# **Supplementary Information**

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# **Materials and Methods**

Diethyl carbonate (>99%), salicylic alcohol (99%) and trifluoroacetic acid (99%) were purchased from Alfa Aesar. *m*-Methoxybenzyl alcohol (98%), tetraethylorthosilicate (99%), tetramethylorthosilicate (98%) and 1,3,5-trioxane (98%) were from ABCR. *p*-Methoxybenzyl alcohol (98%) and caesium carbonate (99.5%) were purchased from Acros. Furfuryl alcohol (98%) was purchased from Merck and distilled before usage. The used surfactant Dabco<sup>®</sup> DC 193 was provided from the BASF SE, Lemförde. It is a silicone polyether surfactant with poly(dimethylsiloxane) backbone and ethyleneoxide oligomers as side chains.

**Differential scanning calorimetry** (DSC) was performed in a 40  $\mu$ L aluminum crucible on a DSC1 from Mettler Toledo. The heating rate was 10 K/min under nitrogen atmosphere (50 mL/min).

The images of **scanning electron microscopy** (SEM) and energy dispersive x-ray spectroscopy were taken with a Nova NanoSEM 200 (FEI company). The sample were sputtered with platinum before measurement.

**Thermogravimetric analysis** were carried out in a platinum crucible on a TGA 7 from Perkin Elmer under synthetic air. The heating rate was 40 K/min. The sample was heated until 800 °C and the end temperature was hold for 10 min.

Solution <sup>1</sup>H- and <sup>13</sup>C-{<sup>1</sup>H}-NMR measurements were performed with a Bruker DPX 250 NMR spectrometer in deuterated chloroform (CDCl<sub>3</sub>).

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). <sup>13</sup>C-{<sup>1</sup>H}-CP-MAS NMR was accomplished in 3.2 mm rotors made of zirconium oxide spinning at 15 kHz. Cross polarization with contact times of 3 ms was used to enhance sensitivity. The recycle delay was 5 s.

<sup>29</sup>Si-{<sup>1</sup>H}-CP-MAS NMR was performed in 3.2 mm rotors spinning at 5 kHz. The contact time was 3 ms and the recycle delay 5 s. All spectra were obtained under <sup>1</sup>H decoupling using a TPPM puls sequence. The spectra are referenced with respect to tetramethyl silane (TMS) using TTSS (tetrakis(trimethylsilyl)silane) as a secondary standard (3.55 ppm for <sup>13</sup>C, -9.5 ppm for <sup>29</sup>Si). If not stated otherwise, all spectra were acquired at room temperature.

**ATR-FTIR** spectra were performed on a FTS 165 spectrometer from BioRad equipped with a Golden Gate single ATR accessory from LOT-Oriel GmbH.

**Nitrogen sorption** measurements were carried out at 77 K on an Autosorb IQ2 from Quantachrome. The samples were outgassed for 2 h at 150 °C in vacuum before measurement. The program ASiQwin 4.0 was used for performing the NLDFT analysis for  $SiO_2$  materials (zylindric pores) and QSDFT analysis for the carbon materials (slit, zylindric pores). The adsorption branch of the isotherms was applied for this analysis. The "micropore BET assistant" was used to determine the maximum relative pressure for BET plot.

The **mercury porosimetry** measurements were performed by using two devices. At first, on the Pascal 140 mercury porosimeter (Thermo Scientific) the pores were studied by filling them in vacuum

increasing the pressure up to ambient pressure. In a second step, the dilatometer with the sample and mercury was displaced in a Porosimeter 2000 (Fisons Instruments) to investigate small pores by filling them with increased pressure up to 2000 bar.

**Raman spectroscopy.** The Raman spectroscopic measurements were performed on materialographic prepared samples with a confocal Raman microscope (50x Leica objektive) "inVia Reflex" from Renishaw. A 100mW frequency-doubled Nd:YAG laser with 532 nm wavelength and a deep depletion CCD array detector (1024 x 256 Pixel) were used.

Measurement of **compressive properties** of hybrid material foams were taken on a Zwick Z 005 testing machine according to the DIN norm EN ISO 844 for hard foam materials. The sample geometry was a cylinder with 15 mm in diameter and 15 mm heights. The foam was cut into 3 pieces, the top, center and bottom part. The upper plate of the testing machine compressed the sample with 0.15 mm per minute.

**Electrical conductivity** was determined with a Voltcraft<sup>®</sup> VC820 multimeter. The resistance of the carbon foam was measured in different distances and converted into the electrical conductivity.

# Synthesis of monomers

The synthesis of organic carbonates were performed by a transesterification of diethyl ether and the respective alcohol using potassium or cesium carbonate ( $K_2CO_3$ ,  $Cs_2CO_3$ ) as catalyst. The procedure was described in the literature<sup>1,2</sup>. The twin monomers (TM) TFOS and Spiro were synthesized by a transesterification of tetraethylorthosilicate and tetramethylorthosilicate with furfuryl alcohol and salicylic alcohol, respectively<sup>3,4</sup>.

# Polymerization

The reactions were performed in a Teflon vessel with round bottom within the monomer melt and the mixture was vigorous stirred to emulsify the released carbon dioxide bubbles. The surfactant (1 wt%) was added to the monomers. The DFC&TFOS mixture is a liquid at room temperature (RT). Thus, the acid catalyst trifluoroacetic acid (TFA) ( $n_{TFA} = (n_{DFC}+n_{TFOS})/10$ ) was added at RT and homogenized for two minutes. After that, the vessel was placed for 4 hours in an 80 °C hot oil bath. Under stirring with a magnetic stir bar.

The polymerization of the *m*C&Spiro mixture was performed accordingly. Except, the monomers have to melt at 100 °C and cooled afterwards for five minutes at RT, before addition of the acid. *p*-toluene sulfonic acid monohydrate (*p*TS) ( $n_{pTS} = (n_{mC} + n_{spiro})/10$ ) was used as acid catalyst. The vessel was removed for four hours to the 100 °C hot oil bath.

*p*C and Spiro were polymerized by melting the substances at 80 °C. The method is analog the polymerization of *m*C and Spiro. The gas development starts immediately after addition of *p*TS ( $n_{pTS} = (n_{pC} + n_{Spiro})/10$ ).

All hybrid material foams were heated until 150 °C (2 K min<sup>-1</sup>) to condensate unreacted groups in the polymer network. The end temperature was hold for 2 hours.

# Production of carbon foam

To obtain  $C/SiO_2$  hybrid foams the organic/SiO<sub>2</sub> foams were heated until 800 °C with a rate of 4.3 K min<sup>-1</sup> under argon atmosphere to convert the organic resin into carbon. The final temperature was hold for 2 hours.

After that, the C/SiO<sub>2</sub> foam was treated with 40 % hydrofluoric acid (HF) for 3 days at RT. The HF solution was filtered off and the material was washed with ethanol and water several times. The carbon foam was dried for 2 day at 110 °C in a vacuum furnace.

# Production of silicon dioxide foam

The organic/SiO<sub>2</sub> hybrid foams were thermally treated with 2 K min<sup>-1</sup> until 900 °C in air atmosphere. The temperature was hold for 3 hours (green oxidation step, Scheme 3 article). The same oxidation program was used for silica production from C/SiO<sub>2</sub> foam (orange oxidation step, Scheme 3 article).

## Preliminary investigations and theoretically considerations of foam density

The calculation of the theoretical density is based on the assumptions that all of the released  $CO_2$  is foam-bound, and the volumetric influence of water is neglected for reasons of simplification. The influence of water on the polymerization and foaming process is somehow difficult to judge because it can hydrolyze the twin monomers and also increase the volume of the foam if temperature exceeds its boiling point. Therefore, the values are probable benchmarks.



Theoretical volume expansion  $1 \rightarrow 12$ 

$$\rho_{Hybrid} = \frac{m_{Hybrid}}{V_{Hybrid}} = \frac{m_{SiO_2} + m_{PFA}}{V_{SiO_2} + V_{PFA} + V_{CO_2}} = \frac{4 \ mol \cdot 60.08 \ \frac{g}{mol} + 18 \ mol \cdot 80.08 \ \frac{g}{mol}}{1233.9 \ mL + 22261 \ mL}$$
$$= 0.072 \ g \cdot mL^{-1}$$

1 mole Spiro + 1 mole DFC $\rightarrow$  2 mole PR + 2 mole PFA + 1 mole SiO2 + 1 mole H2O + 1 mole CO21x272.3 mL + 1x222.2 mL $\rightarrow$  2x81.6 mL + 2x64.1 mL + 26.1 mL + 18 mL+ 22261 mL494.5 mL $\rightarrow$  335.5 mL+ 22261 mLTheoretical volume expansion 1  $\rightarrow$  4646

$$\begin{split} \rho_{Hybrid} &= \frac{m_{Hybrid}}{V_{Hybrid}} = \frac{m_{SiO_2} + m_{PR} + m_{PFA}}{V_{SiO_2} + V_{PR} + V_{PFA} + V_{CO_2}} \\ &= \frac{1 \ mol \cdot 60.08 \ \frac{g}{mol} + 2 \ mol \cdot 106.1 \ \frac{g}{mol} + 2 \ mol \cdot 80.08 \ \frac{g}{mol}}{335.5 \ mL + 22261 \ mL} \\ &= 0.019 \ g \cdot mL^{-1} \end{split}$$

4 mole Spiro + 1 mole DFC $\rightarrow$  8 mole PR + 2 mole PFA + 4 mole SiO2 + 1 mole H2O + 1 mole CO21311.4 mL $\rightarrow$  903.4 mL+ 22261 mLTheoretical volume expansion 1  $\rightarrow$  18

$$\begin{split} \rho_{Hybrid} &= \frac{m_{Hybrid}}{V_{Hybrid}} = \frac{m_{SiO_2} + m_{PR} + m_{PFA}}{V_{SiO_2} + V_{PR} + V_{PFA} + V_{CO_2}} \\ &= \frac{4 \ mol \cdot 60.08 \ \frac{g}{mol} + 8 \ mol \cdot 106.1 \ \frac{g}{mol} + 2 \ mol \cdot 80.08 \ \frac{g}{mol}}{903.4 \ mL + 22261 \ mL} \\ &= 0.0539 \ g \cdot mL^{-1} \end{split}$$

1 mole Spiro + 1 mole mC/pC $\rightarrow$  2 mole PR + 2 mole AR + 1 mole SiO<sub>2</sub> + 1 mole H<sub>2</sub>O+ 1 mole CO<sub>2</sub>1x272.3 mL + 1x302.32 mL $\rightarrow$  2x81.6 mL + 2x92.4 mL + 26.1 mL + 18 mL+ 22261 mL574.62 mL $\rightarrow$  392.1 mL+ 22261 mLTheoretical volume expansion  $1 \rightarrow 40$  $\rightarrow$  0

$$\begin{split} \rho_{Hybrid} &= \frac{m_{Hybrid}}{V_{Hybrid}} = \frac{m_{SiO_2} + m_{PR} + m_{AR}}{V_{SiO_2} + V_{PR} + V_{AR} + V_{CO_2}} \\ &= \frac{1 \ mol \cdot 60.08 \ \frac{g}{mol} + 2 \ mol \cdot 106.1 \ \frac{g}{mol} + 2 \ mol \cdot 120.14 \ \frac{g}{mol}}{392.1 \ mL + 22261 \ mL} \\ &= 0.0226 \ g \cdot mL^{-1} \end{split}$$

4 mole Spiro + 1 mole mC/pC $\rightarrow$  8 mole PR + 2 mole AR + 4 mole SiO<sub>2</sub> + 1 mole H<sub>2</sub>O + 1 mole CO<sub>2</sub>1391.5 mL $\rightarrow$  960 mL+ 22261 mLTheoretical volume expansion  $1 \rightarrow 17$ 

$$\begin{split} \rho_{Hybrid} &= \frac{m_{Hybrid}}{V_{Hybrid}} = \frac{m_{SiO_2} + m_{PR} + m_{AR}}{V_{SiO_2} + V_{PR} + V_{AR} + V_{CO_2}} \\ &= \frac{4 \ mol \cdot 60.08 \ \frac{g}{mol} + 8 \ mol \cdot 106.1 \frac{g}{mol} + 2 \ mol \cdot 120.14 \ \frac{g}{mol}}{960 \ mL + 22261 \ mL} \\ &= 0.0572 \ g \cdot mL^{-1} \end{split}$$

# **Supplementary figures**

### **Preliminary Investigations**



Fig S. 1 DSC measurements of organic carbonates and TMs catalysed with pTS (para-toluenesulfonic acid) and TFA (trifluoroacetic acid).

# Foam production experiments

Tab. S 1 Variation of surfactant concentration – Experiments without surfactant (wS), using 0.2 wt% (0.2wS) and 1 wt%	,
surfactant. The conditions of the performed experiments with molar mass of organic carbonate (Carb), TM and acid, th	е
mass of the surfactant and a picture of the obtained foam.	

sample	molar [mc	mass pl%]	mass [m%]	conditions T [°C] /	picture	
	n <sub>Carb</sub> : n <sub>ZM</sub>	n <sub>Carb+TM</sub> :n <sub>A</sub>	m <sub>Carb.+TM</sub> :m <sub>T</sub>	t [min]	p	
DFC&TFOS_1:1_wS	1:1	1:0.1	-	80 / 240		
DFC&TFOS_1:1_0.2S	1:1	1:0.1	1:0.002	80 / 240		
DFC&TFOS_1:1	1:1	1:0.1	1:0.01	80 / 240		
<i>m</i> C&Spiro_1:1_wS	1:1	1:0.1	-	100 / 240	<u>101</u>	
<i>m</i> C&Spiro_1:1_0.2S	1:1	1:0.1	1 : 0.002	100 / 240	<u>100</u>	
mC&Spiro_1:1	1:1	1:0.1	1:0.01	100 / 240	<u>10</u>	
pC&Spiro_1:1_wS	1:1	1:0.1	-	80 / 240	*	
pC&Spiro_1:1_0.2S	1:1	1:0.1	1:0.002	80 / 240		
pC&Spiro_1:1	1:1	1:0.1	1:0.01	80 / 240		

\* hollow inside the foam



Fig S. 2 SEM pictures of organic/SiO<sub>2</sub> hybrid material foams by polymerization of equimolar rations of organic carbonates DFC, mC and pC with twin monomers TFOS and Spiro without and with 0.2 wt% surfactant.

sample	molar [mc	mass pl%]	mass [m%]	conditions T [°C] / t	picture
	n <sub>Carb</sub> : n <sub>ZM</sub>	$n_{Carb+ZM}:n_A$	m <sub>Carb.+TM</sub> :m <sub>S</sub>	[min]	p
DFC&TFOS_1:2	1:2	1:0.1	1:0.01	80 / 240	
DFC&TFOS_1:4	1:4	1:0.1	1:0.01	80 / 240	G
DFC&TFOS_2:1	2:1	1:0.1	1:0.01	80 / 240	
DFC&Spiro_1:2	1:2	1:0.1	1:0.01	80 / 240	and the second s
DFC&Spiro_1:4	1:4	1:0.1	1:0.01	80 / 240	
DFC&Spiro_1:1	1:1	1:0.1	1:0.01	80 / 240	
mC&Spiro_1:2	1:2	1:0.1	1:0.01	100 / 240	
mC&Spiro_1:4	1:4	1:0.1	1:0.01	100 / 240	Section 2.
<i>m</i> C&Spiro_2:1 <sup>*</sup>	2:1	1:0.1	1:0.01	100 / 240	
pC&Spiro_1:2	1:2	1:0.1	1:0.01	80 / 240	Contract of the second s
pC&Spiro_1:4	1:4	1:0.1	1:0.01	80 / 240	
pC&Spiro_2:1*	2:1	1:0.1	1:0.01	80 / 240	

Tab. S 2 Variation of monomer ratios – conditions of the performed experiments with molar mass of organic carbonate, TM and acid, the mass of the surfactant and a picture of the obtained foam. The surfactant concentration was 1 wt%.

#### **Reference experiments**



Fig S. 3 Images of hybrid materials obtained by polymerization of TMs a) TFOS, b) Spiro and c) TFOS&Spiro\_1:1. The images of foams obtained by polymerization of carbonates d) DFC, e) mC and f) pC.

The cationic polymerization of TFOS with 1 wt% surfactant supplies a monolith (Fig S. 3a) without any volume expansion although water as small molecule was released during the polymerization. The SEM image shows a flat surface, too. Spiro is an ideal twin monomer which polymerizes without condensation of small molecules as by-product<sup>9</sup>. As expected, no chemical foaming under addition of a surfactant occurs (Fig S. 3b). The carbon obtained from both silicon containing TM exhibit an approximate equal micro pore volume and specific surface area of 730 m<sup>2</sup>/g which was determined with nitrogen sorption measurements. Unexpectedly, the combination of both TMs TFOS and Spiro in equal portions leads to a foamed hybrid material (Fig S. 3c) if the surfactant was added. This effect occurs may be due to water releasing and increasing resin viscosity. The obtained carbon shows an increase of surface area to 980 m<sup>2</sup>/g in contrast to the carbon material recieved from homopolymers. If the polymerization of TFOS and Spiro was performed in a precipitation polymerization from toluene a surface area of 1290 m<sup>2</sup>/g can be reached<sup>10,11</sup>.



Scheme S. 1 Possible mesomeric structures of the resonance stabilization of a) the p-methoxybenzyl carbenium ion and b) the m-methoxybenzyl carbenium ion. The carbenium ions were intermediately formed during cationic polymerization of the organic carbonates mC and pC.

### Compressive tests of hybrid material foam

However, to determine the mechanical foam parameters many compressing tests have to be done to get reproducible values because it strongly depends on the foam geometry, the composition of the foam and as well the compressing rate during the experiment<sup>12</sup>. Thus, it is difficult to compare the measured values, for example with those of polyurethane or phenolic foams, which are described in literature<sup>12-14</sup>.

The hybrid material foam  $pC\&Spiro_1:4$  was chosen for compressive test. Test specimen from the bottom, centre and top of the foam were taken for this experiment. The strength against the compressing plate was monitored by compressing the sample with 0.15 mm per minute (10 % of the sample height). The obtained curves show strong fluctuations caused by cell collapse by the bending and buckling of the rigid and inelastic cell walls. As can be seen in Fig S. 4, the curves of the top and the centre of the foam exhibit a similar behaviour during the compressive test.



Fig S. 4 The graphs of the compressive test of pC&Spiro\_1:4 hybrid material foam.

Tab. S 3 The results obtained from the compressive test. The compressive stress at 10 % compressing ( $\sigma$ 10) and the cross-sectional area ( $A_0$ ) of the testing samples.

sample	σ <sub>10</sub> [MPa]	A <sub>0</sub> [mm <sup>2</sup> ]
pC&Spiro_1:4 top	0.1096	252
pC&Spiro_1:4 center	0.1353	246
pC&Spiro_1:4 bottom	0.1928	243

### Investigations of hybrid materials



Fig S. 5 ATR-FTIR spectra of polymers obtained after polymerization of organic carbonates with twin monomers.

The hybrid materials were extracted with DCM for two days. The extractable fractions were investigated by means of liquid <sup>1</sup>H- and <sup>13</sup>C-{<sup>1</sup>H}-NMR spectroscopy using CDCl<sub>3</sub> as solvent. The extracts of the hybrid material foams DFC&TFOS\_1:1 and DFC&Spiro\_1:1 show both in <sup>1</sup>H-NMR spectra defined signals for levulinic acid (Fig S. 4, signal I–V). Extractables from *m*C&Spiro\_1:1 and *p*C&Spiro\_1:1 hybrid materials contain soluble phenolic resin or anisolic resin oligomers. The organic resin species cannot be distinguished in <sup>1</sup>H-NMR spectra because the methoxy group of anisolic resin occurs in the same region as the methylene bridges of connected aromatic rings. The anisolic resin in *p*C&Spiro\_1:1-Ex and *m*C&Spiro\_1:1-Ex is clearly included because signals for carbon atoms of the methoxy group were found in <sup>13</sup>C-{<sup>1</sup>H}-NMR spectra.



Fig S. 6 a) <sup>1</sup>H- and b) <sup>13</sup>C-{<sup>1</sup>H}-NMR spectra (CDCl<sub>3</sub>) of the extracts from the hybrid materials.

## Thermal treatments, silica etching and comparison with calculated composition

Tab. S 4 Results of the thermal treatments and SiO<sub>2</sub> leaching with HF compared to theoretical composition of organic resin/SiO<sub>2</sub> and C/SiO<sub>2</sub> hybrid foams obtained by homopolymerization of twin monomers and carbonates.

sample		mass loss Δm [%]				calculated composition [%]				
	150 °C, Ar	800 °C, Ar	HF	900 °C air	organic	SiO <sub>2</sub>	С	SiO <sub>2</sub>		
TFOS	2	39	25	85	84.2	15.8	74.0	26.0		
Spiro	1	30	29	79	77.9	22.1	68.4	31.6		
TFOS&Spiro_1:1	2	39	31	82	81.6	18.4	69.7	30.3		
DFC	10	51	-	-	100	-	100	-		
mC*	16	37	-	-	100	-	100	-		
pC*	23	50	-	-	100	-	100	-		

\*addition of 1,3,5-trioxane, 250 °C

Tab. S 5 Results of the thermal treatments and SiO<sub>2</sub> leaching with HF compared to theoretical composition of PFA/SiO<sub>2</sub> and C/SiO<sub>2</sub> hybrid foams.

sample		mass loss ∆m [%]					mpositic	on [%]
	150 °C, Ar	800 °C, Ar	HF	900 °C air	PFA	SiO <sub>2</sub>	С	SiO <sub>2</sub>
DFC&TFOS_1:4	6	42	24	86	85.7	14.3	75.3	24.7
DFC&TFOS_1:2	6	45	26	87	87.0	13.0	76.4	23.6
DFC&TFOS_1:1	8	48	20	88	88.9	11.1	78.6	21.4
DFC&TFOS_2:1	5	46	15	91	91.4	8.6	84.1	15.9

Tab. S 6 Results of the thermal treatments and  $SiO_2$  leaching with HF compared to theoretical composition of PR/PFA/SiO<sub>2</sub> and C/SiO<sub>2</sub> hybrid foams.

sample		mass loss ∆m [%]					position	ı [%]
	150 °C, Ar	800 °C, Ar	HF	900 °C air	organic	SiO <sub>2</sub>	С	SiO <sub>2</sub>
DFC&Spiro_1:1	7	45	25	86	86.1	13.9	74.6	25.4
DFC&Spiro_1:2	3	41	27	84	82.9	17.1	71.3	28.7
DFC&Spiro_1:4	3	37	28	90	80.8	19.2	69.6	30.4

Tab. S 7 Results of the thermal treatments and  $SiO_2$  leaching with HF compared to theoretical composition of PR/AR/SiO<sub>2</sub> and C/SiO<sub>2</sub> hybrid foams obtained by polymerization of mC and Spiro.

sample	mass loss ∆m [%]				calculated composition [%]			
	150 °C, Ar	800 °C, Ar	HF	900 °C air	organic	SiO <sub>2</sub>	С	SiO <sub>2</sub>
mC&Spiro_1:4	2	24	27	82	79.7	20.3	73.4	26.6
mC&Spiro_1:2	4	31	25	83	81.9	18.1	73.7	26.3
mC&Spiro_1:1	3	42	21	86	84.7	15.3	73.7	26.3
mC&Spiro_2:1*	4	52	23	89	88.3	11.7	75.6	24.4

\*addition of 1,3,5-trioxane

Tab. S 8 Results of the thermal treatments and SiO<sub>2</sub> leaching with HF compared to theoretical composition of PR/AR/SiO<sub>2</sub> and C/SiO<sub>2</sub> hybrid foams obtained by polymerization of pC and Spiro.

sample	mass loss Δr	calculated composition [%]						
	150 °C, Ar	800 °C <i>,</i> Ar	HF	900 °C air	organic	SiO <sub>2</sub>	С	SiO <sub>2</sub>
pC&Spiro_1:4	4	36	29	84	79.7	20.3	71.9	28.1
pC&Spiro_1:2	2	42	27	86	81.9	18.1	73.7	26.3
pC&Spiro_1:1	6	47	24	89	84.7	15.3	77.7	22.3
pC&Spiro_2:1*	4	51	16	93	88.3	11.7	83.7	16.3

<sup>\*</sup>addition of 1,3,5-trioxane







Fig S. 7 Comparison of the composition of a) the organic/ SiO<sub>2</sub> hybrid material and b) C/SiO<sub>2</sub> material determined by TG analysis and thermal treatment in furnace, respectively in air at 900 °C and by determining the residue (R) after HF treatment. The content of the components were compared with theoretical calculated compositions.



Fig S. 8 EDX mapping of PFA/SiO<sub>2</sub> hybrid foams obtained by polymerization of DFC and TFOS. The elemental distribution of carbon (blue) and silica (red) was mapped.



Fig S. 9 EDX mapping of  $AR/SiO_2$  hybrid foams obtained by polymerization of mC and Spiro. The elemental distribution of carbon (blue) and silica (red) was mapped.



Fig S. 10 EDX mapping of AR/SiO<sub>2</sub> hybrid foams obtained by polymerization of pC and Spiro. The elemental distribution of carbon (blue) and silica (red) was mapped.

### Porosity measurements – nitrogen sorption measurements

The surfactant concentration has no influence on the pore size distribution (QSDFT), specific surface area and pore volume of micro- and mesopores in the respective carbon material.



Fig S. 11 The isotherms (inset) from the nitrogen measurements at 77 K of the carbon material produced from polymerization of a) DFC with TFOS, b) mC with Spiro and c) pC with Spiro. The polymerizations were performed in equal molar ratios of the monomers, without surfactant, 0.2 wt% and 1 wt% surfactant concentration. The cumulative pore volume and pore size distribution obtained after calculation with QSDFT and NLDFT method for carbon and silicon dioxide, respectively were show.

Tab. S 9 Results of the nitrogen sorption measurements from carbon foams obtained with different surfactant concentrations and without surfactant.

sample	V <sub>pore</sub> C Q [cm <sup>3</sup> g	SDFT <sup>-1</sup> ]	S <sub>g</sub> <b>C</b> [m <sup>2</sup> g <sup>-1</sup> ]		
	$V_{\text{total}}$	V <sub>micro</sub>	BET	DFT	
DFC&TFOS_1:1_wS_	0.288	0.180	639	638	
DFC&TFOS_1:1_0.2S_	0.334	0.195	676	747	
DFC&TFOS_1:1_	0.280	0.179	629	636	
mC&Spiro_1:1_wS_	0.351	0.276	828	905	
mC&Spiro_1:1_0.2S_	0.371	0.279	847	943	
mC&Spiro_1:1_	0.341	0.239	779	821	
pC&Spiro_1:1_wS_	0.371	0.273	856	958	
pC&Spiro_1:1_0.2S_	0.381	0.292	881	1017	
pC&Spiro_1:1_	0.401	0.246	829	942	

Tab. S 10 Results of the nitrogen sorption measurements from  $SiO_2$  and carbon foams obtained with equal molar monomer ratios and addition of 1 wt% surfactant.

sample	V <sub>pore</sub> C QSD	FT [cm <sup>3</sup> g <sup>-1</sup> ]	S <sub>g</sub> <b>C</b> [n	n²g⁻¹]	V <sub>pore</sub> SiO <sub>2</sub> NLDFT [cm <sup>3</sup> g <sup>-1</sup> ]	S <sub>g</sub> <b>SiO<sub>2</sub></b> [m <sup>2</sup> g <sup>-1</sup>	
	$V_{\text{total}}$	V <sub>micro</sub>	BET	ET DFT V <sub>total</sub>		BET	DFT
TFOS_TFA_	0.386	0.174	761	730	0.286	484	350
DFC&TFOS_1:1_	0.280	0.179	629	636	0.401	444	308
Spiro_TFA_	0.428	0.160	764	730	0.370	519	376
DFC&Spiro_1:1_	0.565	0.306	1105	1195	0.205	238	163
Spiro_pTS_	0.469	0.335	1057	1110	0.180	322	264
mC&Spiro_1:1_	0.341	0.239	779	821	0.390	482	354
pC&Spiro_1:1_	0.401	0.246	829	942	0.117	116	68

 $V_{pore}$  ... pore volume;  $S_g$  ... spezific surface area



Fig S. 12 The isotherms from the nitrogen measurements at 77 K of the carbon and silicon dioxide foams from DFC&TFOS under addition of 1 wt% surfactant. The cumulative pore volume and pore size distribution obtained after calculation with QSDFT and NLDFT method for carbon and silicon dioxide, respectively.

Sample	V <sub>pore</sub> C QSDFT [cm <sup>3</sup> /g]		Vpore SiO <sub>2</sub> NI	S <sub>g</sub> <b>C</b> [m <sup>2</sup> /g]		S <sub>g</sub> <b>SiO<sub>2</sub></b> [m <sup>2</sup> /g]		
	$V_{\text{total}}$	V <sub>micro</sub>	$V_{\text{total}}$	V <sub>micro</sub>	BET	DFT	BET	DFT
DFC&TFOS_1:4_	0.373	0.161	0.346	0.010	674	660	548	399
DFC&TFOS_1:2_	0.180	0.062	0.369	-	279	241	522	369
DFC&TFOS_1:1_	0.280	0.179	0.292	-	629	636	405	308
DFC&TFOS 2:1	0.329	0.124	0.390	0.011	532	562	588	431

Tab. S 11 Results of the nitrogen sorption measurements from  $SiO_2$  and carbon foams obtained with different molar monomer ratios of DCF and TFOS and addition of 1 wt% surfactant.



Fig S. 13 The isotherms from the nitrogen measurements at 77 K of the carbon and silicon dioxide foams from DFC&Spiro under addition of 1 wt% surfactant. The cumulative pore volume and pore size distribution obtained after calculation with QSDFT and NLDFT method for carbon and silicon dioxide, respectively.

Tab. S 12 Results of the nitrogen sorption measurements from $SiO_2$ and carbon foams obtained with different molar	
monomer ratios of DCF and Spiro and addition of 1 wt% surfactant.	

Sample	V <sub>pore</sub> C QSDFT [cm <sup>3</sup> /g]		Vpore SiO <sub>2</sub> NLDFT [cm <sup>3</sup> /g]		S <sub>g</sub> <b>C</b> [m <sup>2</sup> /g]		S <sub>g</sub> <b>SiO</b> <sub>2</sub> [m <sup>2</sup> /g]	
	$V_{\text{total}}$	V <sub>micro</sub>	$V_{\text{total}}$	V <sub>micro</sub>	BET	DFT	BET	DFT
DFC&Spiro_1:4_	0.446	0.347	0.413	0.124	1059	1094	834	710
DFC&Spiro_1:2_	0.432	0.315	0.506	0.077	999	1034	945	737
DFC&Spiro_1:1_	0.580	0.306	0.205	-	1105	1194	238	163



Fig S. 14 The isotherms (a, c) from the nitrogen measurements at 77 K of the carbon and silicon dioxide foams from mC&Spiro under addition of 1 wt% surfactant. The cumulative pore volume and pore size distribution obtained after calculation with QSDFT (b) and NLDFT (d) method for carbon and silicon dioxide, respectively.

Sample	V <sub>pore</sub> C QSDFT [cm <sup>3</sup> /g]		Vpore SiO <sub>2</sub> NI	S <sub>g</sub> <b>C</b> [m <sup>2</sup> /g]		S <sub>g</sub> <b>SiO<sub>2</sub></b> [m <sup>2</sup> /g]		
	$V_{\text{total}}$	V <sub>micro</sub>	$V_{\text{total}}$	V <sub>micro</sub>	BET	DFT	BET	DFT
mC&Spiro_1:4_	0.433	0.373	0.124	0.010	1068	1231	162	136
mC&Spiro_1:2_	0.321	0.249	0.160	0.034	788	631	268	245
mC&Spiro_1:1_	0.341	0.239	0.390	0.005	779	821	482	354
mC&Spiro 2:1	0.082	0.041	0.592	-	164	120	464	368

Tab. S 13 Results of the nitrogen sorption measurements from  $SiO_2$  and carbon foams obtained with different molar monomer ratios of mC and Spiro and addition of 1 wt% surfactant.



Fig S. 15 The isotherms (a, c) from the nitrogen measurements at 77 K of the carbon and silicon dioxide foams from pC&Spiro under addition of 1 wt% surfactant. The cumulative pore volume and pore size distribution obtained after calculation with QSDFT (b) and NLDFT (d) method for carbon and silicon dioxide, respectively.

Sample	V <sub>pore</sub> C QSDFT [cm <sup>3</sup> /g]		Vpore SiO <sub>2</sub> NI	S <sub>g</sub> <b>C</b> [m <sup>2</sup> /g]		S <sub>g</sub> <b>SiO<sub>2</sub></b> [m <sup>2</sup> /g]		
	$V_{\text{total}}$	V <sub>micro</sub>	$V_{\text{total}}$	V <sub>micro</sub>	BET	DFT	BET	DFT
pC&Spiro_1:4_	0.362	0.362	0.015	-	960	1057	13	9
pC&Spiro_1:2_	0.384	0.314	0.066	0.001	931	1031	83	62
pC&Spiro_1:1_	0.401	0.246	0.117	-	829	942	116	68
pC&Spiro 2:1	0.280	0.175	0.390	-	605	678	305	228

Tab. S 14 Results of the nitrogen sorption measurements from  $SiO_2$  and carbon foams obtained with different molar monomer ratios of pC and Spiro and addition of 1 wt% surfactant.

### Raman spectra of carbon foams

The Raman spectra of carbons obtained from hybrid materials, which were synthesized by cationic polymerization of **Spiro** and **TFOS** with TFA, were measured. They show typical D and G band for amorphous carbon with broad peaks. The ratio I(D)/I(G) is in both spectra 0.80. This means a higher intensity of the G band which is characteristic for the graphite like carbon.



Fig S. 16 The Raman spectra of carbon materials obtained from hybrid material, which was synthesized by cationic polymerization of Spiro an TFOS with TFA.

### **Electrical conductivity**

The electrical conductivity was determined according to a methodology described in literature<sup>15</sup>. The resistant was measured in different distances on the surface of the carbon foam  $pC\&Spiro_1:4_C$  and converted by inverting into the electrical conductivity (Tab. S 15). A similar electrical conductivity as for carbon foams in literature<sup>15</sup> were found.

Tab. S 15 Result of the resistance measurement performed with digital multimeter in three-centimetre distance of the carbon foam  $pC\&Spiro_1:4\_C$ .

resistant [Ω]	distance [cm]	spezific resistance [ $\Omega$ cm <sup>-1</sup> ]	conductivity [S cm <sup>-1</sup> ]
17	1	17	0.059
21	2	10.5	0.095
31	3	10.3	0.097

### Porosity measurements - mercury porosimetry

Tab. S 16 Results from the mercury porosimetry of the carbon and SiO<sub>2</sub> obtained from hybrid material of TMs and DFC.

Sample	$\rho_{\text{bulk}}  \boldsymbol{C}$	ε <b>C</b>	ρ <sub>bulk</sub> SiO <sub>2</sub>	ε <b>SiO</b> 2
	[g/cm <sup>3</sup> ]	[%]	[g/cm <sup>3</sup> ]	[%]
DFC_TFA_	0.15	85	-	-
TFOS_TFA_	0.86	12	0.48	24
Spiro_TFA_	1.11	5	0.85	51



Fig S. 17 Pore size distribution and cumulative pore volume of the mercury porosimetry measurements from carbon and silica foams obtained by polymerization of carbonates and twin monomer in equal ratios.



Fig S. 18 Intrusion and extrusion curves of SiO<sub>2</sub> and carbon foams obtained by mercury porosimetry.

Tab. S 17 Results from the mercury porosimetry of the carbon and  $SiO_2$  foams obtained from hybrid foams.

Sample	V <sub>pore</sub> <b>C</b> [cm <sup>3</sup> g <sup>-1</sup> ]	ρ <sub>bulk</sub> <b>C</b> [g cm <sup>-3</sup> ]	ε <b>C</b> [%]	V <sub>pore</sub> SiO <sub>2</sub> [cm <sup>3</sup> g <sup>-1</sup> ]	ρ <sub>bulk</sub> SiO <sub>2</sub> [g cm <sup>-3</sup> ]	ε <b>SiO₂</b> [%]
DFC&TFOS_1:4_	0.5	0.86	46	1.1	0.66	73
DFC&Spiro_1:4_	0.9	0.66	59	0.7	0.99	69
mC&Spiro_1:4_	2.3	0.31	72	2.0	0.40	80
pC&Spiro_1:4_	5.6	0.15	86	3.6	0.25	90



Fig S. 19 Comparison of pore size distribution measured with Hg-porosimetry of carbon and silica foams obtained from ratio 1:1 and 1:4 of methoxybenzyl carbonates to Spiro.

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