaction with phenyl-vinyl-sulfoxide is mainly due to electronic effects and its structure.

4 Conclusion

In summary, a novel route for the formation of porous polymer networks including imidazolium and NHC moieties in the backbone by a polymer analogous reaction from a polyimine network is presented. All networks (PImin, PImCl, PNHC) feature high surface areas, which mostly result from the supercritical drying of polymer networks. The coordination of

metal ions, here copper, on the NHC network could be confirmed by EPR-spectroscopy.

PImCl and PNHC show high activity as metal-free catalysts for the reaction of CO_2 with epoxides to cyclic carbonates, while PCu–NHC is a very active catalyst for the deoxygenation of sulfoxides.

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