

Electronic Supplementary Information

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Porous titanium and zirconium oxo carboxylates at the interface between sol-gel and metal-organic framework structures

Table S1: Stoichiometric ratios and proportions of reagents used in the reactions

TiO_BT3:

Ti/COOH/H ₂ O ratio	Ti(O ⁱ Pr) ₄	BTB3	H ₂ O
1:1:2	0.15 ml (0.50 mmol)	72 mg (0.165 mmol)	18 μl (0.99 mmol)
1:1:4	0.15 ml (0.50 mmol)	72 mg (0.165 mmol)	36 μl (1.98 mmol)
2:1:4	0.3 ml (0.99 mmol)	72 mg (0.165 mmol)	36 μl (1.98 mmol)
2:1:8	0.3 ml (0.99 mmol)	72 mg (0.165 mmol)	72 μl (3.96 mmol)
3:1:6	0.225 ml (0.74 mmol)	36 mg (0.083 mmol)	27 μl (1.49 mmol)
3:1:12	0.225 ml (0.74 mmol)	36 mg (0.083 mmol)	54 μl (2.97 mmol)
4:1:8	0.3 ml (0.99 mmol)	36 mg (0.083 mmol)	36 μl (1.98 mmol)
4:1:16	0.3 ml (0.99 mmol)	36 mg (0.083 mmol)	72 μl (3.96 mmol)
6:1:12	0.45 ml (1.49 mmol)	36 mg (0.083 mmol)	54 μl (2.97 mmol)
6:1:24	0.45 ml (1.49 mmol)	36 mg (0.083 mmol)	107 μl (5.94 mmol)

TiO_TCB:

Ti/COOH/H ₂ O ratio	Ti(O ⁱ Pr) ₄	TCB	H ₂ O
1:1:2	0.2 ml (0.66 mmol)	46 mg (0.22 mmol)	24 μl (1.32 mmol)
1:1:4	0.2 ml (0.66 mmol)	46 mg (0.22 mmol)	48 μl (2.64 mmol)
2:1:4	0.4 ml (1.32 mmol)	46 mg (0.22 mmol)	48 μl (2.64 mmol)
2:1:8	0.4 ml (1.32 mmol)	46 mg (0.22 mmol)	96 μl (5.28 mmol)
3:1:6	0.6 ml (1.98 mmol)	46 mg (0.22 mmol)	72 μl (3.96 mmol)
4:1:8	0.8 ml (2.64 mmol)	46 mg (0.22 mmol)	96 μl (5.28 mmol)
6:1:12	1.2 ml (3.96 mmol)	46 mg (0.22 mmol)	144 μl (7.92 mmol)

TiO_BTBA:

Ti/COOH/H ₂ O ratio	Ti(O ⁱ Pr) ₄	BTB4	H ₂ O
1:1:2	0.1 ml (0.33 mmol)	46 mg (0.083 mmol)	12 µl (0.66 mmol)
1:1:4	0.1 ml (0.33 mmol)	46 mg (0.083 mmol)	24 µl (1.32 mmol)
2:1:4	0.2 ml (0.66 mmol)	46 mg (0.083 mmol)	24 µl (1.32 mmol)
2:1:8	0.2 ml (0.66 mmol)	46 mg (0.083 mmol)	48 µl (2.64 mmol)
3:1:6	0.3 ml (0.99 mmol)	46 mg (0.083 mmol)	36 µl (1.98 mmol)
3:1:12	0.3 ml (0.99 mmol)	46 mg (0.083 mmol)	72 µl (3.96 mmol)
4:1:8	0.4 ml (1.32 mmol)	46 mg (0.083 mmol)	48 µl (2.64 mmol)
4:1:16	0.4 ml (1.32 mmol)	46 mg (0.083 mmol)	96 µl (5.28 mmol)
6:1:12	0.6 ml (1.49 mmol)	36 mg (0.083 mmol)	72 µl (3.96 mmol)

TiO_TCPS:

Ti/COOH/H ₂ O ratio	Ti(O ⁱ Pr) ₄	TCPS	H ₂ O
1:1:2	0.1 ml (0.33 mmol)	42 mg (0.083 mmol)	12 µl (0.66 mmol)
1:1:4	0.1 ml (0.33 mmol)	42 mg (0.083 mmol)	24 µl (1.32 mmol)
2:1:4	0.2 ml (0.66 mmol)	42 mg (0.083 mmol)	24 µl (1.32 mmol)
2:1:8	0.2 ml (0.66 mmol)	42 mg (0.083 mmol)	48 µl (2.64 mmol)
3:1:6	0.3 ml (0.99 mmol)	42 mg (0.083 mmol)	36 µl (1.98 mmol)
3:1:12	0.3 ml (0.99 mmol)	42 mg (0.083 mmol)	72 µl (3.96 mmol)
4:1:8	0.4 ml (1.32 mmol)	42 mg (0.083 mmol)	48 µl (2.64 mmol)
4:1:16	0.4 ml (1.32 mmol)	42 mg (0.083 mmol)	96 µl (5.28 mmol)

ZrO_BTBA3:

Zr/COOH/H ₂ O ratio	Zr(O ⁱ Pr) ₄ ·(<i>i</i> PrOH)	BTB3	H ₂ O
1:1:2	96 mg (0.25 mmol)	36 mg (0.083 mmol)	9 µl (0.496 mmol)
1:1:4	96 mg (0.25 mmol)	36 mg (0.083 mmol)	18 µl (0.99 mmol)
2:1:4	192 mg (0.50 mmol)	36 mg (0.083 mmol)	18 µl (0.99 mmol)
2:1:8	192 mg (0.50 mmol)	36 mg (0.083 mmol)	36 µl (1.98 mmol)
3:1:6	288 mg (0.74 mmol)	36 mg (0.083 mmol)	27 µl (1.485 mmol)
3:1:12	288 mg (0.74 mmol)	36 mg (0.083 mmol)	54 µl (2.97 mmol)
4:1:8	384 mg (0.99 mmol)	36 mg (0.083 mmol)	36 µl (1.98 mmol)
4:1:16	384 mg (0.99 mmol)	36 mg (0.083 mmol)	72 µl (3.96 mmol)

Table S2: Summary of microporous surface areas of TiO₂ carboxylates.

<i>TiO₂_TCB</i>										
Ti:COOH:H₂O	1:1:2	1:1:4	2:1:4	2:1:8	9:1:18	12:1:24	18:1:36			
S_{t-plot} [m²/g]	199.6	203.6	214.5	221.2	227.7	247.6	232.2			
<i>TiO₂_BTB3</i>										
Ti:COOH:H₂O	1:1:2	1:1:4	2:1:4	2:1:8	3:1:6	3:1:12	4:1:8	4:1:16	6:1:12	6:1:24
S_{t-plot} [m²/g]	280.6	336.8	303.4	277.3	256.2	226.5	256.2	276.3	149.8	205.8
<i>Ti₂_BTB4</i>										
Ti:COOH:H₂O	1:1:2	1:1:4	2:1:4	2:1:8	3:1:6	3:1:12	4:1:8	4:1:16	6:1:12	
S_{t-plot} [m²/g]	191.6	284.1	183.5	267.4	191.0	282.2	199.0	246.7	195.5	
<i>TiO₂_TCPS</i>										
Ti:COOH:H₂O	1:1:2	1:1:4	2:1:4	2:1:8	3:1:6	3:1:12	4:1:8	4:1:16		
S_{t-plot} [m²/g]	297.1	174.5	271.3	0	207.5	31.2	223.9	114.5		

Table S3: Summary of microporous surface areas of ZrO₂ BTB3.

<i>ZrO₂_BTB3</i>									
Zr:COOH:H₂O	1:1:2	1:1:4	2:1:4	2:1:8	3:1:6	3:1:12	4:1:8	4:1:16	
S_{t-plot} [m²/g]	267.4	254.4	212.4	192.8	93.1	120.7	158.5	141.2	

Fig. S1 IR spectra of TiO_TCB with a Ti:H₂O ratio of 1:2 and varying Ti:COOH ratios.

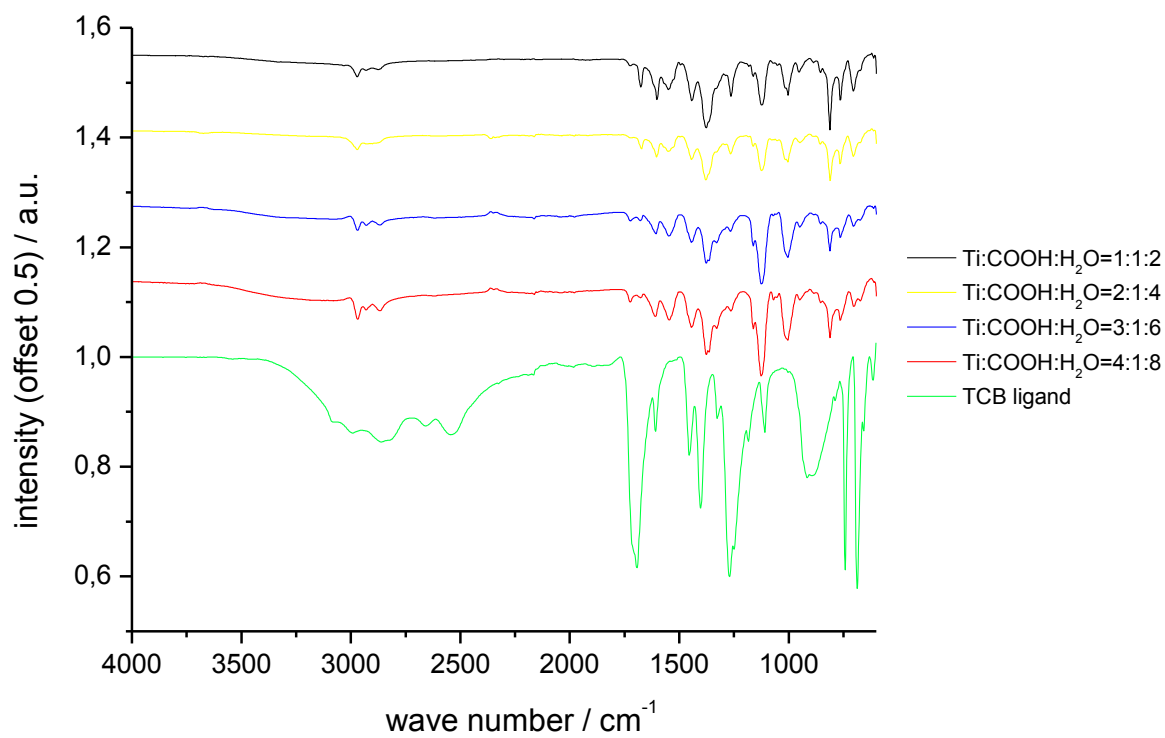


Fig. S2 SAXS patterns of TiO_BT3 with varying Ti:COOH ratios (the SAXS patterns are plotted with an offset of 60% on the y axis). The experimental data are depicted as lines and not as symbols for clarity. Solid lines: Ti:H₂O ratio = 1:2; dotted lines: Ti:H₂O ratio = 1:4 (Note that samples with a Ti:COOH ratio of 1:1 are also included, different to the TiO_BT4 samples in Fig. 6).

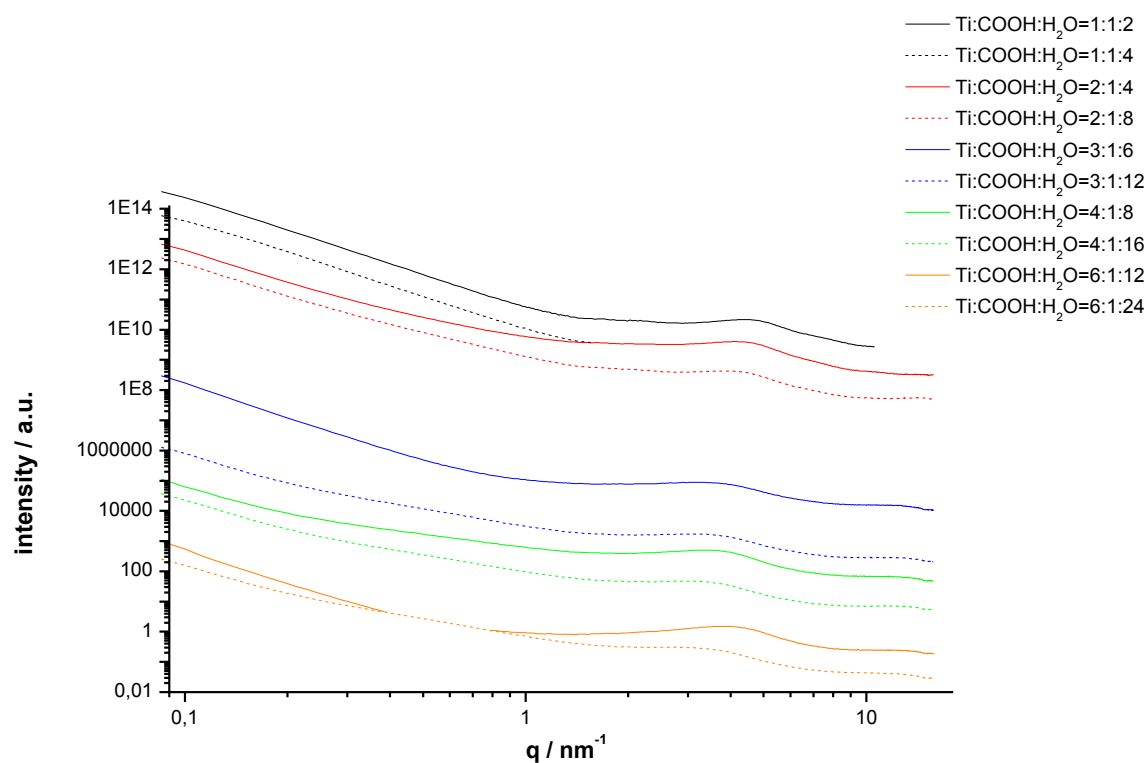


Fig. S3 Fractal dimension (top), hard sphere volume fraction (center) and distance d_{HS} (bottom) for TiO_BT3.

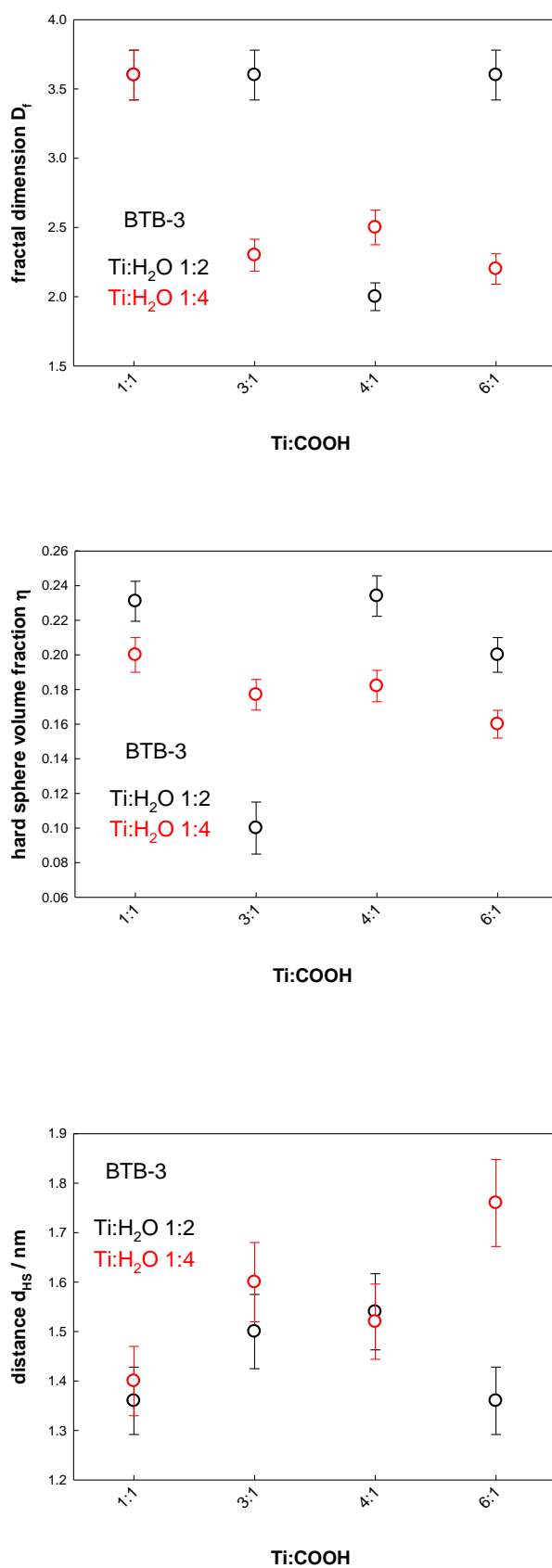


Fig. S4 Fractal dimension (top), hard sphere volume fraction (center) and distance d_{HS} (bottom) for TiO_TCB.

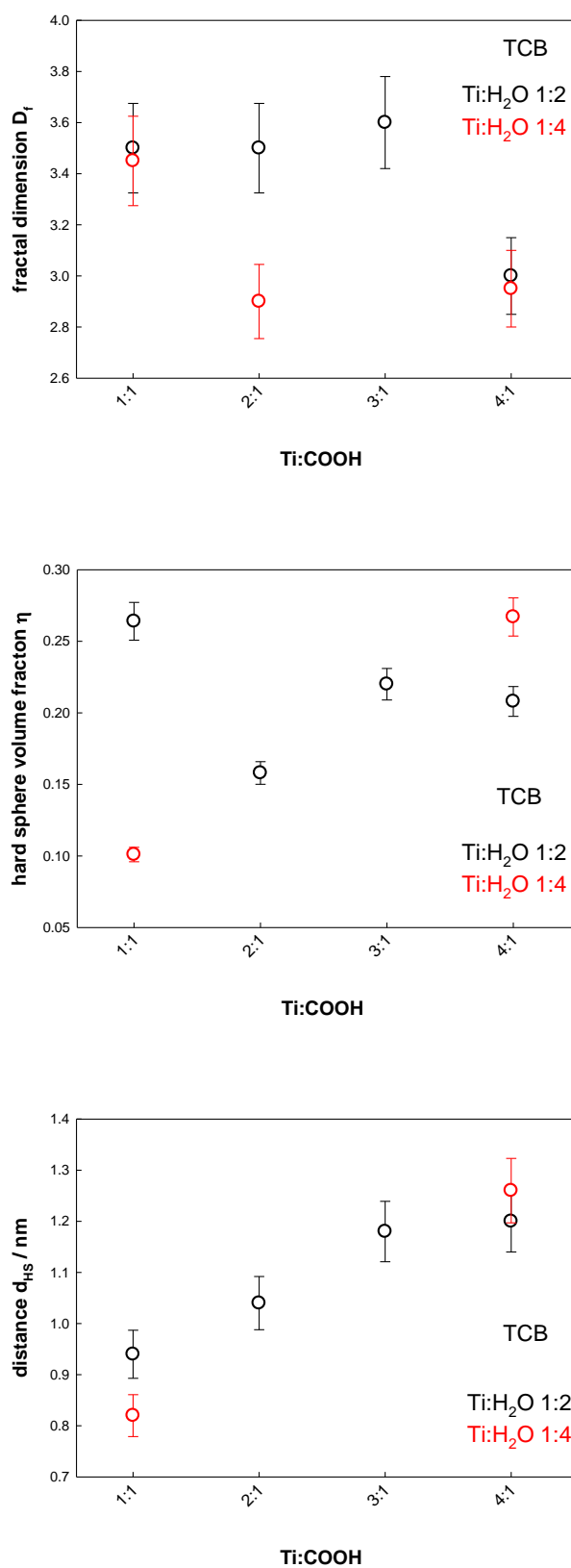
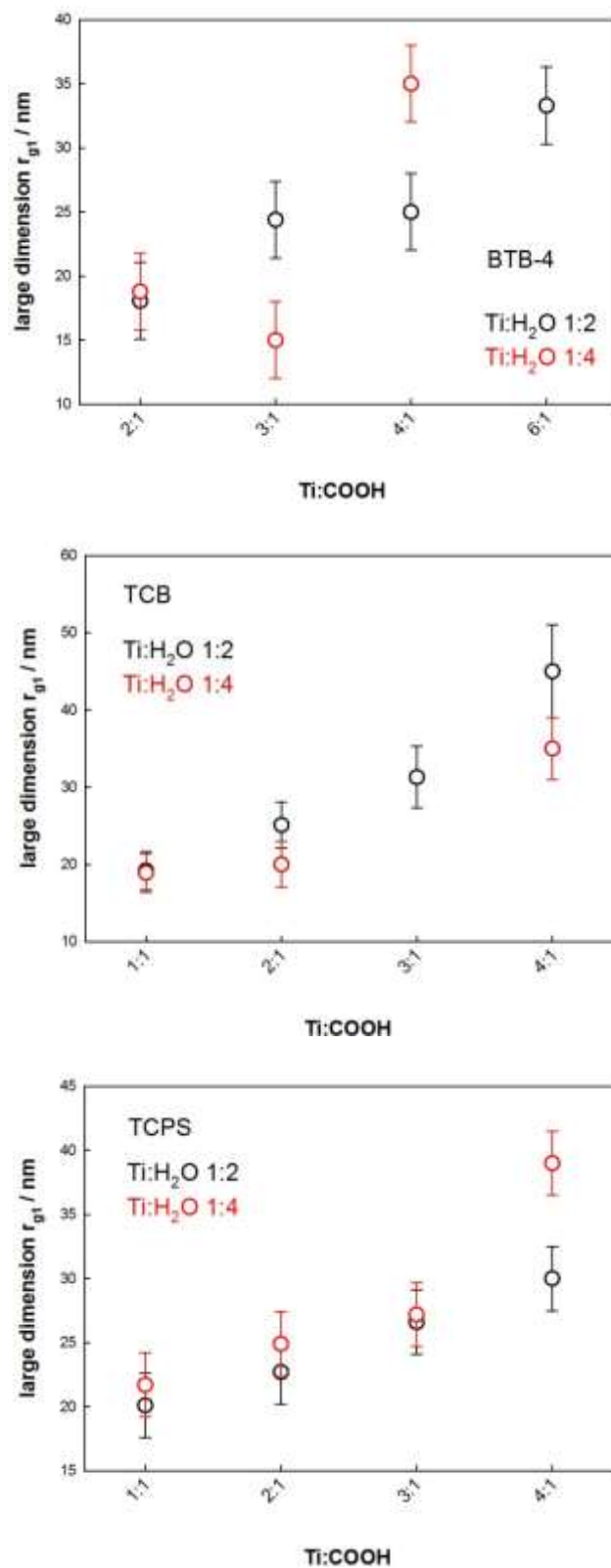


Fig. S5 Radius of gyration r_{g1} of the large dimension of the structure in dependence of the water proportion for TiO_BTb4, TiO_BTb3, TiO_TCPS, and ZrO_BTb3.



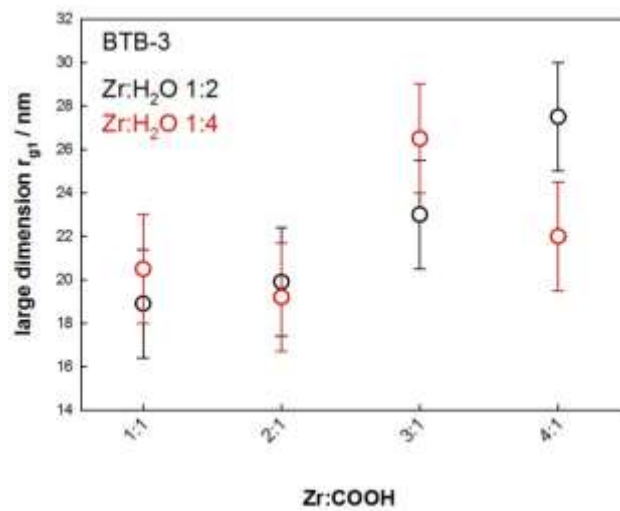


Fig. S6 Fractal dimension (top), hard sphere volume fraction (center) and distance d_{HS} (bottom) for TiO_TCPS.

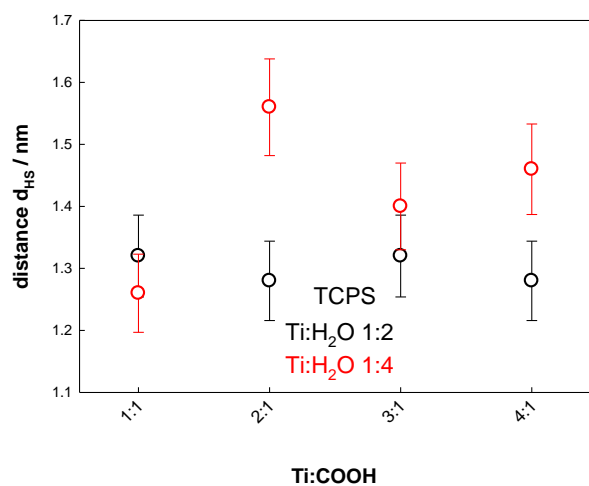
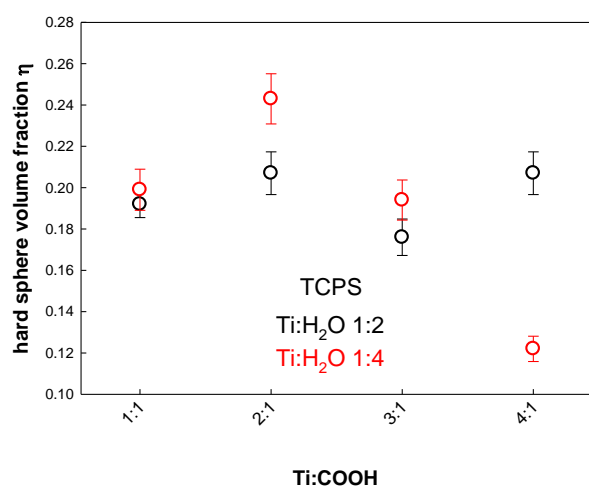
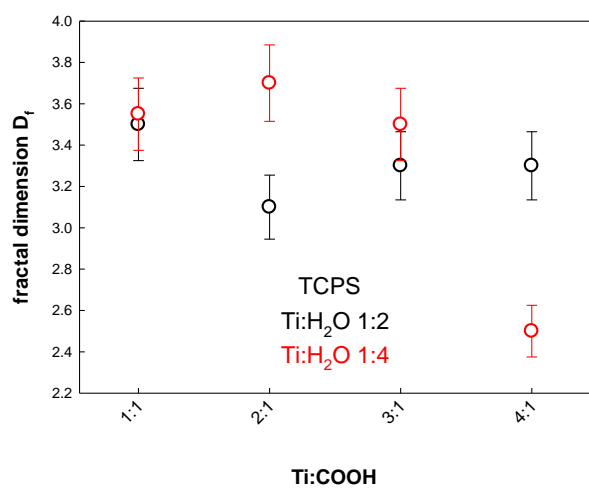


Fig. S7 IR spectra of ZrO_BT3 with Zr:H₂O ratios of 1:2 and varying Zr:COOH ratios.

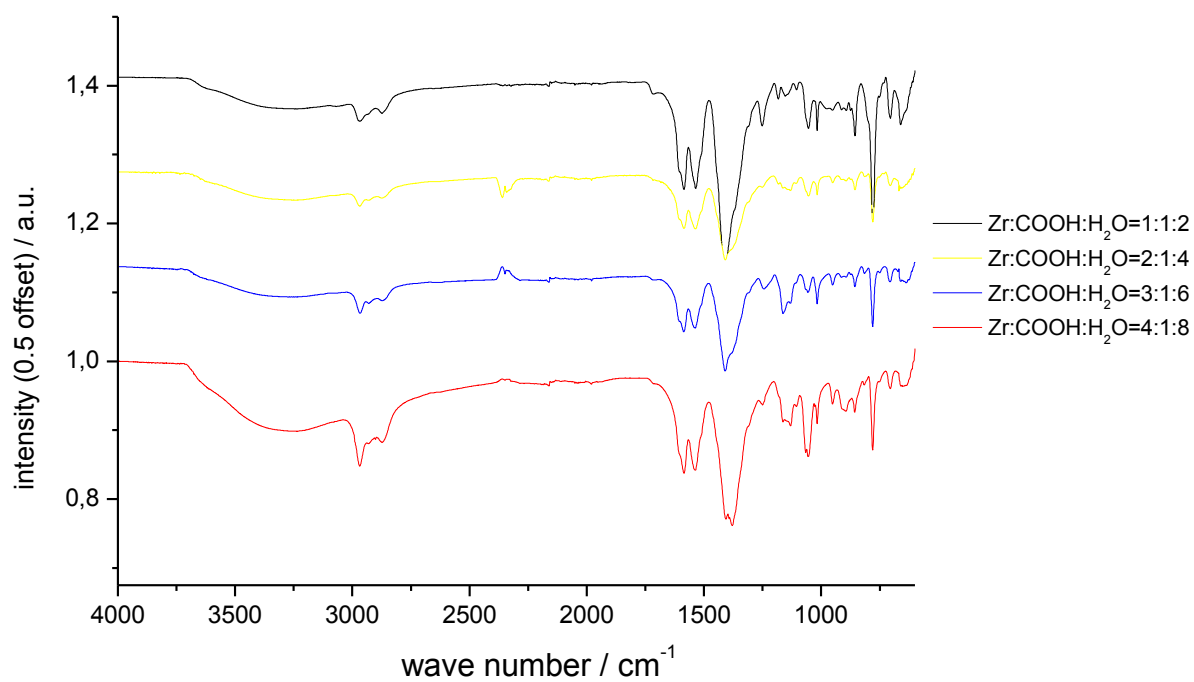


Fig. S8 Fractal dimension (top), hard sphere volume fraction (center) and distance d_{HS} (bottom) for ZrO_BT3.

