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Microporous Polymer Networks (MPNs) Made in Metal-Free Regimes: Systematic Optimization of a Synthetic Protocol toward *N*-Arylcarbazole-Based MPNs

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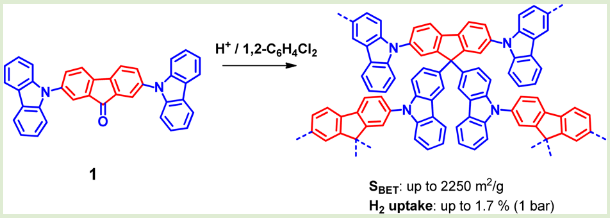
S *Supporting Information*

ABSTRACT: Acidic self-condensation of 2,7-bis(*N*-carbazolyl)-9-fluorenone **1** produces microporous polymer networks (MPNs) with high Brunauer−Emmett−Teller (BET) surface areas of up to 2250 m^2/g and hydrogen storage capacities of up to 1.7% (at 1 bar) in a fully metal-free condensation regime.



Microporous Polymer Networks (MPNs)[1−3] comprise a rapidly growing area of materials science. Especially when prepared under affordable, transition-metal-free regimes (for examples, see refs 4−6), such MPNs will be of high importance toward future mass applications in catalysis, in gas storage/separation, or as porous materials for organic electronic devices.[7−9] Recently, we have developed such transition-metal-free synthesis schemes, one aiming at microporous aromatic ladder polymer networks via self-condensation of bisindanone-type arene precursors[10] and the other focusing on triarylamine-based MPNs derived from self-condensation of 2,7-bis(diarylamino)-substituted fluorenones under acidic conditions.[11] Both approaches yielded microporous materials with high S_{BET} surface areas up to 1800 m^2/g and hydrogen storage capacities up to 1.5% (w/w), respectively.

Here, we present a more in-depth study striving for further optimization of the latter approach particularly considering the choice of (a) best suited acidic reagents and (b) optimum reaction temperature. Notably, after careful optimization of the synthetic protocol, improved MPN materials with distinctly increased S_{BET} surface areas up to 2250 m^2/g could be achieved. Such surface areas are among the highest values until now reported for MPNs made in metal-free condensation regimes (including Schiff base, polyhydroxymethylation, and polyesterfication chemistry[5−7]). The optimum reagents/conditions identified in the case of the investigated condensation process (reagent: trifluoromethane sulfonic acid, TFSA; or methane sulfonic acid/phosphorus pentoxide, MSA/P_4O_{10}; temperature: 140 °C) can be rather easily handled and the acidic reagent simply removed by (sophisticated) washing and drying procedures including supercritical carbon dioxide (sc-CO_2) washing.

Within this study, 2,7-bis(*N*-carbazolyl)-9-fluorenone (**1**) was used as a condensation monomer following monomer design rules established in our previous experiments.[11] The idealized three-dimensional (3D) structure of the target MPN contains regularly arranged tetragonal carbons (in the 9-position of the 9,9-diarylfluorene building blocks) that are connected by *N*-arylcarbazole bridges (Scheme 1). The condensation monomer **1** was generated according to literature procedures.[12] In the condensation experiments with **1** (Scheme 1), we applied four different acidic reagents in *o*-dichlorobenzene (or dichloromethane for room-temperature synthesis) as solvents: (i) methane sulfonic acid (MSA),[11] (ii) methane sulfonic acid/phosphorus pentoxide (MSA/P_4O_{10}),[13] (iii) trifluoromethane sulfonic acid (TFMSA),[14] and (iv) toluene sulfonic acid (TSA) at six different temperatures, (i) 20 °C, (ii) 50 °C, (iii) 80 °C, (iv) 110 °C, (v) 140 °C, and (vi) 160 °C, all with a reaction time of 18 h. Using this 4 × 6 matrix, we synthesized 21 MPN samples followed by standardized workup/drying procedures (including sc-CO_2 washing) as well as structural (solid state ^{13}C CPMAS NMR), thermal (TGA), and surface analytical (S_{BET}) characterization. Hereby, a significant increase of the BET surface area could be observed for most samples after sc-CO_2 washing.

The matrix of the conducted experiments is depicted in Table 1. Table 2 summarizes key characterization data of the MPNs (yield, S_{BET} surface area, maximum pore volume).

In all cases, full conversion of the precursors was monitored by solid-state ^{13}C CPMAS NMR. The representative spectrum

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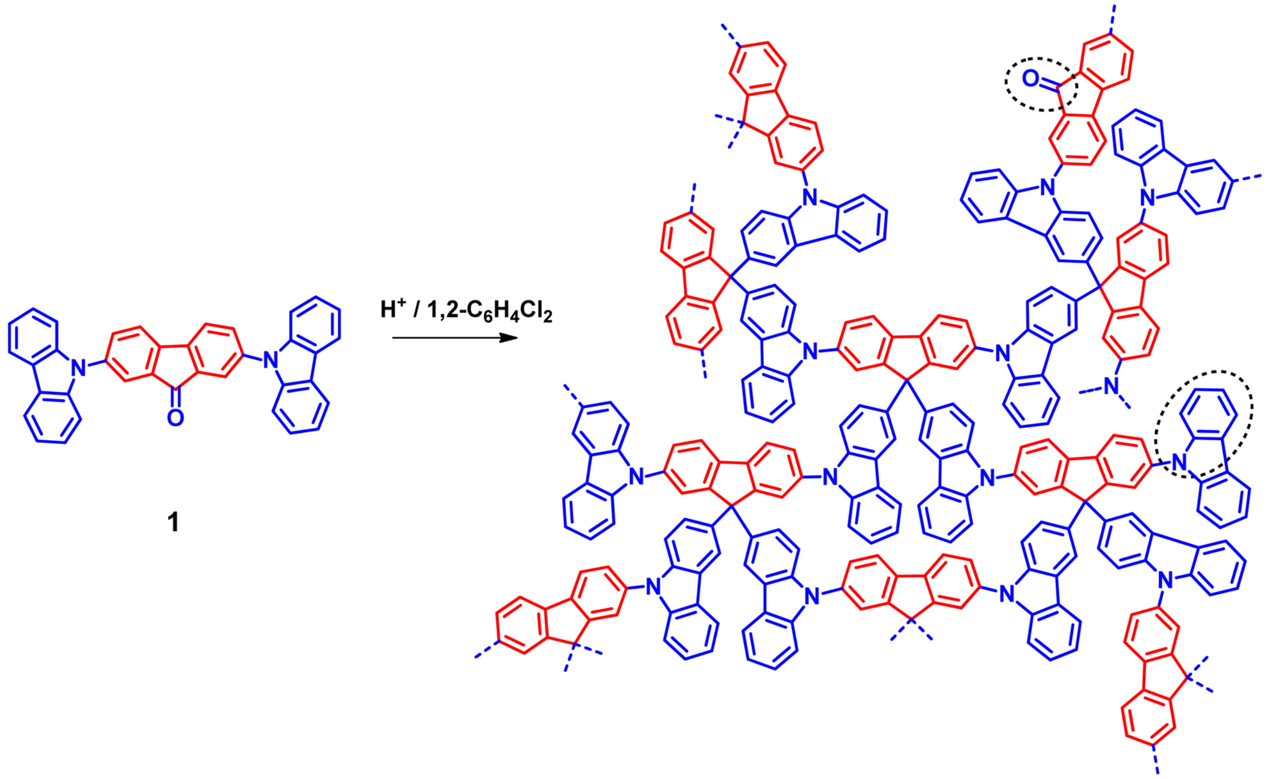
Scheme 1. Idealized Structure for MPNs Obtained by Acid-Catalysed Self-Condensation of Monomer 1[a]



[a]Examples for unreacted aromatic and keto units are encircled; please note that for monomer **1** also 3,6-disubstitution can occur at a single carbazole core.

Table 1. 4 × 6 Matrix of the Synthesized Polymer Samples

	20 °C (RT)[a]	50 °C	80 °C	110 °C	140 °C	160 °C
MSA	--	3	7	11	15	--
MSA/P_4O_{10}	1	4	8	12	16	19
TFMSA	2	5	9	13	17	20
TSA	--	6	10	14	18	21

[a]Dichloromethane as solvent.

of the MPN generated in entry 17 from Table 2 (in Figure 1 together with the ^{13}C CPMAS NMR spectrum of monomer **1**) exhibits five signals of aromatic carbons between 100 and 160 ppm (149, 138, 123, 118, and 108 ppm) as well as a signal at ca. 53 ppm attributed to the aliphatic, tetragonal carbons in the 9-position of the fluorene units. Note that the remaining signals of unreacted keto groups (at 192.2 ppm) could not be detected, thus indicating full conversion of the precursor (please compare the ^{13}C CPMAS NMR spectra of monomer **1** and the corresponding MPN of entry 17). As a characteristic example,

Table 2. Key Characterization Data of the MPNs (S_{BET} Surface Area, Maximum Pore Volume, Yield)[a]

	20 °C (RT)[b]	50 °C	80 °C	110 °C	140 °C	160 °C
MSA	--	*soluble product* 34 m^2/g 0.17 cc/g (73%)	970 m^2/g 1.15 cc/g (83%)	1300 m^2/g 1.48 cc/g (90%)	1200 m^2/g 1.29 cc/g (91%)	--
MSA/P_4O_{10}	*soluble product* 273 m^2/g 0.28 cc/g (85%)	787 m^2/g 1.00 cc/g (53%)	1488 m^2/g 1.39 cc/g (57%)	1467 m^2/g 1.46 cc/g (85%)	2195 m^2/g 2.23 cc/g (quant.)	1430 m^2/g 1.23 cc/g (quant.)
TFMSA	809 m^2/g 0.78 cc/g (90%)	910 m^2/g 0.65 cc/g (quant.)	820 m^2/g 0.71 cc/g (98%)	1700 m^2/g 1.70 cc/g (95%)	2250 m^2/g 2.16 cc/g (95%)	1500 m^2/g 1.64 cc/g (quant.)
TSA	--	*soluble product* 10 m^2/g 0.02 cc/g (51%)	247 m^2/g 0.30 cc/g (31%)	245 m^2/g 0.31 cc/g (50%)	953 m^2/g 1.10 cc/g (quant.)	370 m^2/g 1.87 cc/g (quant.)

[a]Thermal decomposition of MSA starts at 140−150 °C;[13] thermal decomposition of TSA starts at ca. 170 °C;[15] boiling point of TFMSA: 162 °C at 1013 mbar. [b]Dichloromethane as solvent.

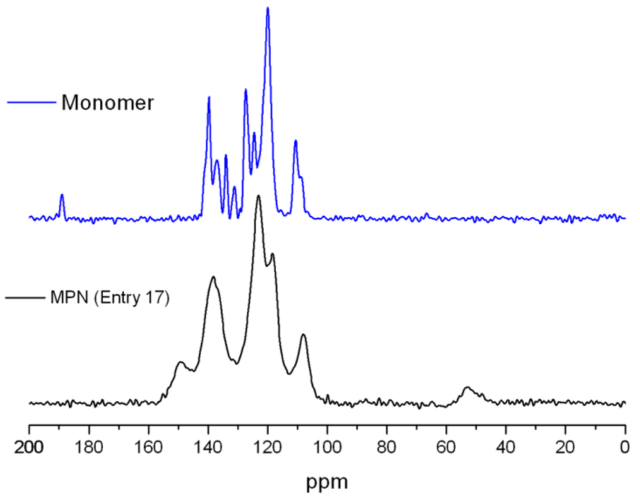


Figure 1. Solid-state ^{13}C CPMAS NMR spectra of monomer **1** and the MPN from entry 17 of Table 2.

this MPN sample reveals high thermal stability up to 380 °C in TGA measurements.

In summary, the main trends reflecting the influence of the tested reaction conditions on the nitrogen sorption properties are: (a) for all acidic reagents optimum reaction temperatures exist (110−140 °C) and (b) trifluoromethane sulfonic acid or methane sulfonic acid/phosphorus pentoxide in *o*-dichlorobenzene are the preferred acidic condensation reagents. In particular, in the case of the highly reactive reagent trifluoromethane sulfonic acid (TFMSA) high BET surface areas can be achieved during condensation even at room temperature (entry 2, Table 2), which is in good agreement with work published by Zolotukhin et al.[14] They applied trifluoromethane sulfonic acid (in dichloromethane) for polyhydroxyalkylation of aromatic monomers with N-methylization at room temperature, thereby yielding high molecular weight linear condensation polymers. Above reaction temperatures of 100 °C, a further increase of S_{BET} up to values of 2200 m^2/g was observed (entries 13 and 17). For methane sulfonic acid (MSA) as condensation reagent, MPNs of moderately high surface area have formed at temperatures of 80 °C or higher, while maximum S_{BET} values of up to 1300 m^2/g were obtained in the case of reaction temperatures of 110 and 140 °C, respectively (entries 11 and 15). For the binary mixture methane sulfonic acid/phosphorus pentoxide (MSA/P_4O_{10}), the surface area of the MPNs increases with increasing temperature (up to 140 °C) toward S_{BET} values of 2200 m^2/g (entry 16). When employing toluene sulfonic acid (TSA), a temperature of 140 °C is needed. The maximum S_{BET} surface areas for TSA as the condensing agent are ca. 1000 m^2/g (entry 18). Note that for all samples a decrease of S_{BET} values could be identified at a condensation temperature of 160 °C. The values for the maximum pore volume roughly correlate with the S_{BET} values, reaching a maximum value of 2.23 cc/g (entry 16) and 2.16 cc/g (entry 17). For the samples with the highest S_{BET} values hydrogen storage capacities have been determined. High hydrogen storage capacities of 1.37% (entry 16) and 1.68% (entry 17) at 1 bar have been observed that are in the range of the highest values reported for microporous polymer networks.[3,16]

In conclusion, self-condensation of 2,7-bis(*N*-carbazolyl)-9-fluorenone **1** under acidic conditions successfully resulted in the formation of microporous networks (MPNs) of the *N*-arylcarbazole type where careful optimization of the reaction conditions (trifluoromethylsulfonic acid or methane sulfonic acid/phosphorus pentoxide in dichlorobenzene at 140 °C) allowed for the generation of novel MPNs with high BET surface areas S_{BET} of up to 2250 m^2/g and hydrogen storage capacities of up to 1.7%. Further experiments applying such carbazole-based, aromatic MPNs in gas separation or as hole conducting components of electronic devices are planned.

■ ASSOCIATED CONTENT

Supporting Information

Experimental details including monomer and polymer synthesis, supercritical carbon dioxide washing, solid-state NMR spectra, pore size distribution, and nitrogen and hydrogen physisorption isotherms. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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