Supporting Information

Chiral Molecular Fluoridosilicates and their Twin Polymerization for the

Preparation of Fluorine-doped Mesoporous Silica and Microporous

Carbon

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Experimental

General remarks

The syntheses were carried out in an argon atmosphere using Schlenk techniques. Solvents were dried over sodium-potassium alloy (n-hexane, n-pentane, THF, toluene) and freshly distilled prior to use. ¹H, ¹³C{¹H} and ²⁹Si{¹H} NMR spectra were recorded on a Bruker spectrometer (Avance III 500, 500 MHz) and ¹⁹F NMR spectra were recorded on a Varian Inova spectrometer (400 MHz) at ambient temperature. The ¹H and ¹³C chemical shifts are reported in δ units (ppm) relative to the residual peak of the deuterated solvent (ref. CDCl₃ ¹H: 7.26 ppm; ¹³C: 77.16 ppm).¹ A Bruker Avance 400 spectrometer was used for the solid state NMR measurements, which were collected at 9.4 T equipped with double-tuned probes capable of magic angle spinning (MAS). ¹³C{¹H} CP MAS NMR spectra were measured at 100.6 MHz, ²⁹Si MAS NMR spectra as well as ²⁹Si¹H} CP MAS NMR spectra were measured at 79.5 MHz and ¹⁹F MAS NMR spectra were measured at 376.5 MHz in 3.2 mm standard zirconium oxide rotors (BRUKER) spinning at 12 kHz (only ²⁹Si{¹H} CP MAS), 15 kHz and 20 kHz, respectively. In case of ¹³C{¹H} CP MAS NMR and ²⁹Si{¹H} CP MAS NMR measurements cross polarization (CP) with a contact time of 3 ms was used to enhance sensitivity with a recycle delay of 5 s. In addition, the spectra were collected with ¹H decoupling using a two-pulse phase modulation sequence. ²⁹Si MAS NMR spectra (Bloch decay) were measured using a 30° puls for direct excitation of ²⁹Si with a recycle delay of 10 s. The spectra were referenced externally to tetramethylsilane (TMS) as well as either to tetrakis(trimethylsilyl)silane (3.55 ppm for ¹³C; 0.27 ppm for ¹H; -9.5 ppm for ²⁹Si) or Teflon® (-122.7 ppm for ¹⁹F) as secondary standard. ATR FTIR spectra were recorded with a BioRad FTS-165 spectrometer. Melting points were measured with a "Melting Point B-540" apparatus from Büchi. Elemental analyses were carried out using a "vario MICRO" from Elementar Analysensysteme GmbH. TGA experiments were determined by using a Mettler Toledo "TGA/DSC1 1600 system" with a MX1 balance. The measurements were performed in a temperature range from 40 to 800 °C with a rate of 10 °C · min⁻¹ and a nitrogen volume flow of 20 mL · min⁻¹. DSC experiments were performed using a Mettler Toledo DSC 30 with 40 µl aluminum crucibles. The measurements were carried out in the temperature range 30 °C to 300 °C with a rate of 10 °C · min⁻¹ and N₂ volume flow of 50 mL · min⁻¹. Nitrogen physisorption isotherms were obtained at -196 °C using an Autosorb IQ2 apparatus from Quantachrome. All samples were activated in vacuum at 150 °C for 5 h prior to the measurements. Specific surface areas were calculated applying the BET equation $(p/p_0 = 0.150 \pm 0.002)$. The pore size distribution was determined according to NLDFT adsorption branch (NLDFT: Non-local Density Functional Theory, for cylindrical pores) for silica samples and QSDFT adsorption branch (QSDFT: Quenched Solid Density Functional Theory, for slit and cylindrical pores) for carbon samples using the Autosorb 1.56 software from Quantachrome.² The specific micropore and total pore volume were also calculated by the above mentioned DFT models. Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy(EDX) were performed on a NovaNano SEM from FEI using following parameters: pressure (~10⁻⁵ mbar), work distance (3 mm to 5 mm) and acceleration voltage (10 kV to 30 kV) using a Si Drift Detector XFlash 3001 from Bruker AXS.

Tetra-*n*-butylammonium fluoride (1 M in THF) was purchased from Alfa Aesar GmbH & Co KG (Karlsruhe), 1,4,7,10,13,16-hexaoxacyclooctadecane (18-crown-6) from ABCR GmbH & Co KG, salicylic alcohol from Merck KGaA, sodium borohydride from Acros Organics, hydrofluoric acid from Carl Roth GmbH + Co. KG and tetramethoxysilane from Aldrich. Potassium fluoride was dried over phosphorus pentoxide before usage. 3-*tert*-butyl-2-hydroxy-benzyl alcohol³ was synthesized by reduction of 3-*tert*-butyl-2-hydroxy-benzaldehyde⁴ using NaBH₄

(quantitative yield). 4H,4H-2,2'-spirobi[benzo[*d*][1,3,2]dioxasiline] (**1**) was synthesized according to the literature.⁵

Single-crystal X-ray diffraction analyses

Single-crystal X-ray data (compounds **3** and **4**) were collected with a Rigaku Oxford Gemini S diffractometer at 120 K with Cu K_a radiation ($\lambda = 1.54184$ Å). The structures were solved by direct methods with SHELXS-2013 and refined by full-matrix-least-squares refinement against F² using SHELXL-2013.⁶ The figures were created with the Diamond program.⁷ A summary of crystallographic and refinement details is given in Table S 1.

In case of **3** the $-CH_2-CH_2$ part of the coordinating THF molecule (O1, C35-38) has been refined disordered to split occupancies of 0.54/0.46 for C36 and C37. A further THF molecule (O12, C39-C42) could be refined reliably as a fully occupied packing solvent molecule. Another THF molecule as packing solvent was refined disordered to split occupancies of 0.54/0.46 (O13, C43-C46). Another THF molecule as packing solvent could not be refined reliably and thus the command SQUEEZE of the PLATON program was applied.⁸ After applying SQUEEZE the unit cell contains solvent-accessible voids of ca. 250 A³ and an electron count per unit cell of 77. Considering that one THF molecule possesses 40 electrons (Z = 2, P-1) the data determined by SQUEEZE agree excellently with the presence of two further THF molecules in the unit cell.

Syntheses of molecular compounds

8,8'-di-tert-butyl-4H,4'H-2,2'-spirobi[benzo[d][1,3,2]dioxasiline] (2)

Tetramethoxysilane (1.64 mL, 11.1 mmol) was added to a solution of 3-*tert*-butyl-2-hydroxybenzyl alcohol (4.00 g, 22.2 mmol) and tetra-*n*-butylammonium fluoride (12 µL of 1M solution in THF, 0.01 mmol) in toluene (40 mL) at 86 °C. Then the solution was stirred for 1.5 hours at this temperature and subsequently the pressure was slowly reduced within four hours to remove methanol. After stirring for 16 hours at room temperature, the mixture was heated to 86 °C and toluene was removed in vacuum. Afterwards, *n*-hexane was added to the residue, while a colorless solid precipitated and was filtered off, washed with a small amount of *n*-hexane and then dried in vacuum.

Yield: 2.07g (49 %), $C_{22}H_{28}O_4Si$ (M = 384.55 g · mol⁻¹) requires C 68.72; H 7.34 %; found: C 69.00; H 7.56 %; m.p. 180-185 °C, ¹H NMR (500.3 MHz, CDCl₃, 298 K): δ 1.39 (s, 18H, CH₃), AB spin system with A at 5.11 and B at 5.23 ppm (4H, ²J_{H-H} = 13.7 Hz), 6.94 (m, 4H), 7.28 ppm (dd, 2H); ¹³C{¹H} NMR (125.8 MHz, CDCl₃, 298 K): δ 29.9 (CH₃), 35.0 (C(CH₃)₃), 66.6 (CH₂), 121.9, 124.3, 126.4, 126.8, 139.7, 151.8 ppm; ²⁹Si{¹H} NMR (99.4 MHz, CDCl₃, 298 K): - 79.9 (s) ppm.

$[(1,4,7,10,13,16-hexaoxacyclooctadecane-\kappa^6O^{1,4,7,10,13,16})$ potassium] fluoridodi[2-(oxido-methyl)phenolate(2-)]silicate [K(C₁₂H₂₄O₆)][C₁₄H₁₂FO₄Si] (**3**)

Compound **1** (1000 mg, 3.7 mmol) was dissolved in 50 mL of THF. Subsequently, 18-crown-6 (971 mg, 3.7 mmol) and potassium fluoride (213 mg, 3.7 mmol) were added in one portion. The suspension was stirred for one day and then filtrated using celite. After removal of the solvent a solid remained, that was purified by stirring in THF/*n*-pentane (ratio 1/1, v/v) solution. Further, the colorless solid was isolated by filtration and dried in vacuum.

Yield: 1.65 g (76 %), colorless crystals suitable for single-crystal X-ray diffraction were grown from THF/*n*-pentane solution at -18 °C, $C_{26}H_{36}KFO_{10}Si$ (M = 594.75 g · mol⁻¹) requires C 52.51; H 6.10 %; found: C 52.31; H 5.86 %; m.p. 131-132 °C, ¹H NMR (500.3 MHz, CDCl₃, 298 K): $\overline{0}$ 3.49 (s, 24H), 4.84 (s broad, 4H, C*H*₂), 6.64 (td, 2H), 6.85 (dd, 2H), 6.88 (dd, 2H), 7.03 ppm (td, 2H); ¹³C{¹H} NMR (125.8 MHz, CDCl₃, 298 K): $\overline{0}$ 65.1 (*C*H₂), 70.0 (18-crown-6), 117.4, 118.7, 124.6, 127.6, 130.8, 159.7 (d, ³J_{C-F} = 2.7 Hz) ppm; ¹⁹F NMR (376.3 MHz, CDCl₃, 298 K): -130.7 ppm (s); ²⁹Si{¹H} NMR (99.4 MHz, CDCl₃, 298 K): - 136.4 (d, ¹J_{Si-F} = 170.8 Hz) ppm.

 $[(1,4,7,10,13,16-hexaoxacyclooctadecane-\kappa^6O^{1,4,7,10,13,16}) potassium] fluoridodi[6-tert-butyl-2-(oxidomethyl)phenolate(2-)]silicate [K(C_{12}H_{24}O_6)][C_{22}H_{28}FO_4Si] (4)$

Compound **2** (1000 mg, 2.6 mmol) was dissolved in 50 mL of THF. Subsequently, 18-crown-6 (687 mg, 2.6 mmol) and potassium fluoride (151 mg, 2.6 mmol) were added in one portion. The suspension was stirred for two days, and then filtrated using celite and the solid was washed twice with 10 mL of THF. After removal of the solvent a solid remained, that was

purified by stirring in THF/*n*-pentane (1/1) solution. Further, the colorless solid was isolated by filtration and dried in vacuum.

Yield: 1.05 g (57 %), colorless crystals suitable for single-crystal X-ray diffraction were grown from THF/*n*-pentane solution at 4 °C, $C_{34}H_{52}$ KFO₁₀Si (M = 706.96 g · mol⁻¹) requires C 57.76; H 7.41 %; found: C 57.52; H 7.47 %; no melting point up to 200 °C, ¹H NMR (500.3 MHz, CDCl₃, 298 K): δ 1.50 (s, 18H), 3.45 (s, 24H), 4.81 (s broad, 4H, C*H*₂), 6.62 (td, 2H), 6.77 (dd, 2H), 7.11 ppm (dd, 2H); ¹³C{¹H} NMR (125.8 MHz, CDCl₃, 298 K): δ 30.1 (*C*H₃), 34.9 (*C*(CH₃)₃), 64.8 (*C*H₂), 70.0 (18-Crown-6), 116.8, 122.9, 124.5, 130.6, 138.7, 157.6 ppm; ¹⁹F NMR (376.3 MHz, CDCl₃, 298 K): -131.0 ppm (s); ²⁹Si{¹H} NMR (99.4 MHz, CDCl₃, 298 K): - 136.7 (d, ¹J_{Si-F} = 174.4 Hz) ppm.

General synthesis protocol for hybrid materials

The respective precursor or mixture of the precursors was polymerized under inert atmosphere for three hours at the temperatures as given below. Subsequently, the as-obtained hybrid material was stirred for two hours in approximately 10-30 mL of CH₂Cl₂, filtered off and dried in vacuum. Hybrid materials were termed as follows: HMX (X: starting material) or HMSi-Spiro\Y (Y: additive; molar ratio 95/5).

Synthesis of HM3: 2.53 g of compound **3**; temperature: 148 °C; yield: 73 % (2.05 g); analysis found: C 50.89; H 5.43 % (ideal polymerization process and removal of 18-crown-6 required: C 50.89; H 3.66 %); BET surface area 9 m²·g⁻¹

Synthesis of HM4: 800 mg of compound **4**; temperature: 148 °C; yield: 28 % (220 mg); analysis found: C 28.13; H 4.17 % (ideal polymerization process and removal of 18-crown-6 required: C 59.70; H 6.38 %); BET surface area 20 m²·g⁻¹

*Synthesis of HM1***3**: 3.0 g of compound **1**; 344 mg of compound **3**; temperature: 157 °C; yield: 88 % (2.95 g); analysis found: C 59.19; H 4.35 % (ideal polymerization process and removal of 18-crown-6 required: C 61.09; H 4.39 %); BET surface area 8 m²·g⁻¹

Synthesis of HM1\TBAF: 2.0 g of compound 1; 0.39 mL of 1 M solution of TBAF in THF; temperature: 148 °C; yield: 83 % (1.755 g); analysis found: C 61.38; H 4.78; N 0.15 % (ideal

polymerization process required: C 62.31; H 4.90, N 0.26 %); BET surface area 18 m²·g⁻¹ Page S 6 *Synthesis of HM1\KF:* 2.5 g of compound **1**; 28.1 mg of KF; temperature: 156 °C; yield: 92 % (2.335 g); analysis found: C 60.89; H 4.42 % (ideal polymerization process required: C 61.06; H 4.39 %); BET surface area 31 m²·g⁻¹

General synthesis protocol for microporous carbon materials

The as-obtained hybrid material was heated under a flow of argon $(11 \text{ L} \cdot \text{h}^{-1})$ in a stove (deposited in a quartz glass tube) for three hours at the final temperature of 800 °C (heating ramp of 10 °C \cdot min⁻¹) to give a black silica/carbon composite.

After treatment of the silica/carbon composites in concentrated hydrofluoric acid (48 %) for three days, washing with aqueous concentrated NaHCO₃ solution (five times with 20 mL) and pure water (five times with 30 mL) the material was dried at 50 °C for 24 h to give microporous carbon. Carbon/silica composites were termed as follows: CSX (X: starting material) or CSSi-Spiro\Y (Y: additive; molar ratio 95/5). Carbon materials were termed as follows: CX (X: starting material) or CSi-Spiro\Y (Y: additive; molar ratio 95/5).

Caution: Hydrofluoric acid is a very toxic (inhalation and skin contact hazard) and corrosive liquid! Avoid direct contact!

*Synthesis of CS***3**: 901 mg of HM**3**; yield: 36 % (326 mg); yield starting from compound **3**: 26 %; analysis found: C 46.77; H 0.21 %; BET surface area 133 m²·g⁻¹ (micropore content 11 %) *Synthesis of CS***1****3**: 500 mg of HM**1****3**; yield: 65 % (324 mg); yield starting from mixture **1****3**: 57 %; analysis found: C 60.58; H 0.44 %; BET surface area 374 m²·g⁻¹ (micropore content 71 %)

Synthesis of CS1\TBAF: 750 mg of HM1\TBAF; yield: 64 % (479 mg); yield starting from mixture 1\TBAF: 53 %; analysis found: C 61.15; H 0.76; N 0.29 %; BET surface area 464 m²·g⁻¹ (micropore content 55 %)

Synthesis of CS1\KF: 850 mg of HM1\KF; yield: 66 % (559 mg); yield starting from mixture 1\KF: 61 %; analysis found: C 57.25; H 0.57 %; BET surface area 39 m²·g⁻¹ (micropore content 0 %)

Synthesis of C3: 313 mg of CS3; yield: 61 % (190 mg); yield starting from compound 3: 16 %; analysis found: C 83.21; H 0.45 %; BET surface area 450 m²·g⁻¹ (micropore content 28 %) Page S 7 *Synthesis of* C1\3: 320 mg of CS1\3; yield: 62 % (197 mg); yield starting from mixture 1\3: 35 %; analysis found: C 84.43; H 0.58 %; BET surface area 1060 m²·g⁻¹ (micropore content 50 %)

Synthesis of C1\TBAF: 370 mg of CS1\TBAF; yield: 60 % (221 mg); yield starting from mixture 1\TBAF: 32 %; analysis found: C 81.44; H 0.52 %; BET surface area 1219 m²·g⁻¹ (micropore content 66 %)

Synthesis of C1\KF: 430 mg of CS1\KF; yield: 66 % (283 mg); yield starting from mixture 1\KF: 40 %; analysis found: C 81.67; H 0.00 %; BET surface area 509 m²·g⁻¹ (micropore content 24 %)

General synthesis protocol for silica materials

The as-obtained hybrid material was oxidized under a flow of air (200 L \cdot h⁻¹) in a stove (deposited in a quartz glass tube) for three hours at the final temperature of either 600 °C, 700 °C or 900 °C (heating ramp of 10 °C \cdot min⁻¹). Silica materials were termed as follows: SX (X: starting material) or SSi-Spiro\Y (Y: additive; molar ratio 95/5).

Synthesis of S**3**_600: 500 mg of HM**3**; yield: 21 % (103 mg); yield starting from compound **3**: 15 %; temperature: 600 °C; analysis found: C 8.11; H 0.22 %; black solid; BET surface area 20 m²·g⁻¹

Synthesis of S**3**_700: 500 mg of HM**3**; yield: 20 % (99 mg); yield starting from compound **3**: 15 %; temperature: 700 °C; analysis found: C 7.79; H 0.52 %; black solid; BET surface area 21 m²·g⁻¹

Synthesis of S**3**_900: 657 mg of HM**3**; yield: 7 % (44 mg); yield starting from compound **3**: 5 %; temperature: 900 °C; analysis found: C 0.41; H 0.00 %; black solid spheres (molten during annealing and stuck at the crucible); BET surface area 48 m²·g⁻¹

Synthesis of S1\3_600: 500 mg of HM1\3; yield: 23 % (114 mg); yield starting from mixture 1\3: 20 %; temperature: 600 °C; analysis found: C 0.11; H 0.31 %; BET surface area 239 m²·g⁻¹ *Synthesis of* S1\3_700: 400 mg of HM1\3; yield: 23 % (92 mg); yield starting from mixture 1\3: 20 %; temperature: 700 °C; analysis found: C 0.14; H 0.16 %; BET surface area 205 m²·g⁻¹

Synthesis of S1\3_900: 420 mg of HM1\3; yield: 22 % (92 mg); yield starting from mixture 1\3: 19 %; temperature: 900 °C; analysis found: C 0.08; H 0.00 %; BET surface area 32 m²·g⁻¹ *Synthesis of* S1\TBAF: 500 mg of HM1\TBAF; yield: 21 % (106 mg); yield starting from mixture 1\TBAF: 17 %; temperature: 900 °C; analysis found: C 0.00; H 0.09 %; BET surface area 687 m²·g⁻¹ (micropore content 12 %)

Synthesis of S**1***KF*: 700 mg of HM**1***K*F; yield: 22 % (155 mg); yield starting from mixture **1***K*F: 20 %; temperature: 900 °C; analysis found: C 0.15; H 0.00 %; BET surface area 229 m²·g⁻¹



c) ¹H NMR spectrum of compound **3**



d) $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of compound $\boldsymbol{3}$



e) ¹H NMR spectrum of compound 4



Figure S 1 NMR spectra of compounds **2-4**; a) ¹H NMR spectrum of **2**, b) ¹³C{¹H} NMR spectrum of **2**, c) ¹H NMR spectrum of **3**, d) ¹³C{¹H} NMR spectrum of **3**, e) ¹H NMR spectrum of **4**, f) ¹³C{¹H} NMR spectrum of **4**. Asterisks mark residue silicon grease or solvents i.e., diethyl ether, THF, toluene or *n*-hexane.



Figure S 2 ATR-FTIR spectra of compounds a) 2, b) 3, c) 4.



ATR-FTIR spectroscopy of hybrid materials HM3, HM1\3, HM1\TBAF and HM1\KF

Figure S 3 ATR-FTIR spectra of hybrid materials a) HM3, b) HM1\3, c) HM1\TBAF, d) HM1\KF.

Molecular structure of compound 4 and crystal data collection and refinement information of

compounds 3 and 4



Figure S 4 Molecular structure of **4**·3 thf (TBPY-5-23'-12'3-A) in the solid state (50% probability level of displacement ellipsoids, hydrogen atoms and non-coordinating THF molecules are omitted for clarity). Selected bond lengths [Å] and bond angles [°]: Si1–O1 1.6558(16), Si1–O2 1.7727(17), Si1–O3 1.7244(17), Si1–O4 1.6906(16), Si1–F1 1.6361(14), K1–F1 2.8248(14), K1–O1 3.7561(17), K1–O3 2.7600(16), K1-O11 2.875(2), O1–Si1–O2 95.64(8), O1–Si1–O3 92.05(8), O1–Si1–O4 120.77(9), O2–Si1–O3 172.17(8), O2–Si1–O4 83.22(8), O3–Si1–O4 94.09(8), F1–Si1–O1 115.24(8), F1–Si1–O2 88.90(8), F1–Si1–O3 86.51(7), F1–Si1–O4 123.92(8), F1–K1–O3 48.71(4).

Nomenclature of fluoridosilicates 3 and 4



TBPY-5-23'-12'3-C and TBPY-5-23'-12'3-A

Figure S 5 Numbering of the ligands in compounds **3** and **4** (Ph = phenyl; Bnz = benzyl). The nomenclature was adopted from the nomenclature of chiral coordination compounds (trigonal bipyramidal geometry) from IUPAC red book.⁹

Table S 1 Compilation of crystal data collection and refinement information

parameters	3	4 ·3 thf
emperical formula	C ₂₆ H ₃₆ FO ₁₀ KSi	C ₄₆ H ₇₆ FKO ₁₃ Si
formula weight	594.74	923.25
temperature / K	120	120
wavelength / Å	1.54184	1.54184
crystal system	orthorhombic	triclinic
space group	P212121	<i>P</i> -1
unit cell dimensions	<i>a</i> = 8.2364(1) Å	<i>a</i> = 13.7772(6) Å
	<i>b</i> = 18.6416(3) Å	<i>b</i> = 13.7838(6) Å
	<i>c</i> = 18.7332(3) Å	<i>c</i> = 14.2885(6) Å
		$\alpha = 95.891(4)^{\circ}$
		$\beta = 96.246(3)^{\circ}$
		$\gamma=92.797(4)^\circ$
volume, Z	2876.29(7) Å ³ , 4	2678.1(2) Å ³ , 2
density (calc.)	1.373 g⋅cm ⁻³	1.145 g⋅cm ⁻³
absorption coefficient	2.541 mm ⁻¹	1.569 mm ⁻¹
<i>F</i> (000)	1256	996
crystal size / mm ³	0.30 x 0.30 x 0.20	0.20 x 0.16 x 0.14
heta range	3.345 to 65.981°	3.2060 to 65.9210°
limiting indices	$-7 \le h \le 9$	-16 ≤ <i>h</i> ≤ 13
	-21 ≤ <i>k</i> ≤ 19	-16 ≤ <i>k</i> ≤ 16
	-21 ≤ <i>I</i> ≤ 21	-16 ≤ <i>I</i> ≤ 16
reflections collected	5882	20665
independent reflections	4353	9210
R _{int}	0.0245	0.0289
completeness to $ heta$	0.982	0.987
absorption correction T_{min} / T_{max}	0.89974 / 1.00000	0.87897 / 1.00000
data/restraints/parameters	4353/459/352	9210/154/624
S	1.022	1.065
final R indices $[l > 2\sigma(l)]$	$R_1 = 0.0979,$	$R_1 = 0.0588,$
	$wR_2 = 0.2532$	$wR_2 = 0.1663$
R indices (all data)	$R_1 = 0.1017,$	$R_1 = 0.0743,$
	$wR_2 = 0.2576$	$wR_2 = 0.1780$
max./min. residual electron density	2.508 / -0.702 e Å ³	0.570 / -0.399 e Å ³
absolute structure parameter ¹⁰	0.023(9)	

¹³C Solid State NMR Spectra of HM1\3, HM1\TBAF and HM1\KF



Figure S 6 ¹³C{¹H} CP MAS NMR spectrum of the phenolic resin/silica hybrid material obtained by simultaneous twin polymerization of a mixture of **1** and **3** (95/5) and additive assisted twin polymerization of a mixture of **1** and TBAF or KF (95/5). The asterisk * mark signals for residual THF, that results from the usage of 1 M TBAF solution in THF.



¹⁹F Solid State NMR Spectra of HM3 and HM4

Figure S 7 ¹⁹F MAS NMR spectra of phenolic resin/silica hybrid materials HM3 and HM4, obtained by twin polymerization of fluoridosilicates 3 or 4, respectively.

¹⁹F Solid State NMR Spectra of silica materials



Figure S 8 ¹⁹F MAS NMR spectra of silica materials S3_900, S1\3_900, S1\TBAF and S1\KF obtained by twin polymerization of either fluoridosilicates 3, simultaneous twin polymerization of compound 1 and 3 or additive assisted twin polymerization of compound 1 with TBAF or KF, respectively. The simultaneous twin polymerization and additive assisted twin polymerization were carried out in a 95/5 molar ratio. A signal in the range of -160 to -200 ppm was received in each spectrum, which was attributed to fluorine containing polymer within the used rotor (see spectrum of *Background*). The asterisk * are assigned to spinning side bands.



Figure S 9 ¹⁹F MAS NMR spectra of silica materials S3_900, S1\3_900, S1\TBAF and S1\KF obtained by twin polymerization of either fluoridosilicates 3, simultaneous twin polymerization of compound 1 and 3 or additive assisted twin polymerization of compound 1 with TBAF or KF, respectively. The simultaneous twin polymerization and additive assisted twin polymerization were carried out in a 95/5 molar ratio. Notably, the signal of the rotor was subtracted in each spectrum! The asterisk * are assigned to spinning side bands.



Figure S 10 ¹⁹F MAS NMR spectra of silica materials S3_600, S3_700, S1\3_600 and S1\3_700 obtained by twin polymerization of either fluoridosilicates **3**, simultaneous twin polymerization of compound **1** and **3** or additive assisted twin polymerization of compound **1** with TBAF or KF, respectively. The simultaneous twin polymerization and additive assisted twin polymerization were carried out in a 95/5 molar ratio. A signal in the range of -160 to -200 ppm was received in each spectrum, which was attributed to fluorine containing polymer within the used rotor (see spectrum of *Background*). The asterisk * are assigned to spinning side bands.



Figure S 11 ¹⁹F MAS NMR spectra of silica materials S3_600, S3_700, S1\3_600 and S1\3_700 obtained by twin polymerization of either fluoridosilicates **3**, simultaneous twin polymerization of compound **1** and **3** or additive assisted twin polymerization of compound **1** with TBAF or KF, respectively. The simultaneous twin polymerization and additive assisted twin polymerization were carried out in a 95/5 molar ratio. Notably, the signal of the rotor was subtracted in each spectrum! The asterisk * are assigned to spinning side bands.

²⁹Si Solid State NMR Spectra of silica materials



Figure S 12 ²⁹Si MAS NMR spectra of silica materials S**3**_900, S**1****3**_900, S**1**\TBAF and S**1**\KF obtained by twin polymerization of either fluoridosilicates **3**, simultaneous twin polymerization of compound **1** and **3** or additive assisted twin polymerization of compound **1** with TBAF or KF, respectively. The simultaneous twin polymerization and additive assisted twin polymerization were carried out in a 95/5 molar ratio.



Figure S 13 ²⁹Si MAS NMR spectra of silica materials S3_600, S3_700, S1\3_600 and S1\3_700 obtained by twin polymerization of either fluoridosilicates 3, simultaneous twin polymerization of compound 1 and 3 or additive assisted twin polymerization of compound 1 with TBAF or KF, respectively. The simultaneous twin polymerization and additive assisted twin polymerization were carried out in a 95/5 molar ratio.



N₂-sorption measurements and pore size distribution of the carbon and silica materials

Figure S 14 N₂-Isotherms of materials a) CS3, b) CS1\3, c) CS1\TBAF and d) CS1\KF.



Figure S 15 N₂-Isotherms of materials a) C3, b) C1\3, c) C1\TBAF and d) C1\KF.





Figure S 16 N₂-Isotherms of materials a) S3_600, b) S3_700, c) S3_900, d) S1\3_600, e) S1\3_700, f) S1\3_900, g) S1\TBAF and h) S1\KF.



Figure S 17 Pore size distribution of CS**3**, CS**1****3**, CS**1**\TBAF and CS**1**\KF. The pore size distributions were determined according to the QSDFT model for slit and cylindrical pores using the adsorption branch for carbon materials.



Figure S 18 Pore size distribution of C**3**, C**1****3**, C**1**\TBAF and C**1**\KF. The pore size distributions were determined according to the QSDFT model for slit and cylindrical pores using the adsorption branch for carbon materials.

EDX analysis of selected materials

EDX analysis of hybrid materials

a)



b)





Figure S 19 Selected EDX analysis of the fluorine-doped hybrid materials a) HM3, b) HM1\3 and c) HM1\TBAF.

Table S 2 EDX-analysis of hybrid materials with resulting fluorine, potassium, silicon, oxygen,carbon and nitrogen contents.

F	К	Si	0	С	Ν
1.49	2.30	1.96	23.13	71.11	/
0.51	1.27	3.41	20.79	74.00	/
0.40	/	3.28	20.31	75.98	0.03
0.34	1.18	1.87	22.32	74.28	/
	F 1.49 0.51 0.40 0.34	F K 1.49 2.30 0.51 1.27 0.40 / 0.34 1.18	FKSi1.492.301.960.511.273.410.40/3.280.341.181.87	FKSiO1.492.301.9623.130.511.273.4120.790.40/3.2820.310.341.181.8722.32	FKSiOC1.492.301.9623.1371.110.511.273.4120.7974.000.40/3.2820.3175.980.341.181.8722.3274.28





b)





Figure S 20 Selected EDX analysis of the fluorine-doped silica materials a) S3_900, b) S1\3_700 and c) S1\TBAF.

Table S 3 EDX-analysis of silica materials with resulting fluorine, potassium, silicon, oxygen,carbon and nitrogen contents.

Atom-%	F	К	Si	0	С	N
S 3 _600	2.29	12.76	17.08	45.04	22.82	/
S 3 _700	0.20	12.59	19.59	46.07	21.54	/
S 3_ 900	0.12	8.83	18.13	56.64	16.27	/
S1\3_600	0.23	1.06	31.86	63.44	3.41	/
S 1∖3 _700	0.24	1.24	32.19	63.04	3.29	/
S 1\3_ 900	0.12	1.07	32.71	61.99	4.12	/
S1\TBAF	0.27	/	33.46	62.40	3.77	0.10
S1\KF	0.21	0.35	32.08	62.67	4.69	/

Material	F:K ratio	F:Si ratio	K:Si ratio
HM3	1:1.5	1:1.3	1:0.9
HM1\3	1:2.5	1:6.6	1:2.7
HM1\TBAF	/	1:8.2	/
HM1\KF	1:3.5	1:5.5	1:1.6

Table S 4 Different ratios of elements within the hybrid materials determined by EDX-analysis.

Table S 5 Different ratios of elements within the silica materials determined by EDX-analysis.

Material	F:K ratio	F:Si ratio	K:Si ratio	
S 3 _600	1:5.6	1:7.5	1:1.3	
S 3 _700	1:61.6	1:95.9	1:1.6	
S 3 _900	1:71.4	1:146.6	1:2.1	
S 1\3_ 600	1:4.6	1:137.8	1:30.1	
S 1\3 _700	1:5.1	1:132.6	1:25.9	
S 1\3_ 900	1:9.2	1:281.9	1:30.5	
S1\TBAF	/	1:122.5	/	
S1\KF	1:1.7	1:154.1	1:91.9	
	l			

Polymerization mechanism of compound 3 and 4



Figure S 21 Reaction cascade as postulated for fluoride-initiated twin polymerization of a) compound **3** and b) compound **4**. Quinone methides and the silicon species [FSi(OR)₂O]⁻ are assumed as reactive intermediates.¹¹

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