Supporting Information

Porous Organic-Inorganic Hybrid Aerogels Based on Cr^{3+}/Fe^{3+} and Rigid Bridging Carboxylates

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Table S1. Gelation tests of $Fe(NO_3)_3 \cdot 9H_2O$ and various ligands.[a]

Ligand	H_3BTC	H_2BDC[b]	H_2BPDC	H_2FDC	H_3BTB	H_2BuDC	H_2ADC
Fe:L	1.5:1	1:1	1:1	1:1	1:1	1:1	1:1
Solvent	EtOH	EtOH-DMF	EtOH-DMF	EtOH	EtOH-DMF	EtOH	EtOH-DMF
c/mol L^{-1}	0.2	0.2	0.1	0.2	0.1	0.1	0.05
Result	**gel**	**gel**	ppt	**gel**	ppt	**gel**	ppt
Time	5 s	10 min		5 min		5 min	

Ligand	H_2NDC	H_2FDC	H_2FDC	H_4aobtc	$H_2(4\text{-Py})DC$	$H_2(4\text{-Py})DC$	$H_2(3\text{-Py})DC$
Fe:L	1:1	1:1	1:1	1.33:1	1.5:1	2:1	1.5:1
Solvent	EtOH	EtOH	EtOH-H_2O	DMF	DMF-H_2O	DMF-H_2O	DMF-H_2O
c/mol L^{-1}	0.1	0.1	0.1	0.075	0.02	0.02	0.02
Result	ppt	**gel**	**gel**	**gel**	**gel**	**gel**	**gel**
Time		1 min	1 min	1 d	1 d	1 d	1 d

[a] All the tests were performed at RT unless otherwise stated. [b] FeBDC gel was formed at 80 °C. [c] ppt = precipitate.

Table S2. Gelation tests of $Cr(NO_3)_3 \cdot 9H_2O$ and various ligands at 80 °C.

Ligand	H_2BDC	H_2BPDC	H_2FDC	H_3BTB	H_2BuDC	$H_2(4\text{-PyDC})$	$H_2(3\text{-Py})DC$	H_2ADC	H_2NDC
Cr:L	0.67:1	0.67:1	0.67:1	1:1	0.67:1	1:1	1:1	0.67:1	0.67:1
Solvent	EtOH-DMF	EtOH-DMF	EtOH	EtOH-DMF	EtOH	EtOH-DMF	EtOH-DMF	EtOH	EtOH
c/mol L^{-1}	0.2	0.1	0.8	0.1	0.4	0.04	0.04	0.3	0.1
Result	**gel**	ppt	**gel**	**gel**	**gel**	**gel**	**gel**	**gel**	**gel**
Time	12 h		1 d	12h	4h	12h	12h	0.5h	12h

[a] *c* is based on the ligand. [b] ppt = precipitate.

Table S3. Gelation tests of $Cr(NO_3)_3 \cdot 9H_2O$ and H_3BTC (Cr:BTC = 1:1) in various solvents and concentrations at 80 °C.

Solvent	EtOH	EtOH	EtOH	EtOH	EtOH	EtOH	EtOH	EtOH	EtOH
c/mol L^{-1}	0.8	0.6	0.4	0.2	0.1	0.05	0.04	0.03	0.025
Result	**gel**	**gel**	**gel**	**gel**	weak gel	weak gel	weak gel	sticky solution	sticky solution
Time	4 h	4 h	3 h	4 h	overnight	1 d	2 d	4 d	4 d

Solvent	DMF	DMF-MeCN-H_2O	DMF-MeCN-MeOH
c/mol L^{-1}	0.08	0.08	0.08
Result	**gel**	**gel**	**gel**
Time	2 d	3 h	6 h

[a] *c* is based on the ligand.

Table S4. Gelation tests of $Cr(NO_3)_3 \cdot 9H_2O$ and BDC (Cr:BDC = 0.67:1) in different solvents at 80 °C.

Solvent	EtOH -DMF (3:2)	EtOH -DMF (6:5)	EtOH -DMF (1:2)	EtOH -DMF (2:5)	DMF	EtOH-DMF (1:2)
c/mol L^{-1}	0.06	0.11	0.1	0.17	0.3	0.2
Result	**gel**	**gel**	**gel**	**gel**	**gel**	**gel**
Time	6 h	1.5 d	overnight	overnight	2 d	overnight

[a] *c* is based on the ligand.

Table S5. Gelation tests of $Cr(NO_3)_3 \cdot 9H_2O$ and H_3BTC (Cr:BTC = 1.5:1) in different solvents and concentrations at 80 °C.

Solvent	EtOH	EtOH	EtOH	EtOH	EtOH	EtOH
c/mol L^{-1}	0.08	0.1	0.2	0.4	0.6	0.8
Result	**gel**	**gel**	**gel**	**gel**	**gel**	**gel**
Time	1 h	overnight	4 h	3 h	4 h	4 h

Solvent	DMF	DMF-H_2O	DMF-EtOH
c/mol L^{-1}	0.08	0.08	0.08
Result	**gel**	**gel**	**gel**
Time	2 d	overnight	overnight

[a] *c* is based on the ligand.

Table S6. Gelation tests of different Fe sources at RT.

Fe source	Fe^{3+}/mmol	L	L/mmol	Fe:L	Solvent	Result	Time
$FeCl_3 \cdot 6H_2O$	0.30	H_3BTC	0.20	3:2	EtOH	**gel**	1 d
$FeCl_3 \cdot 6H_2O$	1.0	H_3BTC	0.20	5:1	EtOH	**gel**	1 min
$FeCl_3$	1.0	H_3BTC	0.20	5:1	EtOH	solution	
$FeCl_3 \cdot 6H_2O$	0.25	H_3BTC	0.05	5:1	EtOH	**gel**	5 h

Table S7. Gelation tests of $CrCl_3 \cdot 6H_2O$ and H_3BTC (Cr:BTC = 1:1) in various solvents at 80 °C.

Solvent	EtOH	MeOH	DMF	DMF-H_2O	DMF-MeOH	DMF-EtOH
c/mol L^{-1}	0.067	0.067	0.067	0.1	0.1	0.1
Result	solution	solution	**gel**	**gel**	**gel**	**gel**
Time			6 d	6 h	overnight	2 d

[a] c is based on the ligand.

Table S8. Gelation tests of $CrCl_3 \cdot 6H_2O$ and H_3BTC (Cr:BTC = 1.5:1) in various solvents at 80 °C.

Solvent	EtOH	DMF	DMF-H_2O	DMF-EtOH
c/mol L^{-1}	0.08	0.067	0.08	0.08
Result	solution	**gel**	**gel**	**gel**
Time		5 d	overnight	2 d

[a] c is based on the ligand.

Table S9. Gelation tests of $Fe(NO_3)_3 \cdot 9H_2O$ and H_3BTC at RT at various Fe:L ratios.

Fe^{3+}/mmol[a]	H_3BTC/mmol[a]	Fe:L	Result	Time
0.30	0.10	3:1	**gel**	1 min
0.25	0.10	2.5:1	**gel**	1 min
0.15	0.10	1.5:1	**gel**	1 min
0.10	0.066	1.5:1	**gel**	1 min
0.10	0.10	1:1	**gel**	5 min
0.066	0.066	1:1	**gel**	overnight
0.066	0.10	0.67:1	**gel**	2 d
0.05	0.10	0.5:1	**gel**	4 d

[a] Dissolved in 1 mL of EtOH.

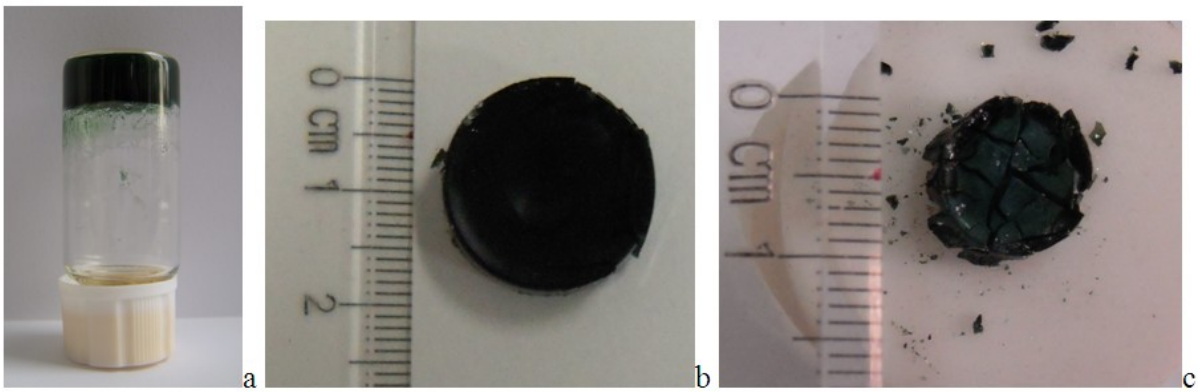


Figure S1. Photographic images of a,b) the wet gel, and b) the aerogel of CrBTC-1:1-0.2.

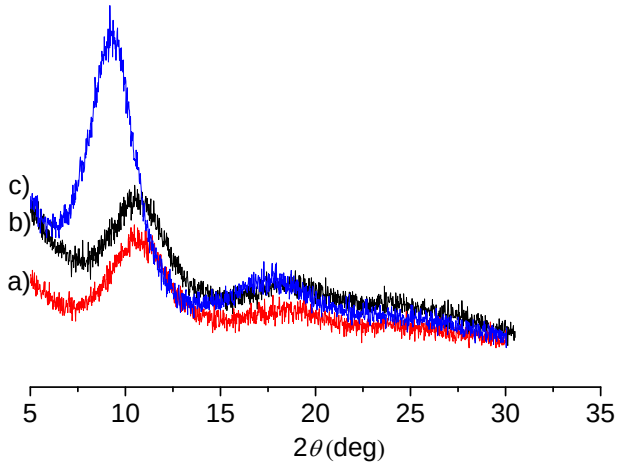


Figure S2. Powder X-ray diffraction patterns of the aerogels a) CrBTC-3:2-0.6, b) CrBTC-1:1-0.6, c) CrBDC-2:3-0.2.

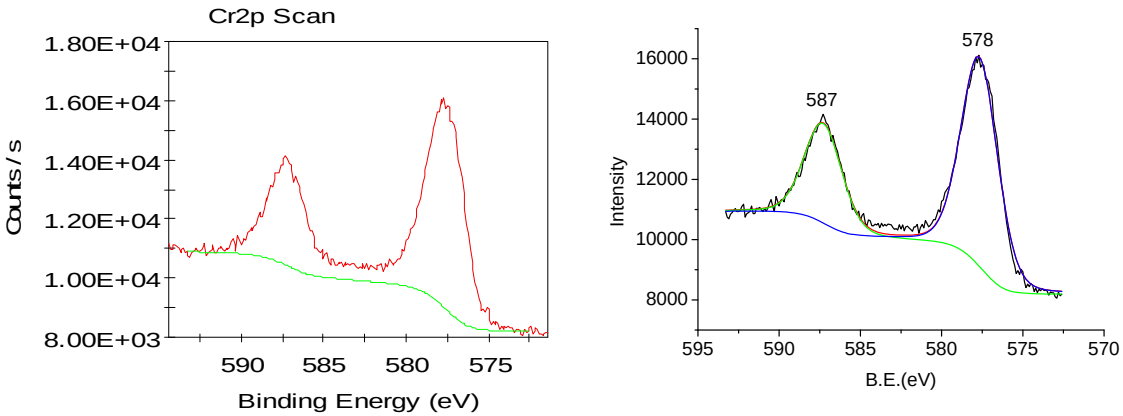


Figure S3. XPS Cr 2p spectrum and the deconvoluted spectrum for the aerogel CrBTC-1:1-0.4.

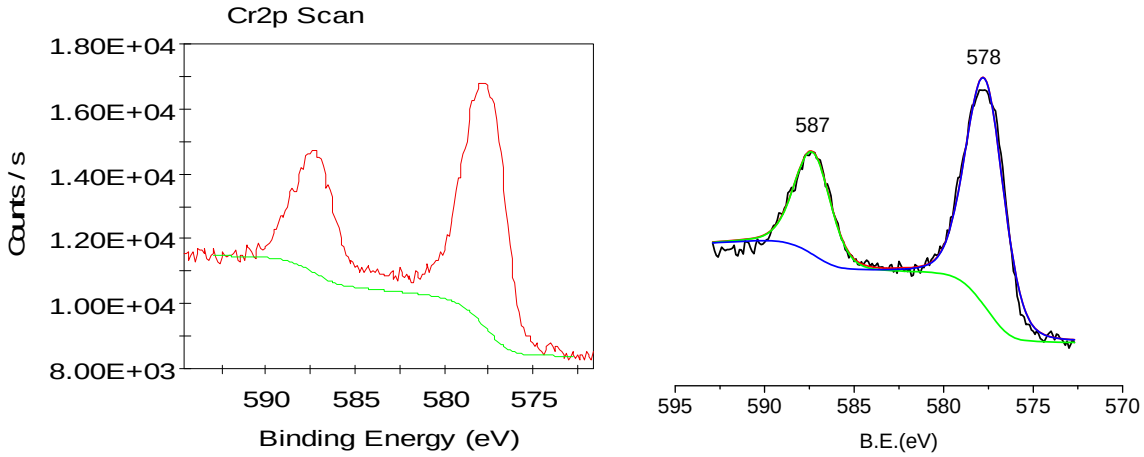


Figure S4. XPS Cr 2p spectrum and the deconvoluted spectrum for the aerogel CrBDC-2:3-0.2.

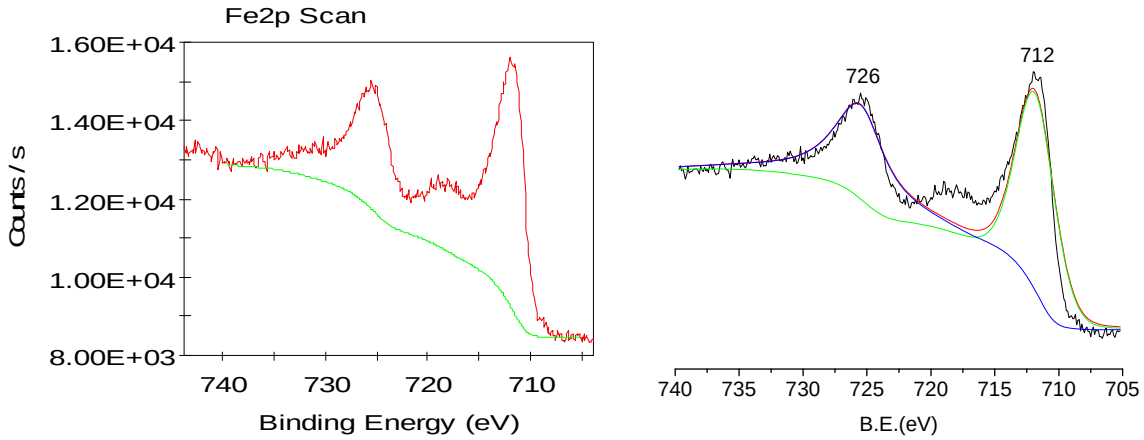


Figure S5. XPS Fe 2p spectrum and the deconvoluted spectrum for the aerogel FeBDC-1:1-0.1.

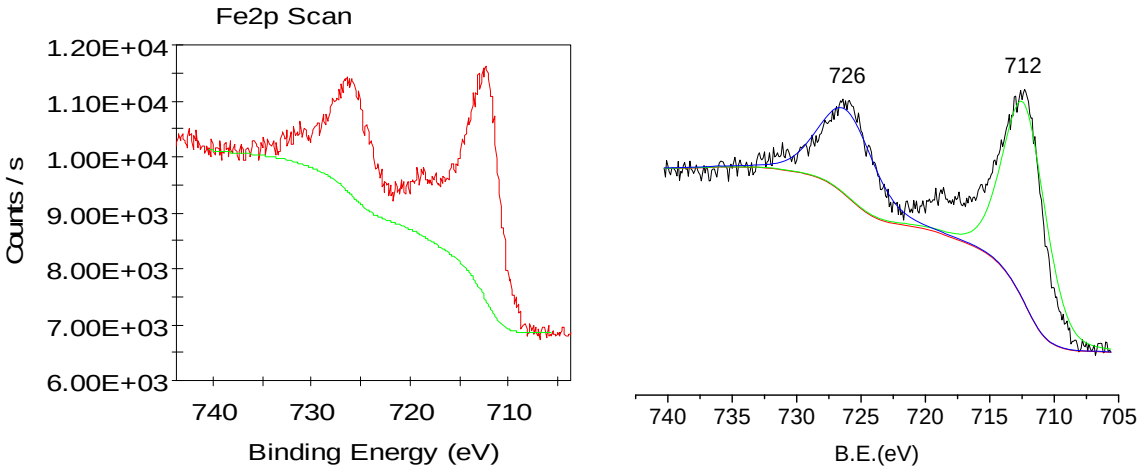


Figure S6. XPS Fe 2p spectrum and the deconvoluted spectrum for the aerogel FeBuDC-1:1-0.1.

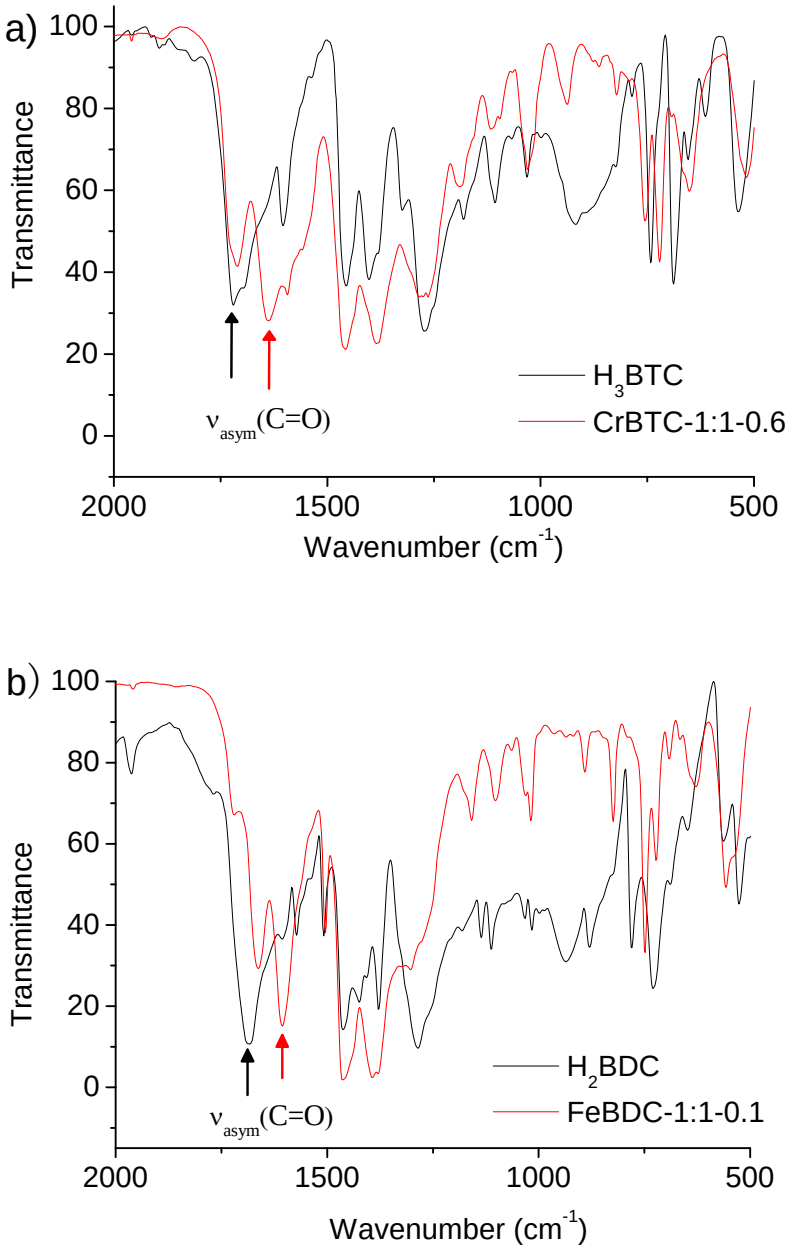
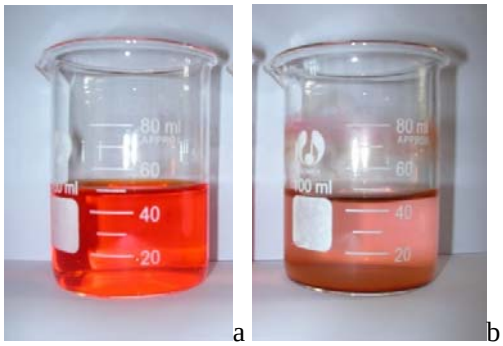


Figure S7. IR spectrum of the aerogels (a) CrBTC-1:1-0.6 and (b) FeBDC-1:1-0.1 (nujol).



a b

Figure S8. Pictures of the dye removal with 0.190 g of aerogel CrBTC-1:1-0.6 in 50 mL of dye solution (0.3 mmol L^{-1}), a) solution of methyl orange in water, b) solution of dimethyl phthalate with the aerogel deposited at the bottom of the beaker after 1 d.

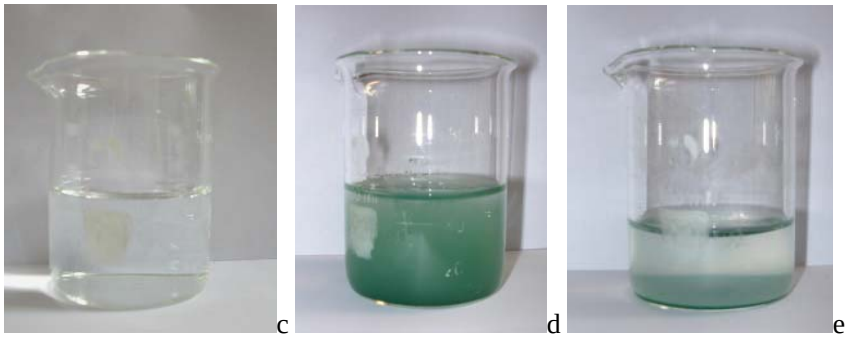
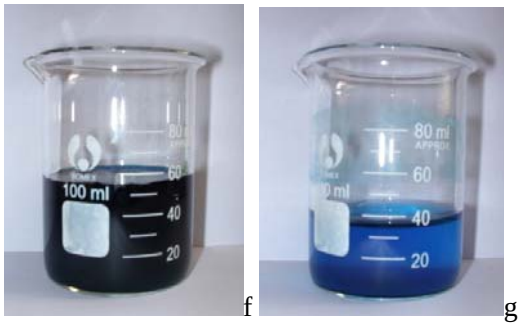

c d e

Figure S9. Pictures of the dye removal with 0.190 g of aerogel CrBTC-1:1-0.6 in 50 mL of dye solution (0.3 mmol L^{-1}), c) solution of dimethyl phthalate in water, d) solution of dimethyl phthalate with the aerogel deposited at the bottom of the beaker, e) picture of the dimethyl phthalate system after 1 d.



f g

Figure S10. Pictures of the dye removal with 0.190 g of aerogel CrBTC-1:1-0.6 in 50 mL of dye solution (0.3 mmol L^{-1}), f) solution of methylene blue with the aerogel deposited at the bottom of the beaker, g) picture of the dimethyl phthalate system after 1 d.