**Supplementary Information**

# Synthesis of microporous polymers by Friedel-Crafts reaction of 1-bromoadamantane with aromatic compounds and their surface modification

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## Measurements

$N_2$ and $CO_2$ uptake amounts were measured by using a Belsorp-Max (BEL Japan, Inc.) apparatus. Ultra-high purity grade $CO_2$ and $N_2$ were used for all adsorption measurements. Solid state NMR measurements were carried out on a Bruker 400 Solid/Micro-Imaging High Resolution NMR with resonance frequencies of 100 MHz. A 4 mm triple resonance CP/MAS NMR probe with a rotation frequency of 7 kHz was used. Fourier transform infrared (FT-IR) measurements were recorded on a PERKIN ELMER Spectrum GX I using KBr pellets. Elemental analyses were performed by an EA 1110 (CE Instrument) and a Flash 1112 (Thermo Electron corporation).

## Synthesis of polymers 1-3

A typical procedure is as follows: To a solution of 1-bromoadamantane (1g, 4.6 mmol) in nitrobenzene (50 ml) were added tert-butyl bromide (1.9 g, 13.8 mmol), aluminum chloride (2.4 g, 18.4 mmol) and an aromatic compound (benzene, biphenyl, or terphenyl, 9.2 mmol). After stirring for 24 h at 150 $^{o}$C, the precipitated polymers were isolated by filtration, washed with methanol, acetone and DMF. Further purification was done by Soxhlet extraction with

methanol. For polymer **1**: $^{13}$C CP/MAS NMR δ 144, 122, 115, 34, 25; IR (cm$^{-1}$, KBr pellet) 3034, 2930, 2900, 2852, 2210. For polymer **2**: $^{13}$C CP/MAS NMR δ 144, 134, 121, 119, 34, 25; IR (cm$^{-1}$, KBr pellet) 3034, 2930, 2900, 2852. For polymer **3**: $^{13}$C CP/MAS NMR δ 144, 134, 121, 119, 34, 25; IR (cm$^{-1}$, KBr pellet) 3034, 2930, 2900, 2852.

**Post-modification of polymers 1-3 with nitronbenzoyl chloride**

A typical procedure is as follows: Polymer **1** (0.2 g) was stirred in nitrobenzene (50 ml) for 1 h at 150 $^{o}$C. To the mixture was added aluminum chloride (0.20 g, 1.50 mmol) and 4-nitrobenzoyl chloride (0.30 g, 1.60 mmol). After stirring for 24 h at 150 $^{o}$C, the polymer was isolated by filtration, washed with methanol, acetone and DMF. Further purification was done by Soxhlet extraction with methanol. For polymer **1'**: $^{13}$C CP/MAS NMR δ 144, 122, 115, 34, 25; IR (cm$^{-1}$, KBr pellet) 3034, 2930, 2900, 2852, 1671, 1526, 1350. For polymer **2'**: $^{13}$C CP/MAS NMR δ 144, 134, 121, 119, 34, 25; IR (cm$^{-1}$, KBr pellet) 3034, 2930, 2900, 2852, 1671, 1526, 1350. For polymer **3'**: $^{13}$C CP/MAS NMR δ 144, 134, 121, 119, 34, 25; IR (cm$^{-1}$, KBr pellet): 3034, 2930, 2900, 2852, 1671, 1526, 1350.

**Post-modification of polymer 3 with benzyl chloride**

Polymer **3** (0.20 g) was stirred in nitrobenzene (50 ml) for 1 h at 120 $^{o}$C. To the mixture was added aluminum chloride (0.70 g, 5.40 mmol) and benzyl chloride (0.60 g, 5.0 mmol). After stirring for 24 h at 120 $^{o}$C, the polymer was isolated by filtration, washed with methanol, acetone and DMF. Further purification was done by Soxhlet extraction with methanol. $^{13}$C CP/MAS NMR δ 144, 134, 121, 119, 34, 25; IR (cm$^{-1}$, KBr pellet) 3034, 2930, 2900, 2852.

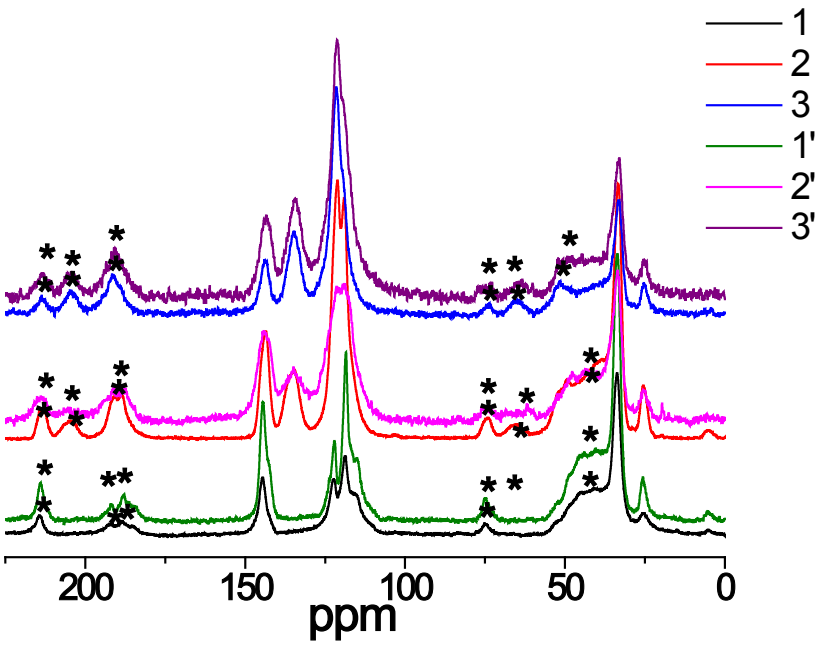


**Fig. S1** $^{13}$C CP/MAS NMR spectra of polymers **1-3'.** The asterisk marks a rotational sideband.

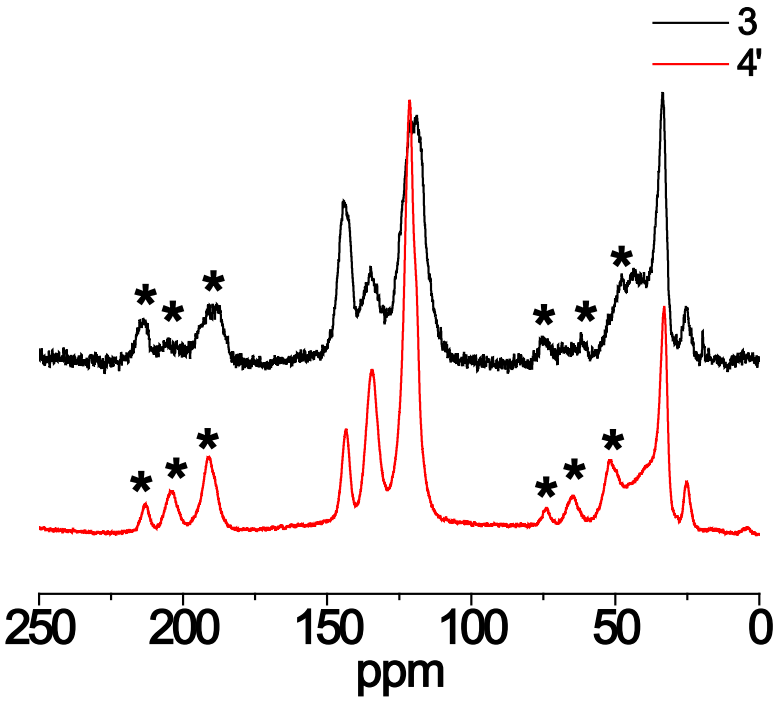


**Fig. S2** $^{13}$C CP/MAS NMR spectra of polymers **3** and **4'.** The asterisk marks a rotational sideband.

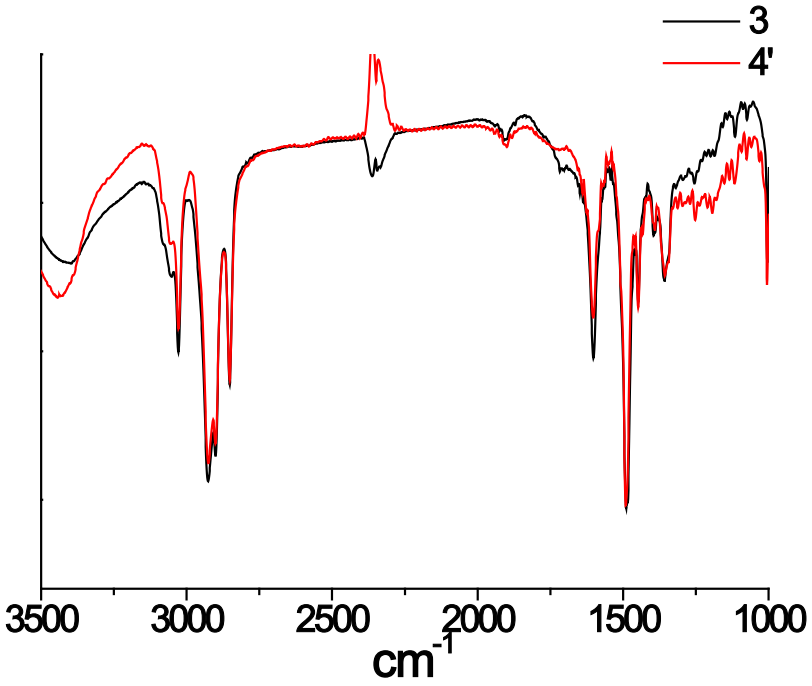


**Fig. S3** FT-IR spectra of polymers **3** and **4'.**

**Table S1** Elemental analysis results of polymers 1-3'

| Polymers | N (%) | C (%) | H (%) |
|---|---|---|---|
| **1** | - | 89.28 | 7.18 |
| **1'** | 0.70 | 86.95 | 6.71 |
| **2** | - | 88.08 | 6.52 |
| **2'** | 2.73 | 76.04 | 4.51 |
| **3** | - | 80.63 | 5.52 |
| **3'** | 1.82 | 79.41 | 4.80 |

**Table S2** Pore volumes of the polymers

| Polymer | [a]$V_{total}$/cm$^3$ g$^{-1}$ | [b]$V_{micro}$/cm$^3$ g$^{-1}$ | $V_{micro}/V_{total}$ |
|---|---|---|---|
| **1** | 2.74 | 0.64 | 0.23 |
| **1'** | 2.49 | 0.62 | 0.25 |
| **2** | 2.00 | 0.46 | 0.23 |
| **2'** | 1.94 | 0.43 | 0.22 |
| **3** | 0.64 | 0.28 | 0.43 |
| **3'** | 1.08 | 0.40 | 0.37 |
| **4'** | 0.76 | 0.31 | 0.40 |

[a]Total pore volume determined from the $N_2$ isotherm at $P/P_0$ = 0.995. [b]Micropore volume determined from the $N_2$ isotherm at $P/P_0$ = 0.050.

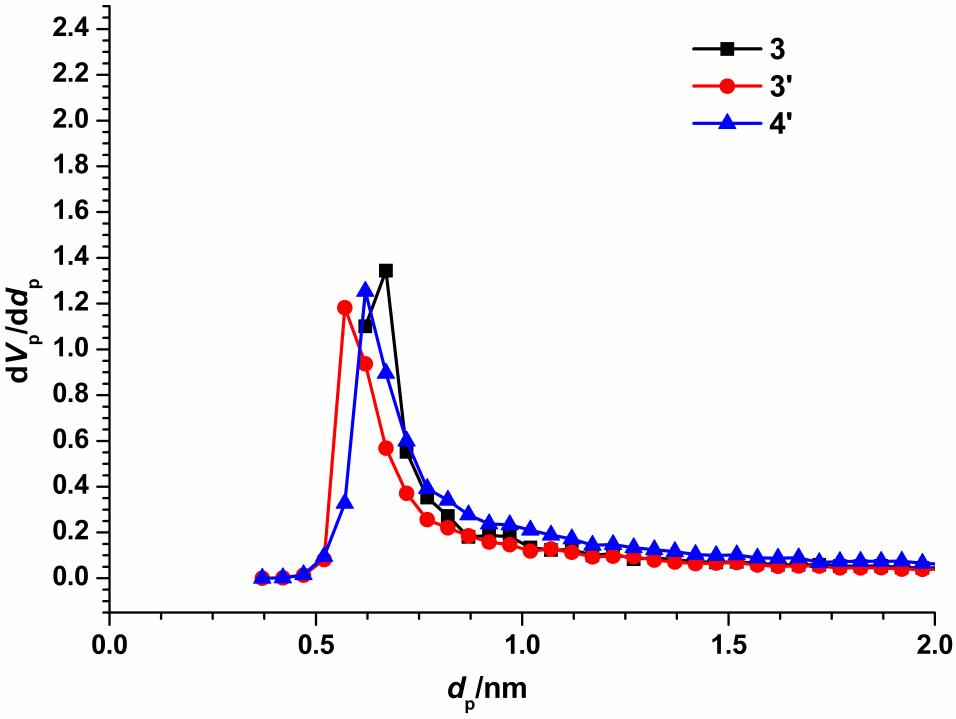


**Fig. S4** Micropore size distribution of polymers **3, 3'** and **4'** calculated by the Horvath-Kawazoe method.