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LETTER

Click chemistry produces hyper-cross-linked polymers with tetrahedral cores†

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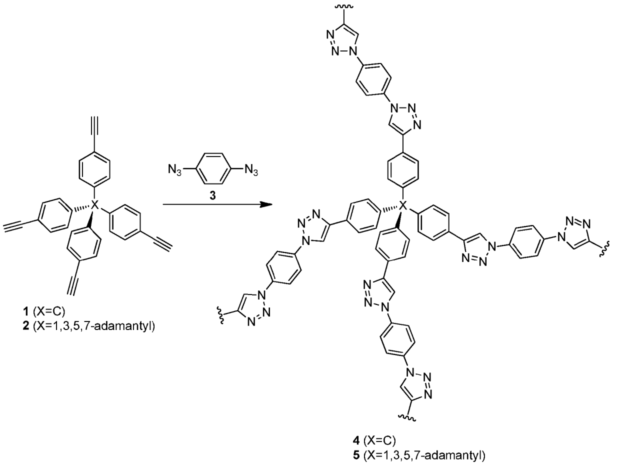
Methane and adamantane based hyper-cross-linked polymers have been prepared by click chemistry reacting the corresponding tetraalkynes with 1,4-diazidobenzene. The adamantane based HCP proved to be very efficient for CO_2 capture at low pressures.

Recently, several ***H****yper-****C****ross-linked* ***P****olymers* (*HCPs*) and ***P****olymers of* ***I****ntrinsic* ***M****icroporosity* (*PIMs*) based on precisely defined rigid three-dimensional monomers have been reported.[1,2] These novel materials exhibit a variety of remarkable properties that derive from their high surface areas, ranging from adsorption and selective capture of gases to catalysis and chemical sensing. Further advantages of applicative value comprise high mechanical strength, thermal stability and resistance to water, air and chemical agents. Especially tetrakisphenylmethane and -adamantane derivatives are appealing as monomers, because they assemble during self- or co-condensation into well-defined and predictable three-dimensional networks. Yaghi had pioneered the field of crystalline networks, so-called ***C****ovalent* ***O****rganic* ***F****rameworks* (*COFs*), by connecting tetrahedral methane cores through reversible boronate ester[3] or imine[4] formation. Kuhn and Antonietti *et al.* developed a reversible triazine formation under ionothermal conditions in molten zinc chloride to obtain an amorphous adamantane based polymer.[5] Wang *et al.* reported methane core based polymers connected by cyanate esters or polyimides with very narrow pore size distributions of 4–6 Å[6] and 4–8 Å,[7] respectively. More recently, we[8] and others[9] have used irreversible organo-metallic cross-coupling reactions to obtain the corresponding tetrakisphenylmethane and -adamantane based polymers. Using the more rigid spirobifluorene monomer, Weber and Thomas generated the corresponding PIMs.[10]

A primary aim is the generation of molecular building blocks[11] and their efficient coupling into supramolecular assemblies[12] and networks.[8,13] Here we report the synthesis and characterization of novel triazole-linked HCPs obtained by copper catalyzed Huisgen 1,3-dipolar cycloaddition—the so-called click reaction[14]—of tetraphenylalkynyl methane and adamantane derivatives **1** and **2** with 1,4-diazidobenzene (**3**)—**Caution**: 1,4-diazidobenzene is potentially explosive—(Scheme 1). Although the click reaction is known as a high-yielding reaction of mild conditions with a broad functional group tolerance, it has not yet been much explored to generate conjugated polymers,[15] and only two HCPs have been reported by Cooper[9b] and Nguyen *et al.*[16] respectively.

Our recently optimized reaction conditions for the fourfold click reaction on tetraphenylalkynyl and -azido methane and



Scheme 1 Synthesis of HCPs **4** and **5**. *Reagents and conditions*: $CuSO_4 \cdot 5H_2O$, sodium ascorbate. For the methane core **1**: *t*-BuOH/H_2O (1 : 1), 60 °C, 3 days, 48–76%; for the adamantane core **2**: DMSO/H_2O (20 : 1), 80 °C, 3 days, quant.

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adamantane derivatives[11c]—$CuSO_4 \cdot 5H_2O$ and sodium ascorbate, in *t*-BuOH/H_2O (1 : 1) for the methane core, and in DMSO/H_2O (20 : 1) for the adamantane core—were adapted to the synthesis of click-HCPs. We first tried to react tetrapodal alkyne and azide cores. Our aqueous reaction conditions failed, however, to deliver the corresponding HCP. Even after reaction times of several days and elevated temperatures (up to 100 °C), only the unreacted starting material was recovered (results not shown).

Nevertheless, click-HCPs could be obtained by co-condensation of tetrapodal cores with linear cross-linkers. HCPs **4** and **5** were prepared by reacting tetraphenylalkynyl methane or adamantane derivatives **1** and **2** with 1,4-diazidobenzene (**3**) (Scheme 1). As already observed for discrete molecular fourfold click products,[11c] best results in the methane series were obtained using an exact stoichiometry of tetraalkyne **1** to diazide **3** of 1 : 2, whereas in the adamantane series mostly in scale-up an excess of diazide **3** was used (up to 1 : 6). Reacting the corresponding methane and adamantane tetraazides with 1,4-diethynylbenzene also resulted in click-HCPs. This strategy appeared to be less effective, however, as the yields were generally lower and the homogeneity of the formed materials was inferior compared to **4** and **5** (data not shown). We thus focused on the reactions depicted in Scheme 1. Upon scale-up, adamantane based HCP **5** was still obtained in excellent yield, whereas methane based HCP **4** was obtained only in moderate amounts using a large excess of copper and ascorbate (see ESI† for details).

The resulting networks **4** and **5** were characterized by IR spectroscopy, solid-state ^{13}C NMR CP/MAS, differential scanning calorimetry (DSC), and gas adsorption. The corresponding discrete molecules **6** and **7**—obtained in high purity from the tetrafunctional molecules and monofunctional 1-azidobenzene,[11c] and bearing the same structural triazole motifs as HCPs **4** and **5**—served as reference compounds for most analytical measurements (Fig. 1).

FT-infrared spectra of all compounds, **1–7**, were recorded (Fig. 2 and 3). The presence or absence of characteristic vibration bands of alkyne and azide groups provides insight into the efficiency of the hyper-cross-linked polymerization reaction. For both HCPs **4** and **5**, residual azide vibration bands at ~2100 cm^{-1} and very weak alkyne vibration bands at ~3300 cm^{-1} are still observed. No isolated vibration bands can be attributed to the characteristic bands of the triazole moiety, thus it was not possible to establish the conversion to the product at this stage.

Solid-state ^{13}C NMR CP/MAS was performed on HCPs **4** and **5** (Fig. 4) and discrete compound **6** (see ESI†). The spectra

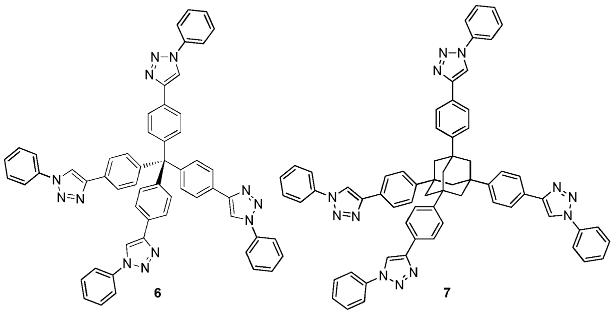
6 **7**

Fig. 1 Reference compounds **6** and **7**.[11c]

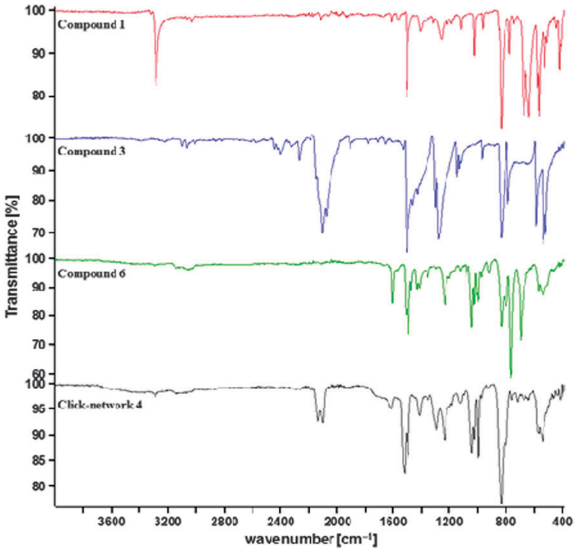

Fig. 2 FT-infrared spectra of compounds **1**, **3**, **6**, and HCP **4**.

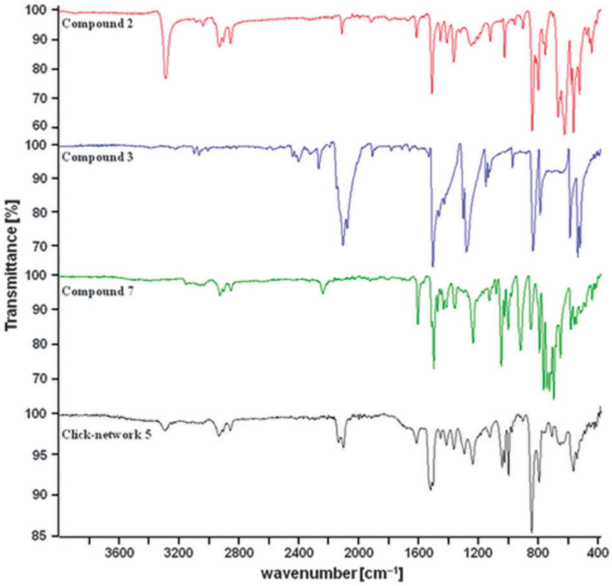

Fig. 3 FT-infrared spectra of compounds **2**, **3**, **7**, and HCP **5**.

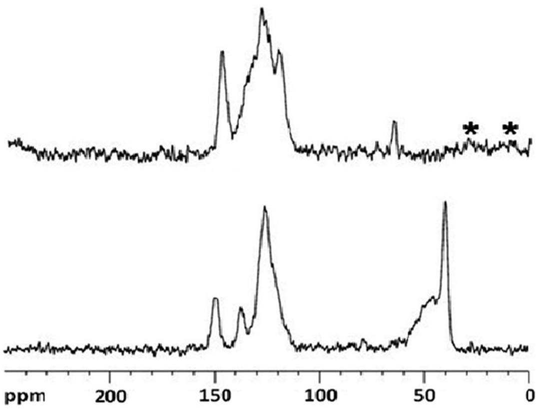

Fig. 4 Solid-state ^{13}C NMR CP/MAS spectra of HCP **4** (upper) and HCP **5** (lower). Spinning side bands are marked with asterisks.

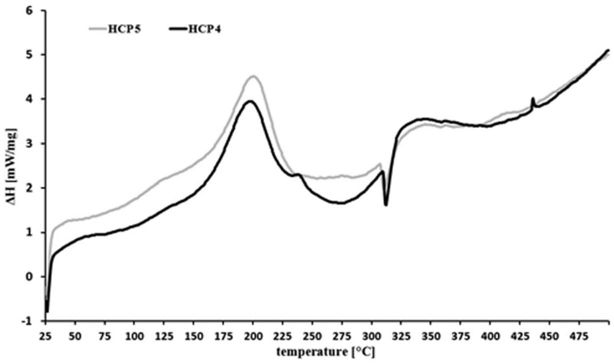

Fig. 5 DSC curves of the HCPs **4** (black curve) and **5** (grey curve).

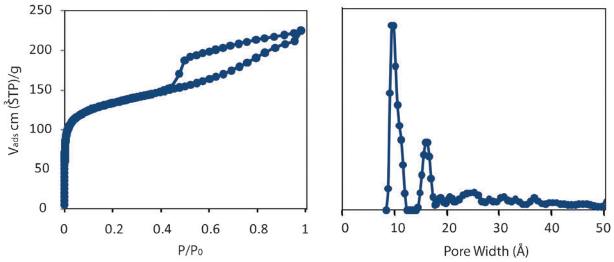

Fig. 6 N_2 adsorption isotherm of the HCP **5** compound at 77 K (left) and pore size distribution as determined by non-linear density functional theory (right).

of **4** and **5** show essentially no traces of residual alkyne groups, as there are no peaks in the range of 75 to 95 ppm. Any residual amount of unreacted alkyne groups seems to be below the detection threshold, suggesting a high conversion of tetraalkyne monomers **1** and **2**.

This interpretation is supported by the pronounced peak at ~150 ppm, which can be assigned to the C4-triazole carbon. This signal is also observed for the discrete compound in the solid (see ESI†) and solution ^{13}C NMR,[11c] indicating that the expected click reaction did take place. The linewidths in the solid-state ^{13}C NMR spectra of HCPs **4** and **5** indicate that the carbon atoms have a heterogeneous surrounding. The rather broad signals were indeed expected, as the click reaction is kinetically controlled and irreversible under our reaction conditions, thereby leading to an amorphous material. X-Ray powder diffraction confirmed the amorphous state of HCPs **4** and **5** (data not shown).

Differential scanning calorimetry (DSC) measurements were performed on HCPs **4** and **5** (Fig. 5) and reference compounds **6** and **7** (see ESI†). The DSC curves indicate that unreacted alkyne groups (shoulder at 245 °C) are present in HCP **4** in barely detectable amounts, while unreacted azide moieties (intense peak at 200 °C) are present in both HCPs **4** and **5**. The characteristic broad peak in the range of 350 °C appears to be caused by decomposition of the triazole rings. The assignment of peaks to the corresponding unreacted functional groups was based on a comparison with the curves of the starting materials **1** and **2** and the reference compounds **6** and **7** (see ESI†). All these observations are in good agreement with the results obtained by other characterization methods.

Furthermore, the porosity of the materials has been explored by adsorption measurements of N_2 and CO_2. An adsorption isotherm of N_2 at 77 K for HCP **5** shows a profile with a prevailing type I component, followed, in the higher pressure range, by a type-IV like contour (Fig. 6, left). The former is indicative of an extensive microporosity, while the latter suggests the presence of pores larger than 2 nm. A similar profile has also been observed in hyper-cross-linked polymers of different chemical constitution.[9b] The surface area was calculated to be 493.62 $m^2\ g^{-1}$ by the BET method and 585.56 $m^2\ g^{-1}$ by the Langmuir model.[17] The pore size distribution was determined by nonlocal density functional theory and presents two sharp peaks at 0.95 and 1.6 nm followed by minor peaks in the mesopore region (Fig. 6, right). The presence of pores as large as 8–10 nm (not shown) is likely due to interparticle cavities generated by the aggregation of the nanoparticles. The total pore volume capacity amounts to 0.27 $cm^3\ g^{-1}$ and the large hysteresis in the desorption curve confirms the presence of a mesoporous character of the material.

CO_2 adsorption isotherms have been performed at variable temperatures and up to 5 atm (Fig. 7). The adsorption isotherm, recorded at 195 K, exhibits a steep slope at low CO_2 pressures and reaches the absorption value of 155 mg g^{-1} at relative p/p0 pressures of 0.97.

The profile was identified as a Langmuir function that reaches 90% of the pore filling even at the relative pressure as low as 0.2 (Fig. 7). The Langmuir profile is ascribed to the micropores whilst the larger pores might contribute with a minor amount to the CO_2 absorption value at higher p/p_0 values.[18] A similar behavior was also observed for the CO_2 isotherm at room temperature and measured up to 5 atm. From the comparison of the adsorption values at variable temperatures performed at low coverage we calculated, by

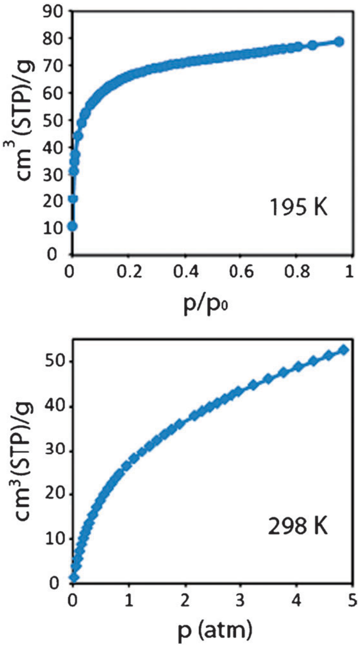

Fig. 7 CO_2 adsorption isotherm of the HCP **5** at 195 K showing a Langmuir profile (upper) and CO_2 adsorption isotherm at 298 K and up to 5 atm. (lower).

applying Clausius–Clapeyron equation, the isosteric heat of adsorption of 28.5 kJ mol^{-1}. The initial steep increase of the CO_2 uptake combined with the relatively high adsorption energy led to the conclusion that the micropores are very efficient for the capture of CO_2 at low pressures.

In conclusion, we have reported preliminary results on the formation of novel hyper cross-linked polymers by exploiting the unconventional synthetic route based on click chemistry. As polyfunctional building elements, tetrahedral-core monomers have been employed, comprising tetrakisphenylmethane and an alternative node of T_d symmetry such as adamantane. This knot combined with the rigidity of *p*-phenylene spacers guarantees the robustness of the network. The adamantane-based compound shows remarkable efficiency for CO_2 capture under the mild conditions of low pressure or, alternatively, of room temperature.

Conceivably, the optimization of the process with the new substrates is expected to provide ameliorated properties and permits us to envisage the scale-up at least for the adamantane derivative. Indeed, further studies to implement HCP production, a better control of particle size formation, enhanced surface areas and anchorage of functional groups are under investigation.

Experimental section

SAFETY STATEMENT: 1,4-diazidobenzene is potentially explosive. Due to high nitrogen content (ratio of carbon to nitrogen should be larger than 3 : 1) it should be handled with extraordinary care. All reactions and handlings were performed behind a blast shield in a closed fume hood.

^1H NMR spectra were recorded on a Bruker AM 400 (400 MHz) spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS, $\delta = 0$) and are referenced to $CHCl_3$ (7.26 ppm), as internal standard. All coupling constants are absolute values and J values are expressed in Hertz (Hz). The description of signals include: s = singlet, bs = broad singlet, d = doublet, m = multiplet, dd = doublet of doublets. The spectra were analyzed according to first order. ^{13}C NMR spectra were recorded on a Bruker AM 400 (100 MHz) spectrometer as solutions in $CDCl_3$. Chemical shifts are expressed in parts per million (ppm, δ) downfield from tetramethylsilane (TMS, $\delta = 0$) and are referenced to $CDCl_3$ (77.4 ppm).

Synthesis of hyper cross-linked polymer 5 (HCP 5)

Typical procedure. In a sealed reaction vessel, 1,3,5,7-tetrakis(4-ethynylphenyl)adamantane (**2**, 35 mg, 0.065 mmol, 1.00 equiv.) was solved in 5 mL DMSO under an argon atmosphere at 100 °C. Then, $CuSO_4{\cdot}5H_2O$ (4.75 mg, 0.019 mmol, 0.20 equiv.), sodium ascorbate (7.50 mg, 0.038 mmol, 0.40 equiv.), both dissolved in 0.25 mL H_2O (total), and 1,4-diazidobenzene (**3**, 21 mg, 0.13 mmol, 2.00 equiv.) were added slowly. The reaction mixture was heated for 72 h at 80 °C. The precipitate was filtered off and extensively washed with chloroform and water. After this, the obtained solid was extensively washed with THF and then dried *in vacuo* for 72 h to yield 35 mg (>99%) of HPC **5** as brown powder. EA ($C_{54}H_{40}N_{12}$): calcd C 75.68, H 4.70, N 19.61; found C 66.66, H 4.94, N 16.46%.

Scale-up reaction procedure. In a 100 mL sealed tube, 1,3,5,7-tetrakis(4-ethynylphenyl)adamantane (**2**, 243 mg, 0.45 mmol, 1.00 equiv.) was solved in 35 mL DMSO under an argon atmosphere at 100 °C. Then, $CuSO_4{\cdot}5H_2O$ (22.6 mg, 90.6 μmol, 0.20 equiv.), sodium ascorbate (35.9 mg, 181.2 μmol, 0.40 equiv.), both dissolved in 1.75 mL H_2O (total), and 1,4-diazidobenzene (**3**, 435 mg, 2.72 mmol, 6.00 equiv.) were added slowly. The reaction mixture was heated for 7 days at 80 °C. The precipitate was filtered off and extensively washed with chloroform and water. Isolation and purification of the formed HCP was identical to that of the above mentioned procedure to yield 380 mg (98%) of HCP **5** as a brown powder.

Acknowledgements

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