Supplementary information

Acid Catalyzed Synthesis of Carbonyl-Functionalized Microporous Ladder Polymers with High Surface Area

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Monomers and reagents

The monomers **A**-**C** have been prepared according to known literature procedures (**A**[1], **B**[2], **C**[3]). The reagents and solvents were used in commercial p.a. quality.

Measurements

The ^{13}C NMR MAS spectra were recorded on a Bruker Advance 400 spectrometer in the MAS double resonance technique with a spinning frequency of 10 kHz. The ^{13}C {^{1}H} cross polarization magic angle spinning (CP MAS) spectra were measured with a contact time of 2s and referenced to tetramethylsilane (TMS) with adamantane as secondary standard.

The thermogravimetric measurements were carried out on a Mettler 1 STAR^{e} system (Mettler-Toledo) with a heating rate of 10°/min.

The adsorption isotherms leading to the Brunauer-Emett-Teller (BET) surface areas (S_{BET}) were measured on a Quantochrome Instruments machine at 77K. The samples (20-50 mg) were dried at 373K/10^{-3} mbar. The S_{BET} values were calculated in the pressure region P/P_0 as described in the literature[4] based on a specific surface of 16.2 Å^2/N_2 molecule.

Cyclotrimerization experiments

Monomer **A**

Entry 1: A 100 mL flask was filled with 1.82 mL (16.6 mmol) titanium tetrachloride and 20 mL of 1,2-dichlorobenzene (ODCB) and heated to reflux. To this mixture 250 mg (1.34 mmol) *s*-hydrindacene-1,7-dione (monomer **A**) in 35 mL of ODCB were added via a syringe. The mixture was refluxed for 72 h under argon. After cooling down to room temperature the dark colored mixture was poured into ice/conc. aqueous hydrochloric acid. After stirring for 48 h, the precipitate was isolated by filtration, neutralized with 5 M aqueous sodium hydroxide solution and extracted with water, acetone and chloroform. After drying, 214 mg (106 %) of a brownish product were isolated. The yield of >100% points for the presence of non-reacted –CH_2–CO– end groups and/or titanium oxide impurities (see Figure S1).

Monomer **B**

Entry 2: A 100 mL flask filled with 500 mg (2.07 mmol) 2,3,6,7-tetrahydro-3,3,7,7-tetramethyl-*s*-indacene-1,5-dione (monomer **B**), 2.76 g (14.5 mmol) *p*-toluenesulfonic acid (PTSA), and 1.1 mL (14.5 mmol) of propionic acid in 40 mL of 1,2-dichlorobenzene (ODCB) was heated up to 105°C for 72 h. The reaction mixture was poured into 300 mL of methanol and neutralized with 5 M aqueous sodium hydroxide solution. The precipitate was isolated and extracted with acetone and chloroform. 135 mg (31.7 %) of dried product were isolated as a beige colored solid.

Entry 3: A 100 mL Schlenk tube was filled with 500 mg (2.07 mmol) 2,3,6,7-tetrahydro-3,3,7,7-tetramethyl-*s*-indacene-1,5-dione (monomer **B**) and 10.6 g polyphosphoric acid (PPA). The mixture was heated up to 80°C for 1 h and to 160°C for 72 h under argon. After cooling down to room temperature the mixture was poured into ice water. The solid was isolated by filtration, neutralized with 5 M aqueous sodium hydroxide solution and extracted with acetone and chloroform. After drying, 301 mg (70.6 %) of a dark colored product were isolated.

Entry 4: A 100 mL Schlenk tube was filled with 500 mg (2.07 mmol) 2,3,6,7-tetrahydro-3,3,7,7-tetramethyl-*s*-indacene-1,5-dione (monomer **B**) and 2.87 g (20.66 mmol) water-free zinc chloride. The mixture was heated up to 400°C for 72 h under argon. After cooling down to room temperature the mixture was poured into 2M aqueous hydrochloric acid and stirred for additional 72 h. The solid was isolated by filtration, neutralized with 5 M aqueous sodium hydroxide solution and extracted with water, acetone, tetrahydrofurane and chloroform. After drying, only 44 mg (10.3 %) of a dark colored product were isolated.

Entry 5: A 100 mL flask was filled with 2.81 mL (25.6 mmol) titanium tetrachloride and 40 mL of 1,2-dichlorobenzene (ODCB) and heated to reflux. To this mixture 500 mg (2.07 mmol) 2,3,6,7-tetrahydro-3,3,7,7-tetramethyl-*s*-indacene-1,5-dione (monomer **B**) in 20 mL of ODCB were added via a syringe. The mixture was refluxed for 72 h under argon. After cooling down to room temperature the dark colored mixture was poured into ice/conc. aqueous hydrochloric acid. After stirring for 48 h, the precipitate was isolated by filtration, neutralized with 5 M aqueous sodium hydroxide solution and extracted with water, acetone and chloroform. After drying, 360 mg (84.5 %) of a brownish product were isolated.

Monomer **C**

Entry 6: In a 250 ml flask 500 mg (2.33 mmol) *s*-indacene-1,3,5,7(2H,6H)-tetraone (monomer **C**) were mixed with 60 mL of an 20% aqueous sulphuric acid. The mixture was heated up to 100°C for 24 h under argon. After cooling down to room temperature the dark colored product was isolated by filtration and extracted with water, ethanol, acetone and chloroform. After drying, 471 mg (113 %) of a dark solid were isolated. The yield >100% points for the presence of non-reacted $–CH_2–CO–$ end groups and/or adsorped sulphuric acid.

Entry 7: A 100 mL flask was filled with 500 mg (2.33 mmol) *s*-indacene-1,3,5,7(2H,6H)-tetraone (monomer **C**) and 20 mL of ODCB. 3 mL of methanesulfonic acid (MSA) were added via a syringe. The mixture was heated up to 180°C for 3 h under argon. After cooling down to room temperature the dark colored product was isolated by filtration and extracted with water, acetone and chloroform. After drying, 448 mg (108 %) of a dark solid were isolated. The yield >100% points for the presence of non-reacted $–CH_2–CO–$ end groups and/or adsorped MSA (see the occurrence of two carbonyl bands – truxenone core units, end groups – in the ^{13}C $\{^1H\}$ CP/MAS NMR spectrum spectrum of Figure S3).

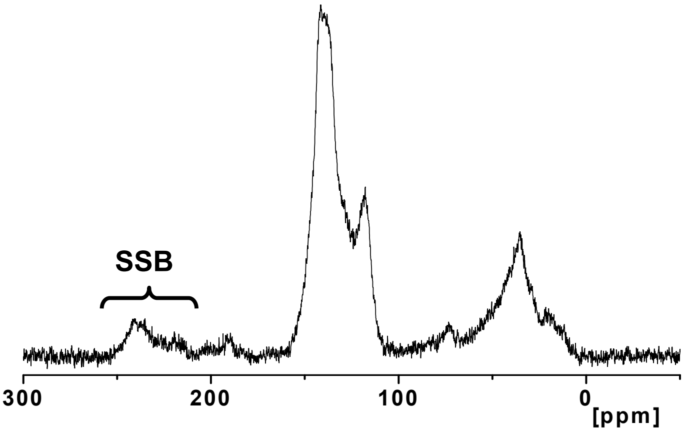

Figure S1: ^{13}C {^{1}H} CP/MAS NMR spectrum (10 kHz MAS) of the cyclotrimerization product of monomer **A** (entry 1); SSB: spinning side bands.

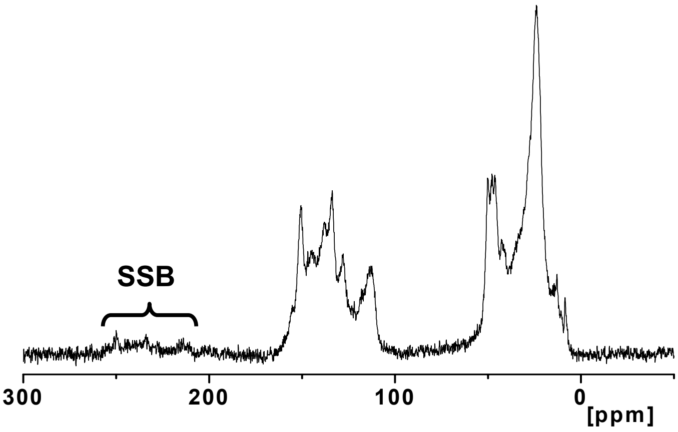

Figure S2: ^{13}C {^{1}H} CP/MAS NMR spectrum (10 kHz MAS) of the cyclotrimerization product of monomer **B** (entry 5); SSB: spinning side bands.

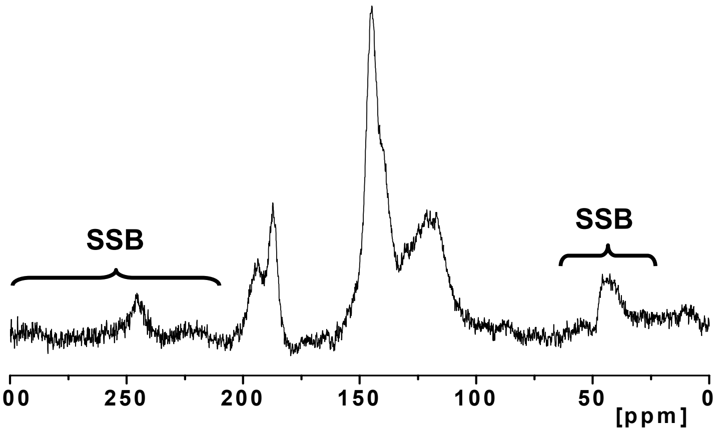

Figure S3: $^{13}C\ \{^{1}H\}$ CP/MAS NMR spectrum (10 kHz MAS) of the cyclotrimerization product of monomer **C** (entry 7); SSB: spinning side bands.

The assignment of the spinning side bands (SSB) is based on the signal patterns and the symmetry of the SSBs. In Figure S1 the labelled SSB mirrors the aromatic signals in the 110-160 ppm region. The corresponding high field SSB is superimposed by the broad aliphatic methylene signal. The low field SSB of the methylene signal falls into the 110-160 ppm region. In Figure S2 again, the labelled SSB mirrors the aromatic signals in the 110-160 ppm region. The corresponding high field SSBs are superimposed by the aliphatic signal group. The low field SSB of the aliphatic signals falls into the 110-160 ppm region. In Figure S3, both wings of the SSBs of the aromatic/carbonyl signal group are identifiable. The high field wing in the 0-75 ppm region may be overlaid by a weak aliphatic signal due to end groups.

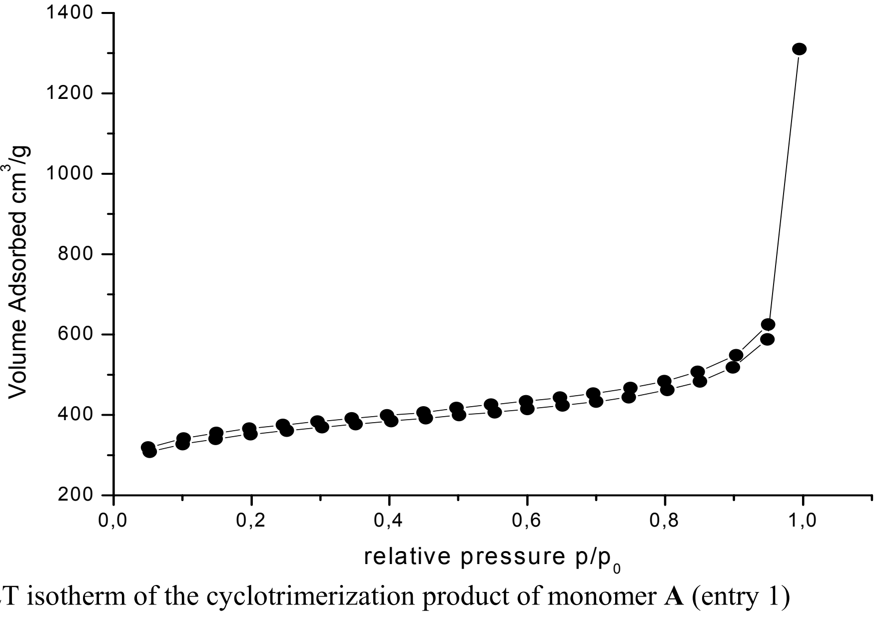

Figure S4: BET isotherm of the cyclotrimerization product of monomer **A** (entry 1)

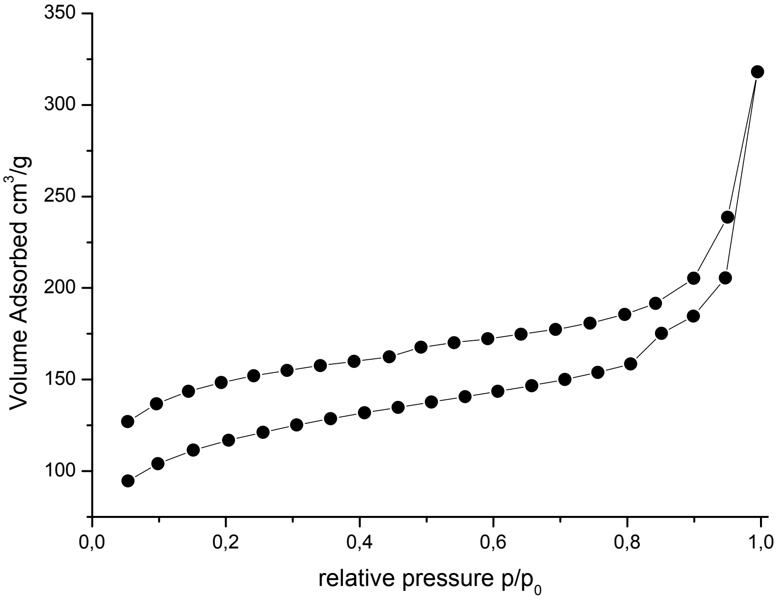

Figure S5: BET isotherm of the cyclotrimerization product of monomer **B** (entry 5)

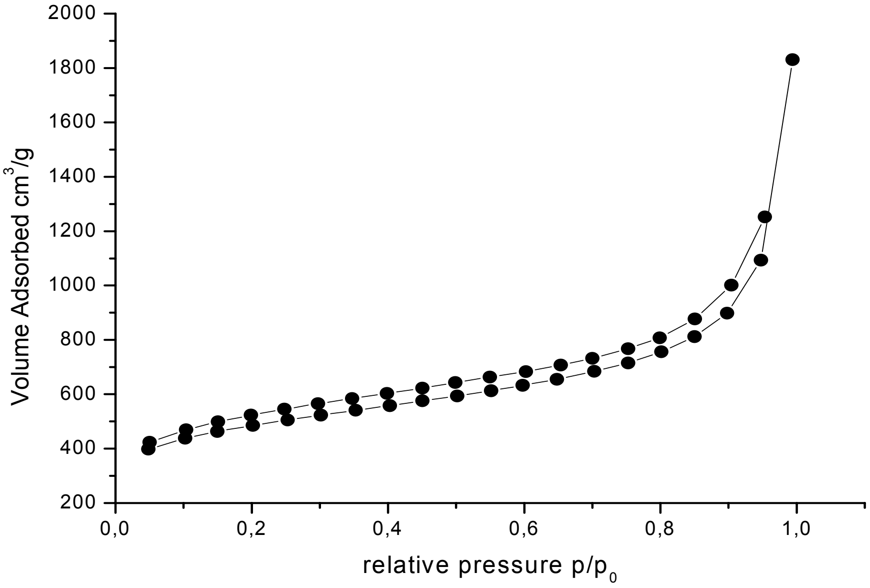

Figure S6: BET isotherm of the cyclotrimerization product of monomer **C** (entry 7)

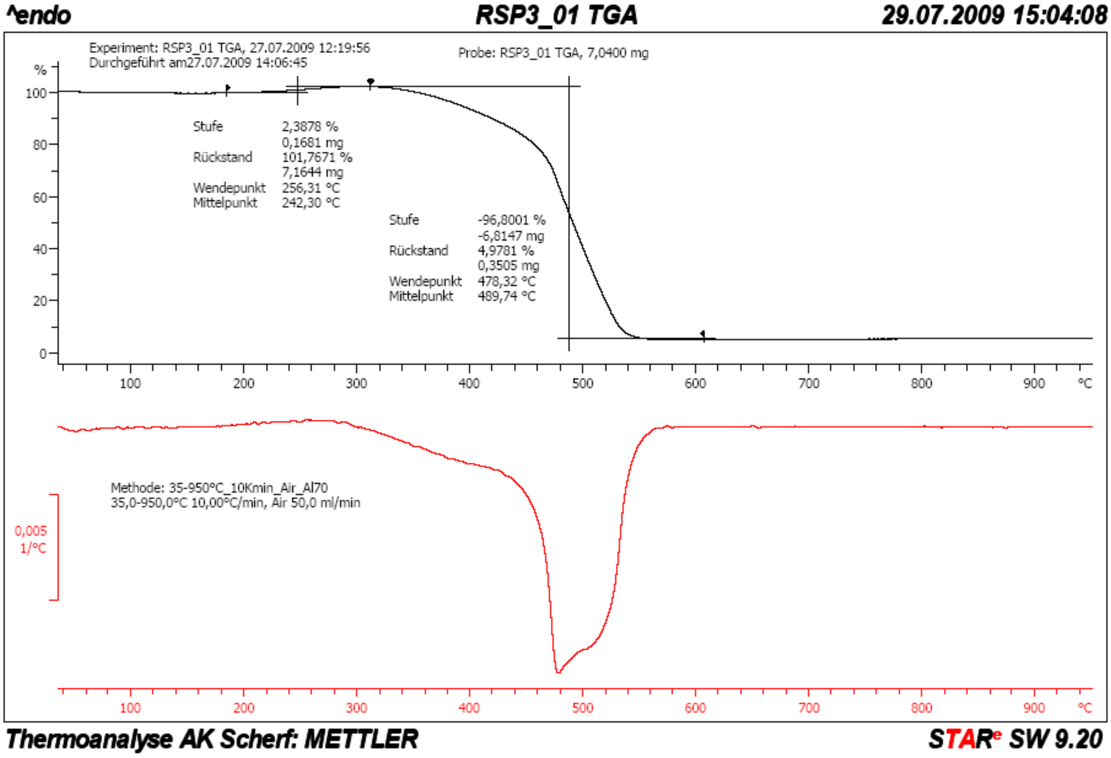

Figure S7: TGA analysis of the cyclotrimerization product of monomer **A** (entry 1)

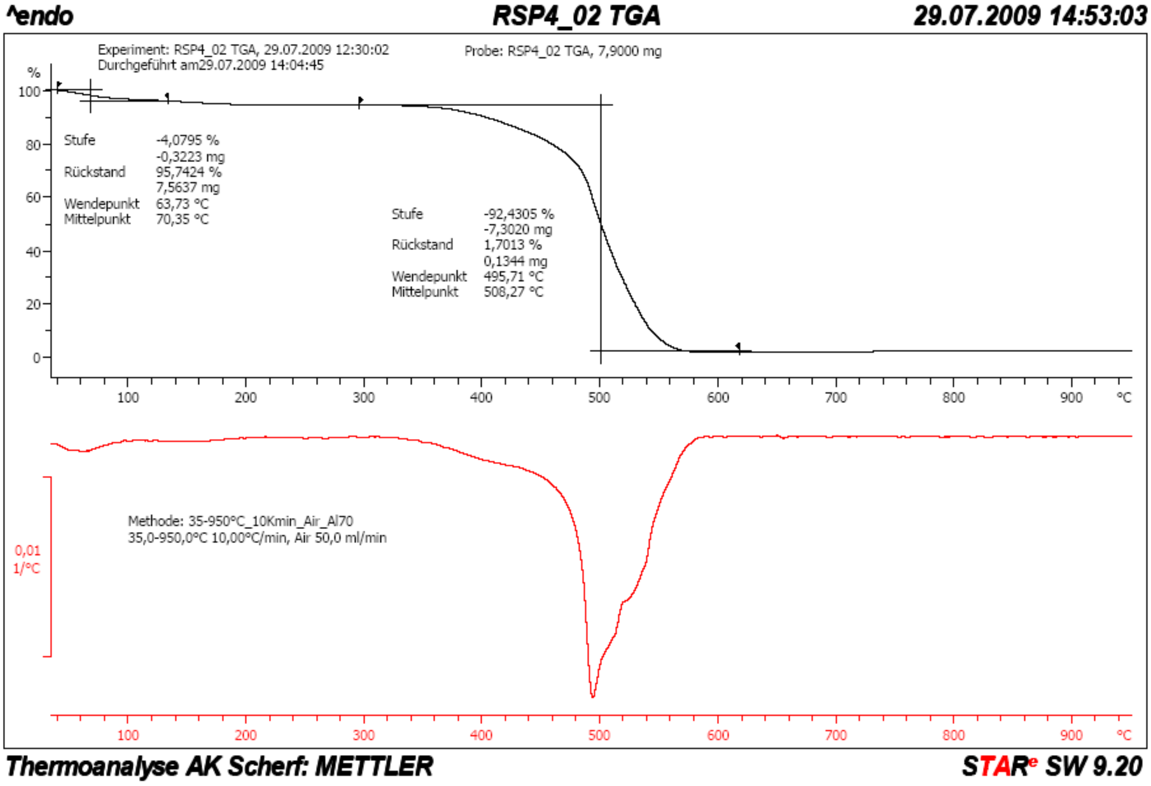

Figure S8: TGA analysis of the cyclotrimerization product of monomer **C** (entry 7)

References

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(3) Krief, P.; Becker, J. Y.; Ellern, A.; Khordorkovsky, V.; Neilands, O. *Synthesis* **2004**, 2509-2514.

(4) Walton, K. S.; Snurr, R. Q. *J. Am. Chem. Soc.* **2007**, *129*, 8552-8556.