Supporting information

Ab initio Structure Determination of Interlayer Expanded Zeolites by Single Crystal Rotation Electron Diffraction

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Table S1 Crystal data and structure refinement details of COE-3 and COE-4 against the PXRD data.

Sample	COE-3	COE-4
Framework composition/unit cell	$Si_{39.3}O_{74.6}(CH_3)_{6.6}(OH)_{1.4}$	$Si_{38.7}O_{73.4}(OH)_8$
Temperature	room temperature data collection	
Wavelength [Å]	1.5418	1.5418
2θ range [°]	5.004°< 2θ < 90.004°	5.008°< 2θ < 90.008°
2θ step size [°]	0.017	0.017
Space group	*Cmcm*	*Cmcm*
Lattice parameters		
a [Å]	7.400 (0)	7.397(1)
b [Å]	23.426(2)	23.289(2)
c [Å]	14.008 (1)	13.994(1)
Total number of data points	5000	5000
Distance restraints [Å]	*d*(Si−O) = 1.61, *d*(O−O) = 2.62	
Number of distance restraints	90	90
R_B	0.017	0.015
R_p	0.033	0.039
R_{wp}	0.043	0.049
GOF	2.5	2.0

Table S2 Representative bond distances and angles of the COE-3 structure refined against the RED data and PXRD data.

	Refine against RED data	Refine against PXRD data
Si1 – O2	1.60(4)	1.584(7)
Si1 – O5	1.56(4)	1.603(7)
Si2 – O3	1.54(4)	1.604(6)
Si2 – O1	1.65(4)	1.610(5)
Si2 – O5	1.45(4)	1.610(8)
Si3 – O1	1.52(4)	1.587(4)
Si3 – O7	1.59(4)	1.583(4)
Si3 – O4	1.54(4)	1.590(5)
Si3 – O6	1.53(2)	1.614(3)
Si4 – O4	1.56(4)	1.581(4)
Si4 – O2	1.53(5)	1.589(5)
Si4 – O8	1.53(5)	1.611(5)
Si5 – O8	1.60(5)	1.655(5)
Si5 – C1	1.59(5)	1.661(10)
Si2 – O1 – Si3	140(3)	145.9(4)
Si4 – O2– Si1	155(4)	155.7(5)
Si2 – O3 – Si2	164(8)	159.0(12)
Si3 – O4 – Si4	143(4)	153.0(3)
Si1 – O5 – Si2	154(4)	152.5(5)
Si3 – O6 – Si3	180	180
Si3 – O7 – Si3	138(5)	139.3(5)
Si4 – O8 – Si5	125(4)	135.6(2)

Table S3 Representative bond distances and angles of the COE-4 structure refined against the RED data and PXRD data.

	Refine against RED data	Refine against PXRD data
Si1 – O2	1.58(4)	1.591(6)
Si1 – O5	1.60(4)	1.573(6)
Si2 – O3	1.61(4)	1.589(6)
Si2 – O1	1.58(3)	1.597(5)
Si2 – O5	1.56(4)	1.593(7)
Si3 – O1	1.63(3)	1.586(4)
Si3 – O7	1.53(3)	1.594(4)
Si3 – O4	1.60(3)	1.596(5)
Si3 – O6	1.59(2)	1.609(3)
Si4 – O4	1.56(3)	1.597(4)
Si4 – O2	1.61(4)	1.592(5)
Si4 – O8	1.55(4)	1.602(6)
Si5 – O8	1.61(5)	1.617(6)
Si5 – O9	1.60(5)	1.608(8)
Si2 – O1 – Si3	151(3)	150.2(4)
Si4 – O2 – Si1	154(4)	165.3(5)
Si2 – O3 – Si2	147(5)	152.7(11)
Si3 – O4 – Si4	154(3)	151.2(3)
Si1 – O5 – Si2	154(3)	153.4(5)
Si3 – O6 – Si3	180	180
Si3 – O7 – Si3	140(4)	142.7(5)
Si4 – O8 – Si5	132(3)	129.6(3)

Table S4 Comparison of atomic positions of COE-3 refined against the RED and PXRD data. The unit cell parameters obtained from the PXRD data were used to calculate the deviations.

Coordinates from the PXRD data				Coordinates from the RED data				Deviation Δ (Å)
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	
Si1	0.000	0.326	0.250	Si1	0.000	0.322	0.250	0.092
Si2	0.213	0.271	0.750	Si2	0.212	0.272	0.750	0.027
Si3	0.299	0.311	0.547	Si3	0.294	0.313	0.545	0.064
Si4	0.000	0.382	0.451	Si4	0.000	0.386	0.451	0.090
Si5	0.138	0.500	0.500	Si5	0.142	0.500	0.500	0.031
O1	0.271	0.310	0.659	O1	0.277	0.316	0.656	0.162
O2	0.000	0.367	0.340	O2	0.000	0.368	0.342	0.036
O3	0.000	0.259	0.750	O3	0.000	0.282	0.750	0.552
O4	0.180	0.359	0.498	O4	0.189	0.367	0.499	0.189
O5	0.181	0.289	0.250	O5	0.183	0.284	0.250	0.105
O6	0.750	0.750	0.500	O9	0.750	0.750	0.500	0.000
O7	0.500	0.331	0.527	O7	0.500	0.337	0.532	0.166
O8	1.000	0.549	0.544	O8	1.000	0.544	0.557	0.216
C1	-0.278	0.517	0.411	C1	-0.266	0.539	0.426	0.561

$$\Delta = \sqrt{\Delta x^2 a^2 + \Delta y^2 b^2 + \Delta z^2 c^2}$$

Table S5 Comparison of atomic positions of COE-4 refined against the RED and PXRD data. The unit cell parameters obtained from the PXRD data were used to calculate the deviations.

Coordinates from the PXRD data				Coordinates from the RED data				Deviation Δ (Å)
Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*	
Si1	0.000	0.324	0.250	Si1	0.000	0.328	0.250	0.099
Si2	0.209	0.271	0.750	Si2	0.211	0.270	0.750	0.039
Si3	0.296	0.312	0.546	Si3	0.303	0.311	0.544	0.057
Si4	0.000	0.386	0.450	Si4	0.000	0.385	0.451	0.021
Si5	0.131	0.500	0.500	Si5	0.132	0.500	0.500	0.008
O1	0.263	0.308	0.658	O1	0.247	0.307	0.657	0.119
O2	0.000	0.362	0.343	O2	0.000	0.370	0.339	0.194
O3	0.000	0.255	0.750	O3	0.000	0.250	0.750	0.127
O4	0.177	0.363	0.503	O4	0.182	0.360	0.493	0.150
O5	0.180	0.287	0.250	O5	0.182	0.289	0.250	0.039
O6	0.750	0.750	0.500	O6	0.750	0.750	0.500	0.000
O7	0.500	0.329	0.524	O7	0.500	0.334	0.546	0.338
O8	1.000	0.545	0.554	O8	1.000	0.547	0.550	0.073
O9	-0.256	0.535	0.427	O9	-0.255	0.532	0.422	0.101

$$\Delta = \sqrt{\Delta x^2 a^2 + \Delta y^2 b^2 + \Delta z^2 c^2}$$

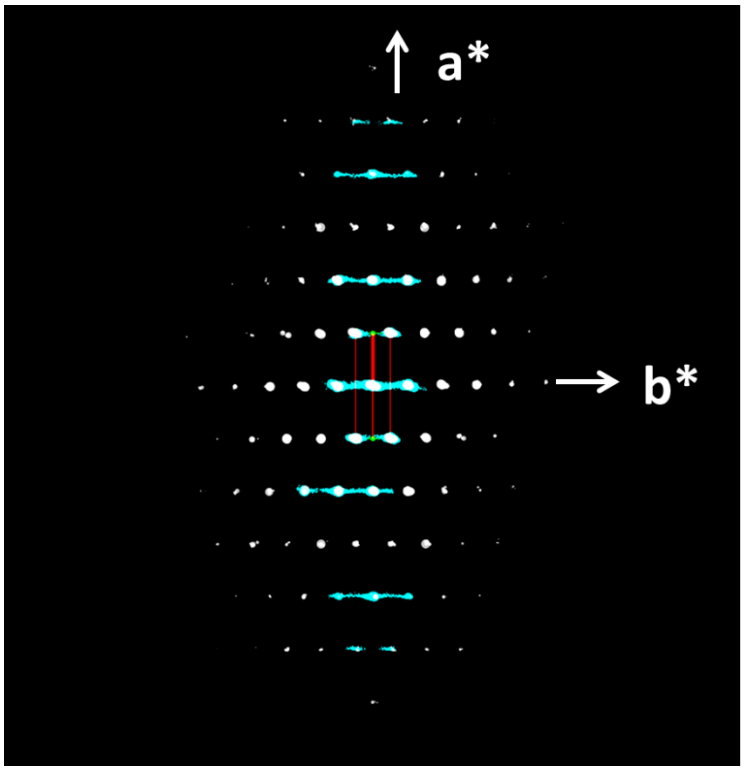

Fig. S1 The 3D reciprocal lattice of COE-3 reconstructed from dataset 1_{COE-3} viewed along the *c*-axis showing the presence of diffuse streaks (marked in light blue) along the *b**-axis.

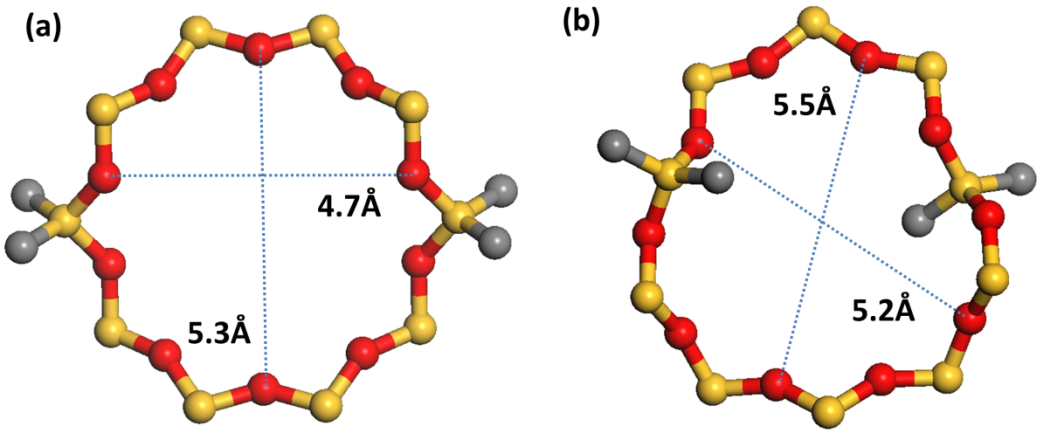

Fig. S2 Maximum effective pore diameters of the different channels in COE-3. (a) The 10-ring channel along the *c*-axis and (b) the 10-ring channel along the *a*-axis. A van der Waals diameter of 2.7 Å for oxygen atoms has been subtracted.

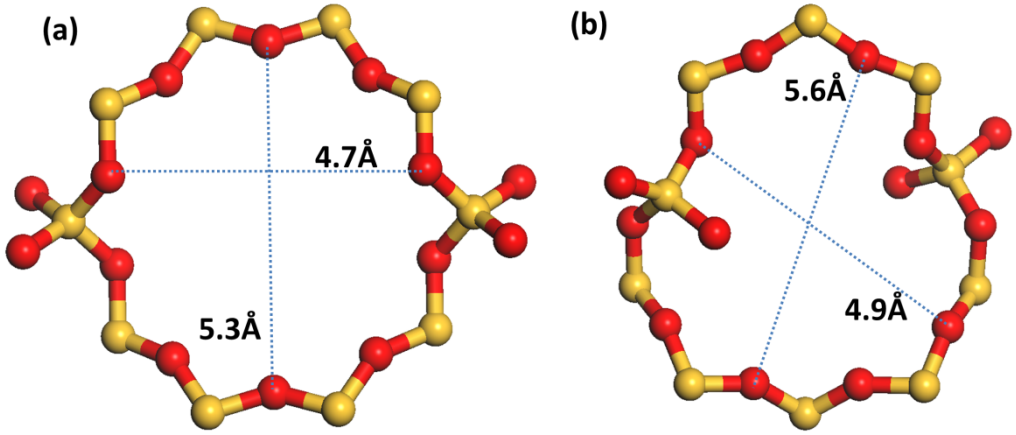

Fig. S3 Maximum effective pore diameters of the different channels in COE-4. (a) The 10-ring channel along the *c*-axis and (b) the 10-ring channel along the *a*-axis. A van der Waals diameter of 2.7 Å for oxygen atoms has been subtracted.