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Tunable porosity of 3D-networks with germanium nodes

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Eight hyper cross-linked polymers based on tetrakis(4-ethynylphenyl)germanium and tetrakis(4-ethynylphenyl)methane are presented. After investigation of their N_2 adsorption properties at 77 K, porosity of the germanium-based porous organic polymers (POPs) was modulated in acidic conditions, offering an easy and direct way, in one single step, to tune the adsorption properties.

First discovered in 2005, three-dimensional porous organic polymers (POPs) have emerged as a new generation of nanoporous materials.[1] The scientific attention in these materials arises from their numbering qualities like their low framework density due to the ordering of the structure, their high surface area and porosity and their low production costs. Extensive interest in such assemblies has led to sub-categories such as covalent organic frameworks,[2] conjugated microporous polymers,[3] polymers of intrinsic porosity[4] and hyper cross-linked polymers (HCPs).[5] Their exhaustive applications include gas storage[6] and separation,[7] heterogeneous catalysis[8] or optoelectronics.[9] From the perspectives of topology chemistry, POPs are exclusively composed of pure organic units containing light elements based on designed building blocks such as aromatic structures[10] and only very recently with non-aromatic building blocks.[11] After an appropriate condensation reaction between the monomers or in the presence of a linker, the macromolecular assemblies are generated with discrete pores in their internal structure, displaying interconnected networks of channels wherein gaseous molecules can be trapped. In the

case of HCPs, the generated frameworks are amorphous due to the kinetic control of the reactions, and the permanent microporosity results from the extensive cross-linking, which prevents the rigid polymeric constructs from close packing. Their strong covalent linkage attests high water, chemical, air and thermal stability. Use of a tetrahedral monomer such as tetraphenylmethane (TPM) is prominent for the generation of 3D-porous assemblies by means of boroxine rings,[12] imines,[13] triazine,[14] C-C bonds[15] or imides.[16] Replacement of the central carbon or silicium atom by germanium in the monomeric skeleton for the production of POPs was already reported by Zhu and coll. in the co-dehydration reaction of tetra(4-dihydroxyborylphenyl)germanium (TBPGe) in presence of 2,3,6,7,10,11-hexahydroxytriphenylene resulting in a Ge-based POP exhibiting a Brunauer-Emmett-Teller (BET) surface area of 747 m^2g^{-1}.[17]

In our quest to develop intensive access to POPs by development of novel monomers, we report herein the synthesis and properties of 3D frameworks based on a tetrahedral monomer incorporating a germanium atom as central node. The focus on germanium was motivated by i) the possibility to explore the properties of POPs with a marginal central atom almost not yet illustrated in this field, ii) the possible detection by NMR of this specific nucleus[18] and iii) the ability of such assemblies to be easily chemically transformed (*vide infra*). To synthetize the 3D materials, the copper-catalyzed Huisgen 1,3-dipolar cyclo-addition (CuAAC) was selected regarding its high yielding conversion under mild conditions with a broad tolerance for diverse functional groups. Effective use of the CuAAC in the formation of POPs was already depicted by Cooper,[19] Nguyen,[20] and Zhu[21] on relevant tetrahedral monomers and by ourselves on a pseudo-octahedral monomer.[22] After generation of the desired 3D-systems, it was taken advantage of the presence of germanium to cleave the resulting POPs, leading to a new way of fine-tuning the properties of the relevant systems by chemical modification. To the best of our knowledge, this is the first time that such an approach is used to modulate porous HCPs.

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Scheme 1. Synthesis of tetrakis(4-ethynylphenyl)germanium **3**
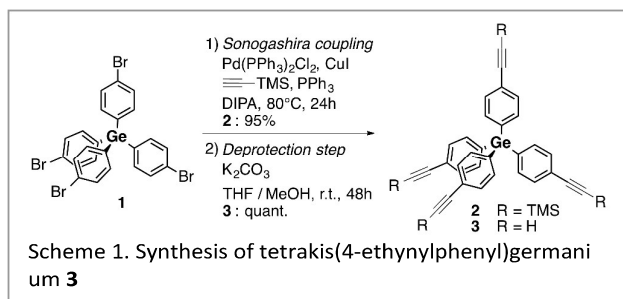
Subsequently, the targeted monomer tetrakis(4-ethynylphenyl)germanium **3** (TEPGe) was easily prepared by a Sonogashira cross-coupling reaction starting from the tetrakisbromoderivative **1** followed by deprotection of the trimethylsilyl groups in presence of potassium carbonate and methanol, yielding in two steps in 95% the desired compound (Scheme 1). The Ge based-monomer was postliminary assembled by means of CuAAC with a series of azido-linkers, whose use has not yet been exemplified in the generation of porous networks (Scheme 2). To determine the effect of the presence of Ge, networks were also generated from tetrakis(4-ethynylphenyl)methane **4** (TEPM) under the same reaction conditions. To ensure solubility of the starting materials and effectiveness of the formation of the macromolecular assemblies, reaction conditions reported by Nguyen were chosen as *in situ* generation of Cu(I) by reducing Cu(II) with sodium ascorbate and employing DMF as solvent. As illustrated in Table 1, the CuAAC reaction occurred between TEPGe **3** and TEPM **4** and the cross-linkers **5**, **6** and **7** at temperature ranging from 100 to 150 °C, leading to materials characterized by their insolubility in common organic solvents. These solids were dried for 24 h *in high vacuo* at 100 °C to remove any guest molecules and were further characterized by relevant solid-state analyses. The FT-IR data revealed no residual trace of the specific vibration band relative to terminal alkynes (v = 3300 cm^{-1}) or azide function (2100 cm^{-1}), therefore assuming a high conversion of the starting monomers (see ESI†). The significant vibration bands of the triazol moiety were detected around 1601 cm^{-1} (broad N=N stretch). For POPs **15** and **16**, the FT-IR spectra revealed vibration bands around 2100 cm^{-1} probably due to azido end groups or to remaining starting material **8**. Interestingly, a broad stretch around 3300 cm^{-1} is also observed for these networks, suggesting that a large amount of water was trapped in the networks. Elemental analysis was in moderate accordance with the theoretical values but ^{13}C CP/MAS NMR corroborated the assumed structures (Fig. 1). Indeed the presence of broad peaks, inherent to a polymeric structure,

Scheme 2. POPs formation

Table 1. Synthesis and BET surface area of HCPs **9-17**
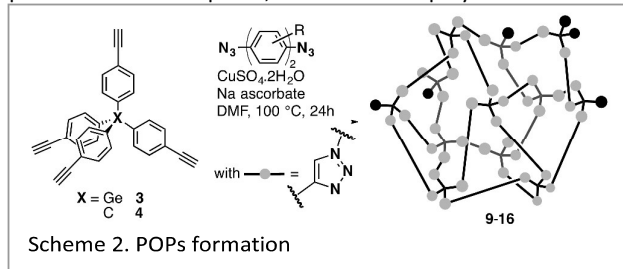
Entry	Monomer	Linker	HCPs	S_{BET} [a]
1	**3**		**9**	/[b]
2[c]	**4**	**5**	**10**	231
3	**3**		**11**	/
4[c]	**4**	**6**	**12**	123
5	**3**		**13**	/
6	**4**	**7**	**14**	134
7[c]	**3**		**15**	881
8[d]	**3/4**:1/1	**8**	**16**	1056
9[d]	**4**		**17**	1080

[a] S stands for specific surface area - Brunauer-Emmett-Teller method - and is calculated over the relative pressure range P/P_0 = 0.05-0.3. Specific surface area is expressed in m^{2}g^{-1}. [b] "/" stands for non porous. [c] CuAAC was performed at 150 °C during 24 h. [d] CuAAC was performed at 100 °C during 48 h.

was detected in the aromatic (around 135-150 ppm) and aliphatic (21 ppm for **12**) domain. No trace of residual alkyne groups was observed in the networks (should be present at approximately 87 ppm as for **4**) and the broad peak at ~150 ppm (C4-triazole carbon) resulted from the CuAAC reaction. Thermal properties were next investigated (see ESI†). DSC analyses did not show glass transitions for these HCPs, due to the high degree of crosslinking. No unreacted azide nor alkyne group (would cause a transition at 200 °C and 213°C, respectively) were present in the frameworks, in accordance with the FT-IR collected data. Decomposition of the triazol moieties occurred around 330–350 °C. Thermogravimetric analysis showed that all HCPs possess a high thermal stability and exhibit a multi-step degradation pattern, with a first transition around 100 °C due to trapped or physisorbed water, followed by decomposition of the triazol moiety around 335 °C, and degradation of the carbon scaffold. On the whole, the HCPs lose less than 20 wt% of their weight below 500 °C. Scanning Electron Microscopy (SEM) image of HCP **15** revealed the fine microporous structure (see ESI†). In addition, the porosity of the HCPs was explored by sorption measurements using nitrogen gas as adsorptive (Fig. 2). The specific surface
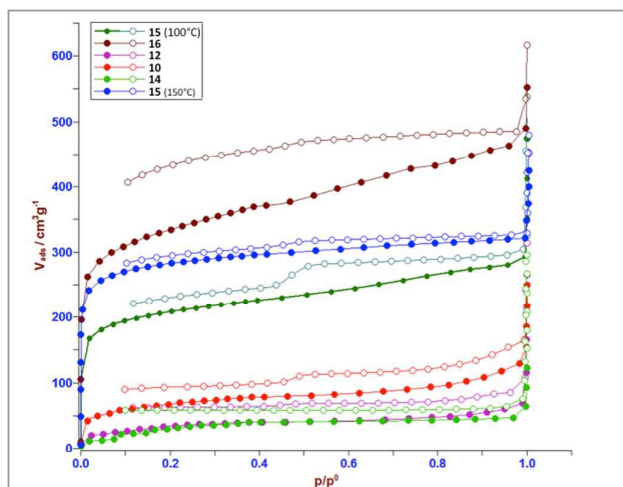

Fig 1. ^{13} CP/MAS NMR of **4**. **12**. **14**. **15** and **16**.

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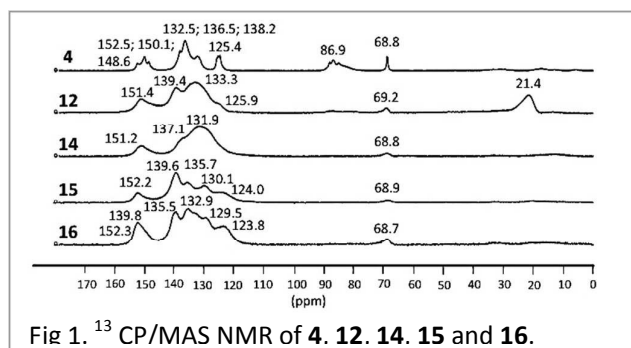
Fig. 2. The 77 K N_2-adsorption isotherms of HCPs **9-16**. Closed and open circles are used for adsorption and desorption data points, respectively.

Scheme 3. Principle of POP decomposition

areas were calculated by the BET nitrogen adsorption method as well as by Langmuir analysis and the pore size was given by the Saito and Foley model (Table 1 and ESI†). Networks **10, 12, 14**-**16** exhibited a type-IV nitrogen gas adsorption isotherm according to IUPAC classification. The pore size distribution showed a microporous structure with a large degree of mesoporosity as corroborated by the fast gas uptake at low pressure (0–0.1 bar) indicating a permanent microporous structure (pores < 2 nm), and the large hysteresis loop in the desorption isotherms revealing a mesoporous character (mesopores 2–10 nm). Overall, the use of TEPGe **3** for generation of networks with di-azidobenzidine derivatives **5-7** did not lead to the formation of porous networks contrary to the common monomer TEPM **4**.[23] A contrario, a high specific surface area of 881 $m^2 g^{-1}$ was reached when **3** and tetra-azidophenylmethane **8** were mixed together in a 1:1 ratio. As a point of comparison, click reaction conditions were applied between **4** and **8**, resulting in **17**, which exhibited a high specific surface area of 1080 $m^2.g^{-1}$ (Table 1, entry 9).

The ability to modulate the surface area was firstly investigated on POP **15**, which exhibited the highest BET surface area obtained in this study in presence of **3**. Two reaction conditions were screened, in presence of iodide monochloride[24] or triflic acid,[25] leading to the specific cleavage of one Ge-C bond (Scheme 3). To assure a complete reaction on the material and not only at its surface, higher amounts than required were engaged (see Table 2). In presence of iodine monochloride, a limited decrease in the value of the surface area was obtained whatever the stoichiometry, probably due to partial disruption of the channels (Table 2, entries 2-3). In the case of triflic acid, the channels were completely destroyed even with one equivalent, leading to an almost non-porous material (Table 2, entries 5-7). The significant vibration bands of the triazol moiety and of azido end groups disappeared in the IR spectrum of the resulting materials, as expected. To modulate this trend, we prepared POP **16** incorporating monomers **3, 4** and **8** in the ratio 1:1:2 (Table 1, entry 8). The IR and DSC
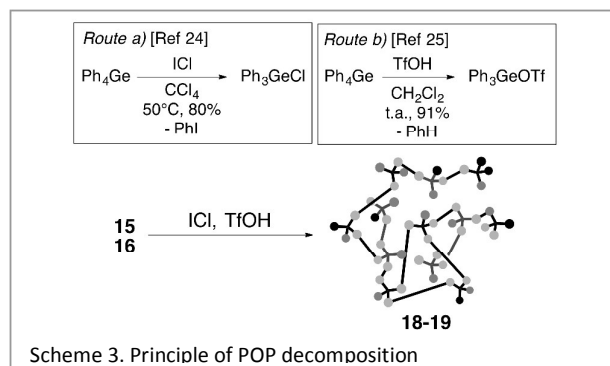
characterization exhibited some azido and ethynyl end groups while thermal properties of **16** were comparable to those of **15** (for details of the structure analysis, see ESI†). N_2 adsorption data revealed a high BET surface area of 1056 $m^2 g^{-1}$ obtained for the "three-component-click" network, which revealed that the presence of germanium central node has a small impact on the properties of relevant network in comparison to **17**, and was therefore subjected to acidic conditions (Table 2, entries 9-10). Even in presence of 100 equivalents of triflic acid, the porous structure was preserved (S_{BET} = 361 $m^2 g^{-1}$), most probably due to the network created between **4** and **8**, while the use of acetic acid did not alter the porous structure (see ESI†). The pore size dramatically increased twofold after acidic treatment with an average value of the pore diameter from 0.44 nm till 0.88 nm for **16** and **19**, respectively. The IR spectrum of **19** revealed no new functionality (*i.e.* as a stretching band arisen from the reaction between TfOH with acetylenic end groups leading to C=C-OTf) while triazol vibration band was still present. Note that only in extreme conditions when 100 equivalents of triflic acid were employed, the stretching band relative to the azido end groups disappeared (due to the protonation of azide function in strong acidic conditions). Thermal properties of the resulting material seem only moderately affected by such a chemical modification (see ESI†). These reaction conditions offer new perspectives in post-functionalization of porous networks and exemplify some specificity of incorporating germanium nodes, allowing an easy and direct way in one single step to tune the

Table 2. Adsorption data of POPs **18** and **19**.

Entry	POP	Acid	Equivalents	$S^{[a]}$	Total Pore Volume[b]
1	**15**		/	881	0.4293
2	**18**	ICl	1	696	0.3410
3	**18**		10	487	0.2250
5	**18**		1	3	0.0023
6	**18**		10	23	0.0065
7	**18**		100	9	0.0030
8	**16**	TfOH	/	1056	0.4903
9	**19**		1	815	0.3901
10	**19**		100	361	0.1719

[a] Surface area calculated over the relative pressure range P/P0 = 0.05-0.3 by using the BET nitrogen adsorption method. Specific surface area is expressed in $m^2 g^{-1}$. [b] Total pore volume for P/P0 = 0.99 and is expressed in $cm^3 g^{-1}$.

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adsorption properties. This can be considered as a future way of releasing adsorbates having strong interactions with the initial material. Work on other ways to generate reversible porous materials will be reported in due course.

In conclusion, we have synthesized the first example of CuAAC-POPs incorporating a germanium node and characterized several novel three-dimensional POPs formed from monomers **3** and **4** as tetrahedral building block and azido linkers **5**-**8**. N$_2$ adsorption measurements performed at 77 K revealed that the CuAAC reaction between the methane and the germanium core yielded the highest values for nitrogen uptake under mild conditions at low pressure. Furthermore, the presence of the germanium atom inside the porous structure was advantageously used for partial decomposition of the resulting network, opening a new way of fine-tuning the size of the channels.

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