Supplementary Material

Synthesis and structure of COE-11, a new borosilicate zeolite with a 2-dimensional pore system of 12 ring channels

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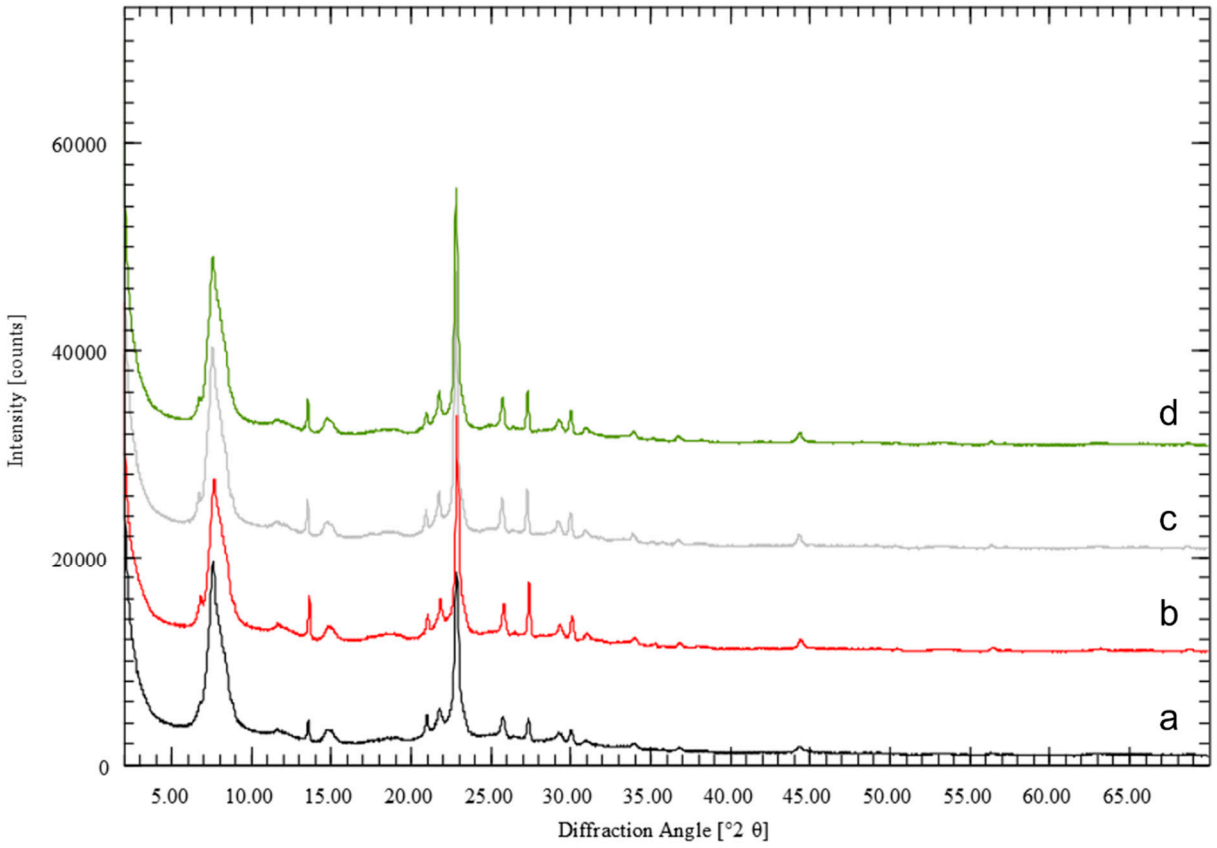

Figure S1: XRD powder patterns of products from 200 ml scale syntheses with gel composition 1 SiO_2 / 0.1 H_3BO_3 / 0.25 NaOH / 0.33 OSDA / 16 H_2O using Ludox HS-30 as Si-source and crystalized for (a) 4 days at 155°C, (b) 4 days at 155°C followed by 3 days at 165°C, (c) 4 days at 155°C followed by 4 days at 165°C and (d) 4 days at 155°C followed by 5 days at 165°C.

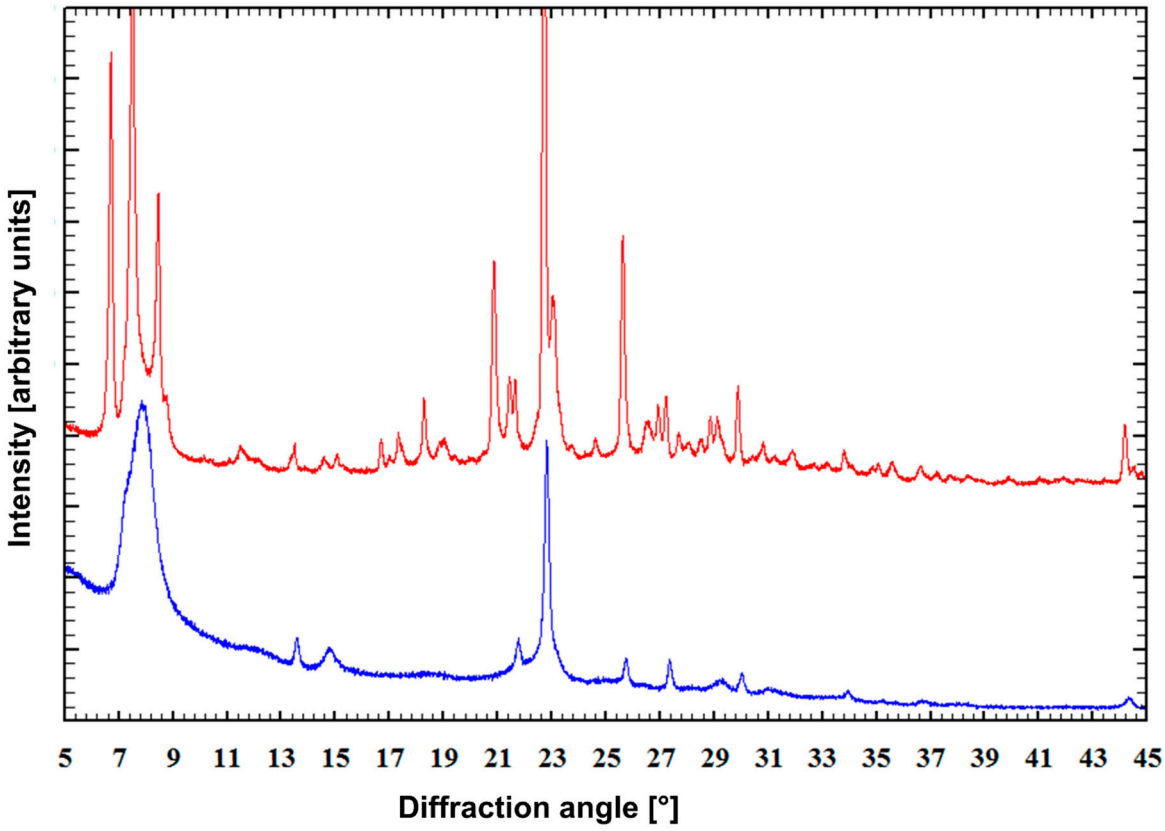

Figure S2: Comparison of XRD powder patterns of COE-11 (sample S21, top) and classical disordered Beta (bottom).

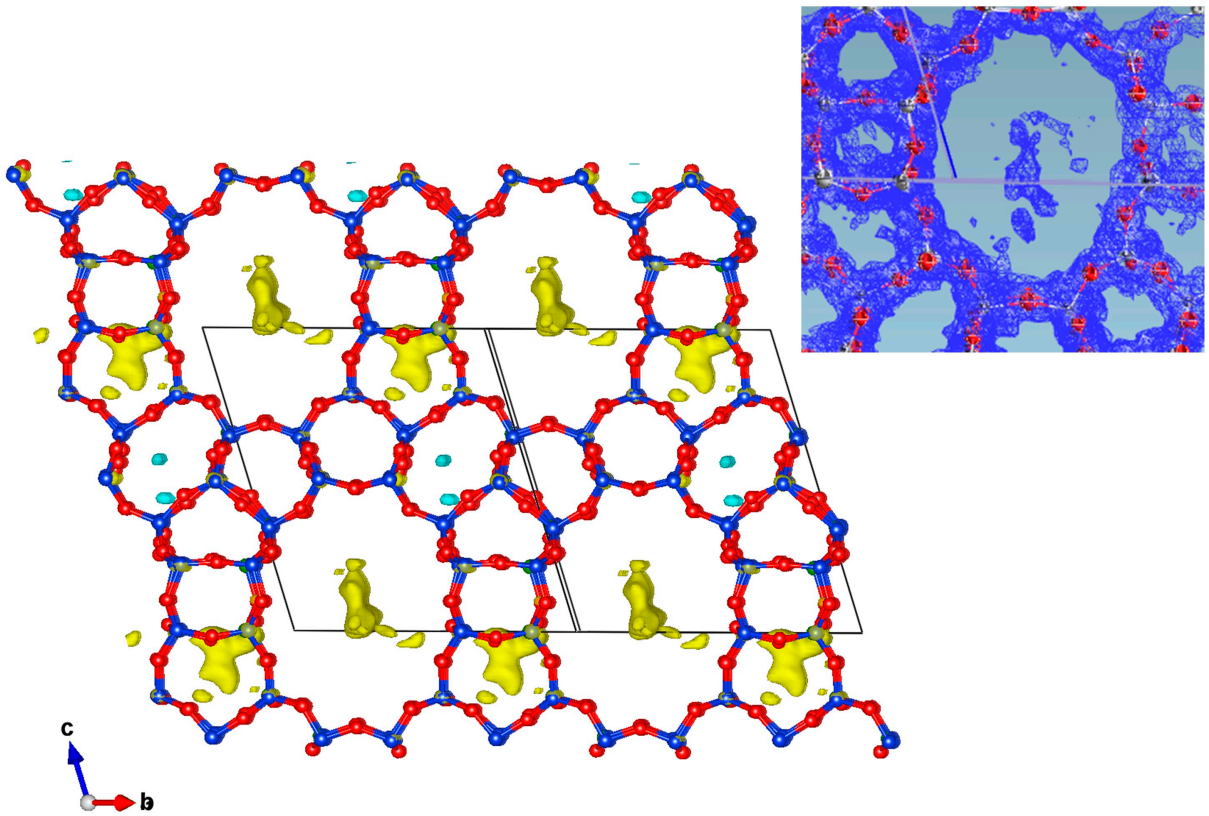

Figure S3: Left: Difference Fourier map based on PXRD data considering only the framework atoms. The remaining positive electron density in the channel-like voids (yellow) represents the TEA cations; right: Section of a Fourier map based on 3D ED data showing a similar potential in the zeolite pores being related to the TEA cation.

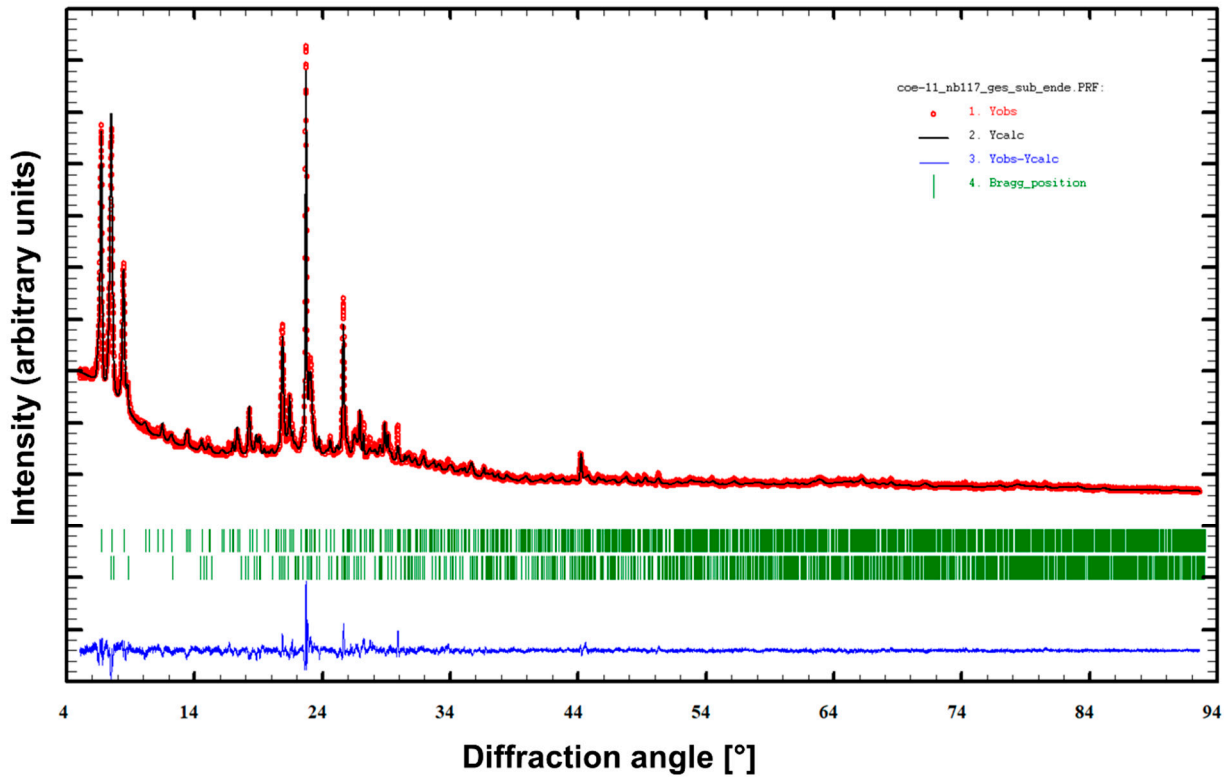

Figure S4: Plot of diffraction patterns after Rietveld analysis: Experimental data (red), calculated data (black) and the difference plot (blue) are presented. Green tick marks indicate allowed reflections.

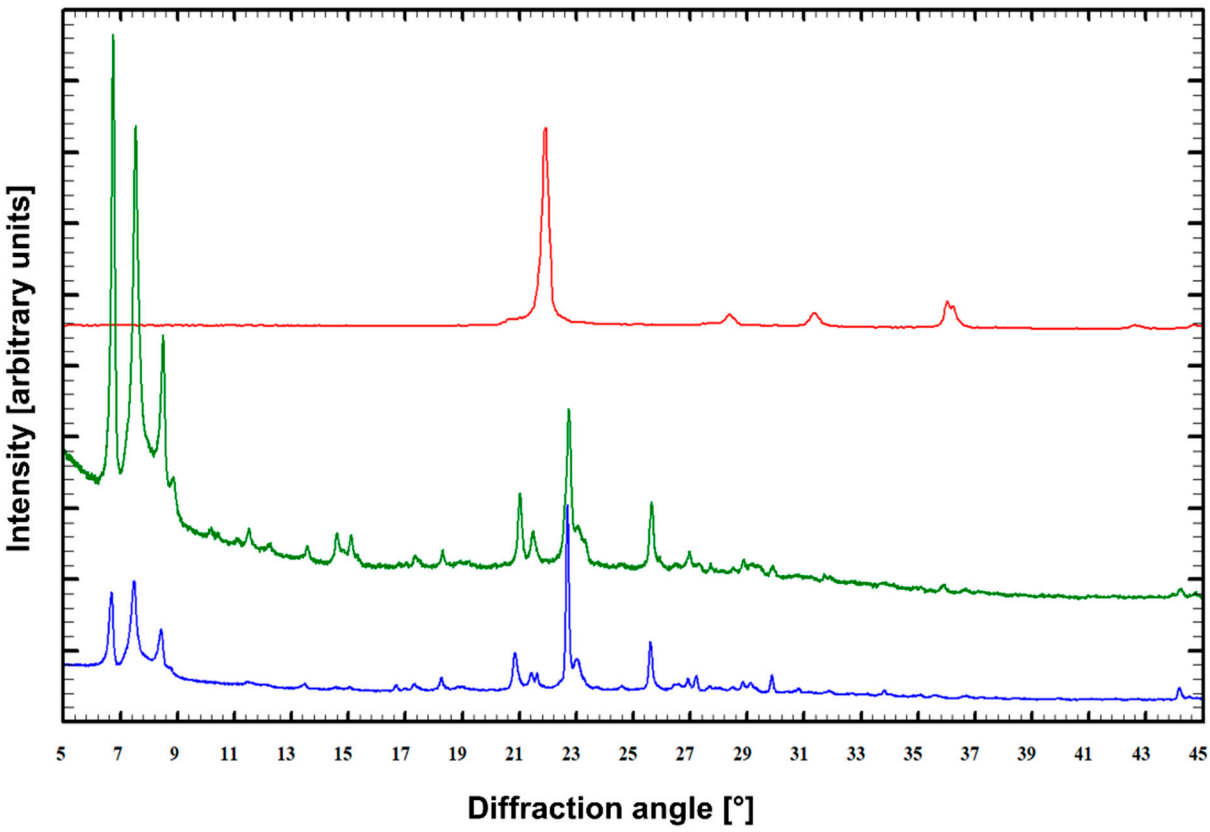

Figure S5: Comparison of PXRD patterns of as-made COE-11 (bottom), calcined and dehydrated COE-11 (middle) and disordered cristobalite obtained by heating COE-11 up to 1000°C (top)

Table S1: Recording conditions of the NMR spectra.

	^{13}C CP MAS	**^{11}B CP MAS**	**^{29}Si CP MAS**	**^{1}H MAS**
Standard	TMS	$NaBH_4$	TMS	TMS
Frequency (MHz)	100.62	128.39	79.50	400.18
Pulse length (10^{-6} s)	10	4	10	6
Contact time (10^{-3} s)	1.5	–	1	–
Recycle time (s)	5	1	**5**	10
Spinning rate (kHz)	4.0	12.5	4.0	12.5
No. of scans	400	6400	800	128

Table S2: Crystallographic information about 3DED/FAST-ADT measurements, structure solution and refinement of COE-11.

Data acquisition			
Tilt range (°)	-60/+70	Temperature	Liq. N_2
Radiation	Electrons	Wavelength λ (Å)	0.0197 (300 keV)
Camera settings (CCD 4Kx4K)	Exposure 2, Bin 4	Diffraction mode	NED
Imaging mode	µ-STEM	Beam size	400 nm
Crystal data (3DED)/XRPD cell parameters used for crystal structure solution			
Space group	*C*2 #5 (*Z*=2)	*V* (Å³) / calc density	3931.7(5) / 1.866 (g/cm^3)
a (Å)	17.18 / 17.3494 (11)	*α* (°)	90.0
b (Å)	17.23 / 17.3409 (11)	*β* (°)	113.69 (5) / 113.762 (2)
c (Å)	14.29 / 14.2789 (4)	*γ* (°)	90.0
No. of indep. Si and O atoms	19 + 33	Chemical content (unit cell)	C16 H40 N2 O132 Si66
Structure solution (SIR2019)			
No. of sampled reflections	8746	No. of independent reflections	2148
Resolution (Å)	1.0	Completeness (%)	99
R_{sym}	0.1181	Overall *U* (Å²)	0.00927
Residual R(*F*) (*SIR*2019)	0.1958	Reflections/parameter ratio	6.37
Structure refinement (SHELXL)			
No. of reflections > 4σ (I)	5423	No. of independent reflections	5891
-h – h	-19 – 19	Parameters (framework only)	199 / 1
-k – k	-19 – 19	Parameters/restraints (framework + TEA)	213 / 209
-l – l	-16 – 16	Reflections/parameter ratio	29.6 resp. 27.7
Resolution (Å)	0.8	Hydrogen treatment TEA	Riding
Refinement results	Framework only (unrestrained)		Framework + TEA (restrained)
R(all)	0.2397	R(all)	0.2281
R > 4σ(I)	0.2304	R > 4σ(I)	0.2181
wR > 4σ(I)	0.5295	wR > 4σ(I)	0.5308
Goodness of fit	3.994	Goodness of fit	4.011
Last shift mean (Å)	0.042	Last shift mean (Å)	0.036

Table S3: Atomic coordinates, isotropic atomic displacement parameters and occupancies of as-made COE-11 (3D ED data).

Atom	x frac	y frac	z frac	Uiso	Occupancy
Si1	0.00000	0.8978(6)	0.500000	0.022(4)	1
Si2	0.8121(7)	0.7031(5)	0.5117(8)	0.024(3)	1
Si3	0.00000	0.5125(5)	0.500000	0.007(3)	1
Si4	0.6804(7)	0.5763(6)	0.4976(9)	0.032(3)	1
Si5	0.9820(6)	0.6253(5)	0.6537(7)	0.015(2)	1
Si6	0.6298(6)	0.8873(4)	0.5065(7)	0.012(2)	1
Si7	0.7895(6)	0.8215(5)	0.6666(8)	0.019(2)	1
Si8	0.8958(7)	0.5628(5)	0.7905(8)	0.025(3)	1
Si9	0.500000	0.7613(7)	0.500000	0.031(4)	1
Si10	0.7908(6)	0.4431(4)	0.6353(7)	0.013(2)	1
Si11	0.8348(6)	0.8149(5)	0.3630(8)	0.017(2)	1
Si12	0.7709(7)	0.6910(5)	0.7938(8)	0.022(3)	1
Si13	0.5979(6)	0.6376(5)	0.6445(8)	0.023(3)	1
Si14	1.0914(6)	0.7595(5)	0.7799(8)	0.022(3)	1
Si15	0.9659(7)	0.8897(5)	0.7869(8)	0.032(3)	1
Si16	0.9761(7)	1.0116(6)	0.6561(9)	0.036(3)	1
Si17	0.8803(7)	0.7169(5)	1.0076(8)	0.029(3)	1
Si18	0.00000	0.5980(8)	0.00000	0.046(5)	1
Si19	0.00000	0.8408(6)	0.00000	0.019(3)	1
O1	0.6139(8)	0.5526(8)	0.3857(10)	0.034(4)	1
O2	1.0209(9)	0.5653(7)	0.5993(8)	0.034(4)	1
O3	0.8028(9)	0.7413(6)	0.4049(9)	0.016(3)	1
O4	0.4610(9)	0.7100(7)	0.3999(8)	0.035(4)	1
O5	0.7117(9)	0.8787(10)	0.6092(12)	0.056(6)	1
O6	0.9416(7)	0.5450(6)	0.9085(7)	0.017(3)	1
O7	0.8690(7)	0.8775(9)	0.7170(13)	0.044(5)	1

O8	1.1425(10)	0.7357(9)	0.8968(9)	0.037(4)	1
O9	0.7950(9)	0.6949(9)	0.9145(8)	0.044(5)	1
O10	0.9834(10)	0.8964(7)	0.9043(7)	0.037(4)	1
O11	0.6507(9)	0.8971(7)	0.4075(11)	0.025(4)	1
O12	0.8328(9)	0.6342(7)	0.7704(13)	0.031(4)	1
O13	0.8443(10)	0.4864(7)	0.7404(10)	0.035(4)	1
O14	0.9790(11)	0.9494(7)	0.5780(10)	0.032(4)	1
O15	0.8400(10)	0.7955(10)	0.2563(11)	0.048(5)	1
O16	0.5808(7)	0.9613(6)	0.5178(13)	0.037(5)	1
O17	0.9178(6)	0.7911(7)	0.9770(13)	0.038(5)	1
O18	1.0205(11)	0.8220(8)	0.7685(16)	0.052(6)	1
O19	0.5712(8)	0.8141(7)	0.4883(14)	0.040(5)	1
O20	0.8013(13)	0.7691(9)	0.5827(13)	0.050(6)	1
O21	0.7750(13)	0.7756(7)	0.7532(13)	0.047(5)	1
O22	0.9575(10)	0.5795(8)	0.7351(12)	0.032(4)	1
O23	0.9452(8)	0.6495(7)	1.0416(11)	0.032(4)	1
O24	0.9007(8)	0.6620(10)	0.5664(13)	0.054(6)	1
O25	0.5472(9)	0.5735(7)	0.6748(13)	0.031(4)	1
O26	0.7374(9)	0.6418(8)	0.4805(13)	0.036(4)	1
O27	1.0521(9)	0.6859(7)	0.7126(11)	0.027(4)	1
O28	0.6306(13)	0.6066(11)	0.5623(14)	0.061(6)	1
O29	0.6758(8)	0.6620(10)	0.7461(12)	0.051(6)	1
O30	0.9227(7)	0.8416(8)	0.4424(12)	0.055(6)	1
O31	0.9933(10)	0.9729(6)	0.7631(9)	0.023(4)	1
O32	0.7379(11)	0.5050(8)	0.5524(13)	0.054(6)	1
O33	0.7702(10)	0.8844(8)	0.3431(15)	0.052(5)	1
N1	0.264(7)	0.476(6)	0.005(10)	0.32(6)	0.50(4)
C2	0.370(10)	0.561(9)	-0.006(15)	0.32(6)	0.50(4)
H2A	0.361930	0.521907	-0.057324	0.480	0.50(4)

H2B	0.423073	0.553680	0.049694	0.480	0.50(4)
H2C	0.367608	0.610860	-0.036003	0.480	0.50(4)
C3	0.243(13)	0.515(10)	-0.188(11)	0.32(6)	0.50(4)
H3A	0.200641	0.554242	-0.203485	0.480	0.50(4)
H3B	0.234820	0.486040	-0.247979	0.480	0.50(4)
H3C	0.297839	0.539513	-0.163036	0.480	0.50(4)
C4	0.239(9)	0.462(7)	-0.106(11)	0.32(6)	0.50(4)
H4A	0.180163	0.447206	-0.130928	0.384	0.50(4)
H4B	0.269322	0.416458	-0.109882	0.384	0.50(4)
C5	0.336(8)	0.440(7)	0.092(12)	0.32(6)	0.50(4)
H5A	0.388630	0.459246	0.093116	0.384	0.50(4)
H5B	0.334513	0.384712	0.083221	0.384	0.50(4)
C6	0.192(8)	0.452(8)	0.029(13)	0.32(6)	0.50(4)
H6A	0.166040	0.498773	0.040832	0.384	0.50(4)
H6B	0.213505	0.423418	0.092137	0.384	0.50(4)
C8	0.123(9)	0.405(10)	-0.049(16)	0.32(6)	0.50(4)
H8A	0.146564	0.375091	-0.087732	0.480	0.50(4)
H8B	0.080479	0.438701	-0.093901	0.480	0.50(4)
H8C	0.099390	0.371352	-0.014488	0.480	0.50(4)
C1	0.300(9)	0.554(6)	0.031(12)	0.32(6)	0.50(4)
H1A	0.322808	0.562023	0.104858	0.384	0.50(4)
H1B	0.257350	0.592915	-0.001122	0.384	0.50(4)
C9	0.330(12)	0.459(10)	0.192(11)	0.32(6)	0.50(4)
H9A	0.362469	0.504759	0.221068	0.480	0.50(4)
H9B	0.351962	0.416913	0.239066	0.480	0.50(4)
H9C	0.272349	0.467982	0.180879	0.480	0.50(4)

Table S4: Experimental and crystallographic parameters for the Rietveld analysis of COE-11.

Sample	S21: COE-11 (+ Beta + MTW)
Diffractometer	Siemens D5000 with 6° PSD
Wavelenght	1.54059 Å
Sample	0.3 mm glass capillary
2Θ range of data used [°]	3.07 - 92.56
Step size [°2Θ]	0.007863
No. contributing reflections	2195
No. geometric restraints	219
No. structural parameters	176
No. profile parameters	18
FWHM at ca. 20°2Θ [°2Θ]	0.10 - 0.24
R_F	0.039
R_{wp}	0.17
R_{exp}	0.09
$\chi 2$	3.53
Space group	C2 (No. 5)
a_0 [Å]	17.3494(11)
a_0 [Å]	17.3409(11)
c_0 [Å]	14.2789(4)
V_{UC} [Å^3]	113.762(2)
Unit cell content	$[(C_2H_5)_4N]_4\,[B_4Si_{62}O_{132}]$