Microporous Poly(tri(4-ethynylphenyl)amine) Networks: Synthesis, Properties and Atomistic Simulation

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SUPPORTING INFORMATION

Synthesis of NCMP-1 to NCMP-4: These networks were synthesized by using the similar method as described for **NCMP-0.**

NCMP-1: This network was produced from *tri*-(4-ethynylphenyl)amine (951 mg, 3.0 mmol), 1,3,5-tris-(4-iodophenyl)amine (1246 mg, 2.0 mmol), tetrakis-(triphenylphosphine)palladium (35 mg), and copper iodide (7 mg). (Yield, 75.4%). Calcd for $C_{21}H_{12}N$: C 90.64, H 4.32, N 5.04; Found: C 87.65, H 3.89, N 4.36.

NCMP-2: This network was synthesized from *tri*-(4-ethynylphenyl)amine (951 mg, 3.0 mmol), 1,3,5-tris(4′-iodophenyl)benzene (1368 mg, 2.0 mmol), tetrakis-(triphenylphosphine)palladium (35 mg), and copper iodide (7 mg). (Yield, 79.5%). Elemental combustion analysis (%) Calcd for $C_{48}H_{27}N$: C 93.35, H 4.38, N 2.27; Found: C 88.92, H 3.79, N 1.98.

NCMP-3: This network was synthesized from *tri*-(4-ethynylphenyl)amine (634 mg, 2.0 mmol), 1,4-diiodobenzene (660 mg, 2.0 mmol), tetrakis-(triphenylphosphine)palladium (25 mg), and copper iodide (5 mg). (Yield, 75.4%).Elemental combustion analysis (%) Calcd for $C_{33}H_{12}N$: C 93.84, H 2.84, N 3.32; Found: C 87.65, H 2.56, N 2.03.

NCMP-4: *tri*-(4-ethynylphenyl)amine (634 mg, 2.0 mmol), 4,4′-diiodobiphenyl (812 mg, 2.0 mmol), tetrakis-(triphenylphosphine)palladium (25 mg), and copper iodide (5 mg) were employed in this polymerization. (Yield, 74.5%). Elemental combustion analysis (%) Calcd for $C_{42}H_{24}N$: C 92.98, H 4.42, N 2.58; Found: C 89.25, H 3.84, N, 1.95.

Table S1. Physical properties of NCMP-0–4 compared with other PAE networks.[S1,S2]

polymer	$L_{AV(strut)}$ (nm)[a]	$L_{AV(cluster)}$ (nm)[b]	S_{BET} (m^2/g)	S_{LANG} (m^2/g)[c]	S_{MICRO} (m^2/g)	V_{MICRO} (cm^3/g)	Bulk density, ρ (g/cm^3)
NCMP-0	0.69	5.40	1108	957	825	0.51	0.83
CMP-0[S2]	0.82	6.30	1018	898	702	0.38	0.94
NCMP-1	0.97	6.20	968	793	648	0.41	0.89
NCMP-2	1.10	7.20	900	685	586	0.32	0.95
CMP-1[S1,S2]	1.11	6.60	834	728	675	0.33	0.98
CPN-2[S2]	1.19	6.68	775	710	548	0.31	0.99
CPN-3[S2]	1.28	6.76	757	669	580	0.30	1.00
CPN-4[S2]	1.36	6.84	749	638	576	0.29	0.99
CPN-5[S2]	1.45	6.92	722	575	526	0.29	1.00
CMP-2[S1,S2]	1.53	7.00	634	562	451	0.25	1.05
NCMP-3	1.63	6.50	866	681	559	0.31	0.96
CMP-3[S1,S2]	1.90	7.50	522	409	350	0.18	1.14
NCMP-4	2.05	8.90	546	472	327	0.20	1.06
CMP-5[S2]	2.55	7.60	512	361	257	0.16	1.16

[a] Average node to node strut length; CMP materials: measured from quaternary carbons, NCMP materials: measured between N nodes and quaternary carbons respectively (measurements involving the N nodes are normalised with respect to the benzene node), CPN materials: strut length taken as a weighted average between the constituent monomer polymer strut lengths; [b] Average overall fragment diameter derived from fragment models. Each model was built to have an average number molecular weight in the range 11020-11319 g/mol. For CPN materials the cluster diameter was taken as a weighted average between the constituent monomer polymer cluster diameters. [c] The Langmuir surface area calculated from the H_2 adsorption isotherm by application of the Langmuir equation.

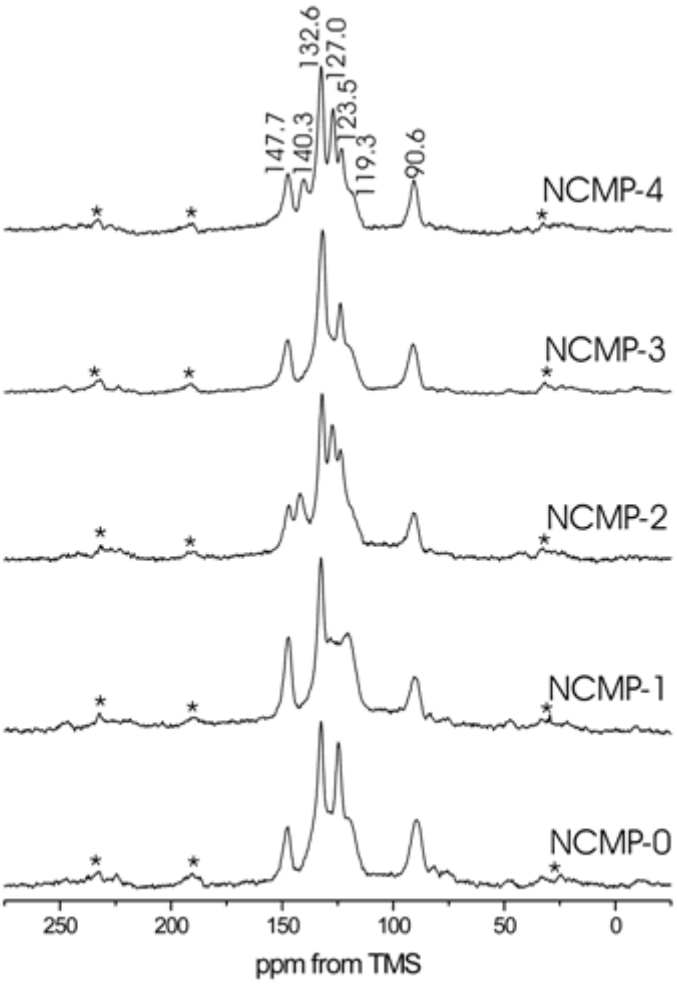

Figure S1. $^{13}C/^{1}H$ MAS NMR spectra of NCMP networks recorded at MAS rate of 10 kHz. Asterisks denote spinning sidebands.

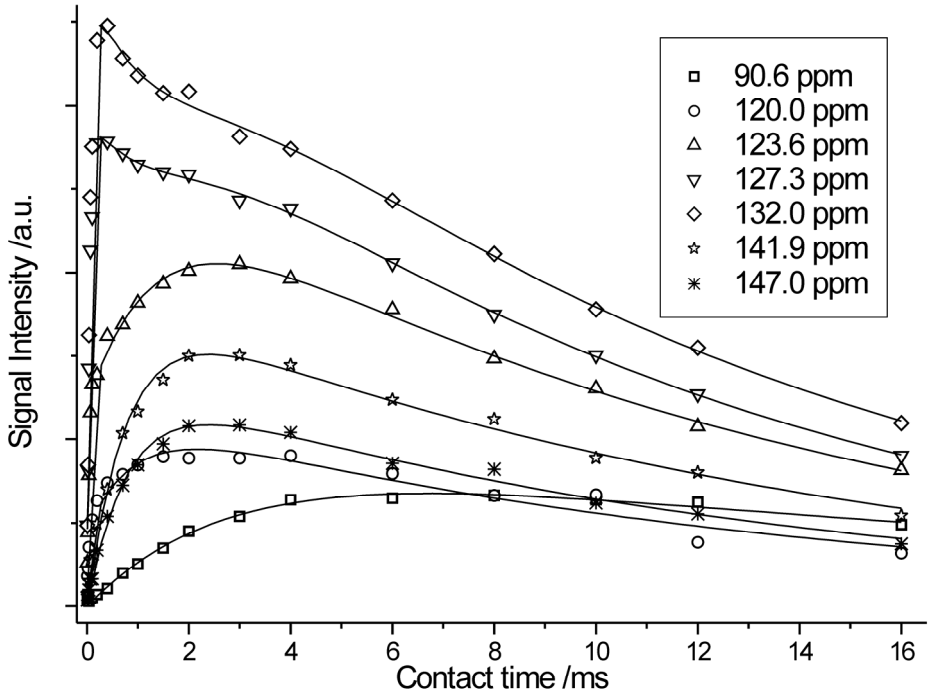

Figure S2. ^{1}H-^{13}C CP/MAS NMR kinetics curves for the NCPM-2 network. Note much faster CP-kinetics for the resonances at 127.3 and 132.0 ppm due to the presence of directly attached protons (C_{ar}-H sites). The resonances at 120.0, 123.6, 141.0 and 147.0 show much slower build up of the signal intensity, confirming their assignment to the quaternary aromatic sites. The line at 90.6 ppm exhibits the slowest CP-kinetics and is due to the -C≡C- linkages.

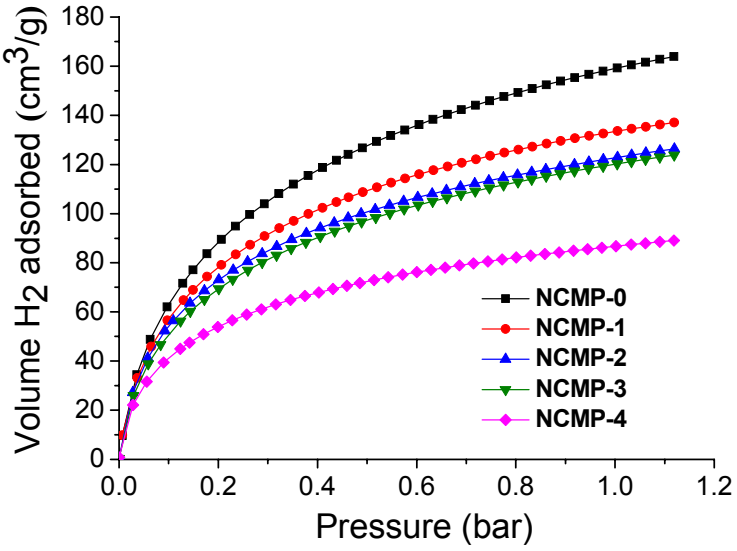

Figure S3. Volumetric H_2 adsorption isotherms for NCMP-0−4 at 77.3 K.

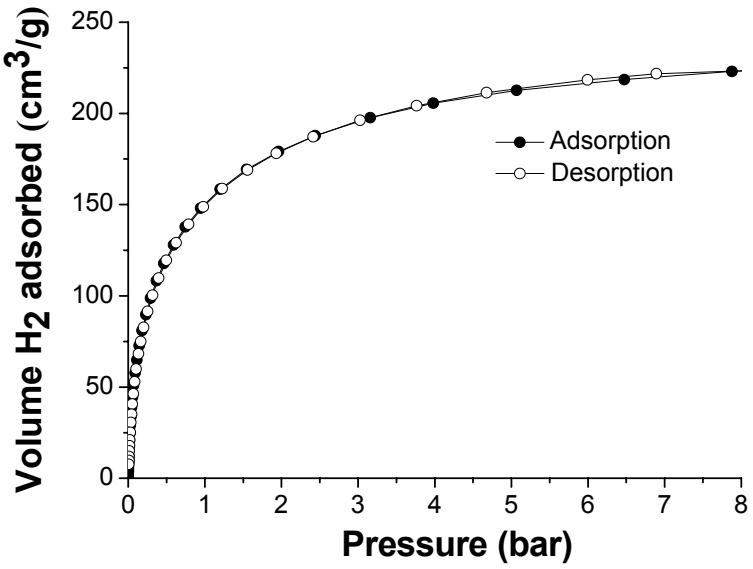

Figure S4. Volumetric H_2 adsorption isotherms for NCMP-0 at 77.3 K up to 8 bar.

References

(S1) (i) Jiang, J.-X.; Su, F.; Trewin, A.; Wood, C. D.; Campbell, N. L.; Niu, H.; Dickinson, C.; Ganin, A. Y.; Rosseinsky, M. J.; Khimyak, Y. Z.; Cooper, A. I. *Angew. Chem., Int. Ed.* **2007**, *46*, 8574-8578. (ii) Jiang, J.-X.; Su, F.; Trewin, A.; Wood, C. D.; Campbell, N. L.; Niu, H.; Dickinson, C.; Ganin, A. Y.; Rosseinsky, M. J.; Khimyak, Y. Z.; Cooper, A. I. *Angew. Chem., Int. Ed.* **2008**, *47*, 1167-1167.

(S2) Jiang, J.-X.; Su, F.; Trewin, A.; Wood, C. D.; Niu, H.; Jones, J. T. A.; Khimyak, Y. Z.; Cooper, A. I. *J. Am. Chem. Soc.* **2008**, *130*, 7710-7720.