Supplementary Information
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Experimental

Materials and methods

Trichloromethylsilane (99%) and hydrofluoric acid (38–40%) were purchased from Merck, 2-hydroxybenzyl alcohol (99%) from ABCR, 1,8-diazabicycloundecene-7-ene (99%) from fluorochem, trifluoroacetic acid (99%) from Alfa Aesar and methanesulfonic acid (99%) from Aldrich. These chemicals were used as received.

Toluene, tetrahydrofuran and triethylamine were dried using standard methods and distilled before use. CDCl3 was dried using molecular sieve 4Å. Furfuryl alcohol (98%) was purchased from Acros and distilled before usage.

Solid state NMR measurements were performed at 9.4 T on a Bruker Avance 400 spectrometer equipped with double-tuned probes capable of MAS (magic angle spinning). The finely powdered samples were packed in 3.2 mm rotors made of zirconium oxide spinning at 15 kHz (13C) and 12 kHz (29Si). All 13C- and 29Si-(1H)-CP-MAS NMR spectra were acquired at room temperature using cross polarization (CP) technique with contact times of 3 ms to enhance sensitivity and 1H decoupling using a TPPM (two puls phase modulation) puls sequence. Several thousand scans were accumulated and the recycle delays were set to 6 s. The spectra are referenced with respect to tetramethylsilane (TMS) using TTSS (tetrakis(trimethyl silyl)silane) as a secondary standard (3.5 ppm for 13C, –9.5 ppm for 29Si).

DSC measurements were performed using a DSC 1 from Mettler Toledo. The samples were prepared in 40 µL aluminum crucibles and measured under a nitrogen flow of 50 mL min-1 in a temperature range of 0–400 °C. For TGA a Thermogravimetric Analyzer TGA 7 from Perkin Elmer was used with heating rates as indicated. Synthetic air or helium with a flow of 20 mL min-1 were selected as atmospheres for the measurements.

ATR-FTIR spectra were recorded with a BioRad FT-IR 165 spectrometer using a Golden Gate ATR accessory from LOT-Oriel GmbH & Co. KG, Darmstadt.

Nitrogen sorption measurements were done with an Autosorb IQ2 apparatus from Quantachrome at 77 K. The samples were outgassed at 150 °C for 2 h before measurement.

For TEM investigations, a JEOL JEM-2100F UHR with a Schottky field-emitter (ZrO2/W (100)) was used at an acceleration voltage of 200 kV. The instrument was operated as a scanning transmission electron microscope (STEM) using a high angle annular darkfield (HAADF) detector.

Synthesis of monomer 1

For the synthesis of 2-methyl-2-chloro-4H-1,3,2-benzoxasiline a solution of 40.0 mL (0.289 mol) dry triethylamine and 15.5 mL (0.132 mol) trichloromethylsilane in 250 mL dry THF were slowly added. The cooling bath was removed and the mixture was stirred at room temperature using a stirring bar. After complete addition, the cooling bath is removed and the mixture is stirred for two hours at room temperature. The formed triethylammonium chloride is filtered off and the remaining volatile educts and the solvent are removed under reduced pressure before the monomer is distilled at 0.2 mbar and 80 °C to yield 13.16 g (54 %) of the colorless liquid.

1H NMR (250 MHz, CDCl3) δ [ppm] 7.28–7.16 (m, 1H, aryl-H), 7.05–6.90 (m, 3H, aryl-H), 5.30–4.90 (2d, 2J 14.1 Hz, 2H, SiOCH2–), 0.72 (s, 3H, –SiCH3). 13C NMR (63 MHz, CDCl3) δ [ppm] 151.6 (C-O), 129.2, 126.1, 125.5, 122.2, 119.5, 64.6 (SiOCH2–), –0.6 (–SiCH3). 29Si NMR (50 MHz, CDCl3) δ [ppm] –20.3.

For the synthesis of monomer 1 18.6 mL (0.133 mol) dry triethylamine and 20.7 g (0.103 mol) 2-methyl-2-chloro-4H-1,3,2-benzoxasiline were added to 250 mL dry toluene under argon atmosphere. The mixture was cooled to 0 °C before 11.6 mL (0.134 mol) furfuryl alcohol dissolved in 100 mL dry toluene were slowly added. The cooling bath was removed and the mixture was stirred at room temperature for two hours before the ammonium chloride was filtered off. The solvent and the educts are removed under reduced pressure before the monomer is distilled at 0.2 mbar and 101 °C. (yield 21.508 g; 80%)
H NMR (250 MHz, CDCl₃) δ [ppm] 7.37 (s, 1H, furan-H), 7.26–7.16 (m, 1H, aryl-H), 7.04–6.88 (m, 3H, aryl-H), 6.34–6.19 (m, 2H, furan-H), 5.07–4.91 (2d, J 14.1 Hz, 2H, SiOCH₂-aryl) 4.8 (s, 2H, SiOCH₂-furan), 0.35 (s, 3H, -SiCH₃).

13C NMR (63 MHz, CDCl₃) δ [ppm] 152.9, 152.7, 142.8, 129.1, 126.6, 126.1, 121.5, 119.3, 110.4, 108.5, 64.9 (SiOCH₂-aryl), 57.7 (SiOCH₂-furan), -6.3 (-SiCH₃).

29Si NMR (50 MHz, CDCl₃) δ [-40.2.

Elemental analysis: (found) C, 59.40; H, 5.52 (calculated) C, 59.52; H 5.38.

Synthesis of hybrid materials

In a typical reaction for the synthesis of hybrid material A 5.154 g (19.6 mmol) of monomer 1 are heated to 50 °C in a PTFE reaction vessel. Under constant stirring with a magnetic stirring bar 0.218 g (0.147 mL; 1.9 mmol) of trifluoroacetic acid (TFA) are added. Immediately after the addition of the acid the liquid turned black and after 90 minutes no more stirring was possible. The reaction was conducted for six hours after the addition of the acid to the monomer to yield 5.357 g black monolithic hybrid material.

In an exemplary reaction, 5.011 g (19.1 mmol) of monomer 1 are heated to 140 °C in a PTFE reaction vessel under constant stirring with a magnetic stirring bar. At 140 °C 0.288 g (0.283 mL; 1.9 mmol) 1,8-diazabicycloundec-7-ene (DBU) are added and the reaction was continued for six hours at this temperature to yield 5.118 g orange, monolithic hybrid material.

Hybrid material T can be obtained by simple annealing of monomer 1 at 250 °C. In a typical reaction 2.823 g (10.8 mmol) monomer 1 are heated to 250 °C in a PTFE reaction vessel under constant stirring. After 50 minutes at this temperature, no more stirring was possible. The reaction was conducted for three hours at 250 °C yielding 2.472 g of a dark, monolithic hybrid material.

Conversion of the hybrid materials into porous carbon

A sample of the hybrid material is put in a platinum crucible and placed into a quartz vessel. The vessel is flushed with argon gas (80 mL min⁻¹) for 30 min before it is heated to 800 °C with 4.3 K min⁻¹ under constant argon flow and maintained at this temperature for 3 h. The carbonized samples are placed into a PE vessel covered with hydrofluoric acid. After 72 h the carbon samples are filtered off, washed thoroughly with water and ethanol and dried in vacuum at 110 °C.

Oxidation of the hybrid material to porous SiO₂

The hybrid material is put in a platinum crucible and placed into a quartz vessel. Under an air flow of 80 mL min⁻¹ the sample is heated to 900 °C with a heating rate of 4.3 K min⁻¹ and maintained at this temperature for 3 h under constant air flow.

Supplementary figures
Figure S1: DSC thermogram of TFOS and TFOS in the presence of a base catalyst. The heat flow is given per mol monomer.

Figure S2: DSC thermogram of 1 with added catalysts and thermograms of the catalysts solely. The heat flow is given per mol monomer 1 for the polymerizations or per mol catalyst for the reference measurements.

* polymerization starts already before sample is placed in DSC.
Fig. S3 $^{13}$C-{'H}-CP-MAS-NMR spectra of hybrid materials obtained from the precipitation polymerization of 1 with methanesulfonic acid in dichloromethane.

Fig. S4 $^{29}$Si-{'H}-CP-MAS-NMR spectra of hybrid materials obtained from the precipitation polymerization of 1 with methanesulfonic acid in dichloromethane.
**Fig. S5.** Differential scanning calorimetry measurements of the hybrid material from the DBU catalyzed polymerization of 1 solely and together with TCA.

**Fig. S6.** Thermogravimetric analysis (30-900 °C) of the carbon material, obtained by carbonizing the hybrid materials and etching with HF, measured under air atmosphere (20 mL min⁻¹) with a heating rate of 40 K min⁻¹ and 60 min at 900 °C.
Fig. S7 Thermogravimetric analysis (30–800 °C) of the hybrid materials measured under air atmosphere (20 mL min⁻¹) with a heating rate of 40 K min⁻¹ and 30 min at 800 °C.

Fig. S8 Thermogravimetric analysis (30–800 °C) of the hybrid materials measured under He atmosphere (20.0 mL min⁻¹) with a heating rate of 10 K min⁻¹.
Fig. S9 Thermogravimetric analysis (30–900 °C) of the carbonized hybrid materials measured under air atmosphere (20 mL min⁻¹) with a heating rate of 40 K min⁻¹ and 60 min at 900 °C.