## **Supporting information**

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

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| Sample                          | COE-3  | COE-4  |  |  |  |
|---------------------------------|--|--|--|--|--|
| Framework composition/unit cell | Si <sub>39.3</sub> O <sub>74.6</sub> (CH <sub>3</sub> ) <sub>6.6</sub> (OH) <sub>1.4</sub> | Si <sub>38.7</sub> O <sub>73.4</sub> (OH) <sub>8</sub> |  |  |  |
| Temperature                     | room temperature data collection   |  |  |  |  |
| Wavelength [Å]                  | 1.5418   | 1.5418   |  |  |  |
| 2θ range [°]                    | $5.004^{\circ} < 2\theta < 90.004^{\circ}$   | $5.008^{\circ} < 2\theta < 90.008^{\circ}$             |  |  |  |
| 2θ step size [°]                | 0.017  | 0.017  |  |  |  |
| Space group                     | Стст   | Стст   |  |  |  |
| Lattice parameters              |  |  |  |  |  |
| a [Å]                           | 7.400 (0)  | 7.397(1)   |  |  |  |
| <i>b</i> [Å]                    | 23.426(2)  | 23.289(2)  |  |  |  |
| <i>c</i> [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 S1 Crystal data and structure refinement details of COE-3 and COE-4 against the 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 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 |
|----------------|-------------------------|--------------------------|
| Si1-02         | 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)                 |
| Si3-07         | 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 S3 Representative bond distances and angles of the COE-4 structure refined against the RED data and PXRD data.

| Coord | Coordinates from the PXRD data |       | Coordinates from the RED data |      |        |       | Deviation $\Delta$ (Å) |       |
|-------|--------------------------------|-------|-------------------------------|------|--------|-------|------------------------|-------|
| Atom  | x                              | У     | Ζ                             | Atom | x      | У     | Ζ                      |       |
| 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 |
| 01    | 0.271                          | 0.310 | 0.659                         | 01   | 0.277  | 0.316 | 0.656                  | 0.162 |
| 02    | 0.000                          | 0.367 | 0.340                         | O2   | 0.000  | 0.368 | 0.342                  | 0.036 |
| 03    | 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 |
| 05    | 0.181                          | 0.289 | 0.250                         | 05   | 0.183  | 0.284 | 0.250                  | 0.105 |
| 06    | 0.750                          | 0.750 | 0.500                         | 09   | 0.750  | 0.750 | 0.500                  | 0.000 |
| 07    | 0.500                          | 0.331 | 0.527                         | 07   | 0.500  | 0.337 | 0.532                  | 0.166 |
| 08    | 1.000                          | 0.549 | 0.544                         | 08   | 1.000  | 0.544 | 0.557                  | 0.216 |
| C1    | -0.278                         | 0.517 | 0.411                         | C1   | -0.266 | 0.539 | 0.426                  | 0.561 |

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.

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

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 $\Delta$ (Å)   |  |
|--------------------------------|--|--|--|--|--|--|--|
| x                              | У  | Z  | Atom   | x  | У  | Ζ  |  |
| 0.000                          | 0.324  | 0.250  | Sil  | 0.000  | 0.328  | 0.250  | 0.099  |
| 0.209                          | 0.271  | 0.750  | Si2  | 0.211  | 0.270  | 0.750  | 0.039  |
| 0.296                          | 0.312  | 0.546  | Si3  | 0.303  | 0.311  | 0.544  | 0.057  |
| 0.000                          | 0.386  | 0.450  | Si4  | 0.000  | 0.385  | 0.451  | 0.021  |
| 0.131                          | 0.500  | 0.500  | Si5  | 0.132  | 0.500  | 0.500  | 0.008  |
| 0.263                          | 0.308  | 0.658  | 01   | 0.247  | 0.307  | 0.657  | 0.119  |
| 0.000                          | 0.362  | 0.343  | O2   | 0.000  | 0.370  | 0.339  | 0.194  |
| 0.000                          | 0.255  | 0.750  | 03   | 0.000  | 0.250  | 0.750  | 0.127  |
| 0.177                          | 0.363  | 0.503  | 04   | 0.182  | 0.360  | 0.493  | 0.150  |
| 0.180                          | 0.287  | 0.250  | 05   | 0.182  | 0.289  | 0.250  | 0.039  |
| 0.750                          | 0.750  | 0.500  | O6   | 0.750  | 0.750  | 0.500  | 0.000  |
| 0.500                          | 0.329  | 0.524  | 07   | 0.500  | 0.334  | 0.546  | 0.338  |
| 1.000                          | 0.545  | 0.554  | 08   | 1.000  | 0.547  | 0.550  | 0.073  |
| -0.256                         | 0.535  | 0.427  | 09   | -0.255   | 0.532  | 0.422  | 0.101  |
|                                | x   0.000   0.209   0.296   0.000   0.131   0.263   0.000   0.177   0.180   0.750   0.500   1.000   -0.256 | x y   0.000 0.324   0.209 0.271   0.296 0.312   0.000 0.386   0.131 0.500   0.263 0.308   0.000 0.362   0.000 0.362   0.000 0.255   0.177 0.363   0.180 0.287   0.750 0.750   0.500 0.329   1.000 0.545   -0.256 0.535 | x $y$ $z$ $0.000$ $0.324$ $0.250$ $0.209$ $0.271$ $0.750$ $0.296$ $0.312$ $0.546$ $0.000$ $0.386$ $0.450$ $0.131$ $0.500$ $0.500$ $0.263$ $0.308$ $0.658$ $0.000$ $0.362$ $0.343$ $0.000$ $0.255$ $0.750$ $0.177$ $0.363$ $0.503$ $0.180$ $0.287$ $0.250$ $0.750$ $0.750$ $0.500$ $0.500$ $0.329$ $0.524$ $1.000$ $0.545$ $0.554$ $-0.256$ $0.535$ $0.427$ | x $y$ $z$ Atom0.0000.3240.250Si10.2090.2710.750Si20.2960.3120.546Si30.0000.3860.450Si40.1310.5000.500Si50.2630.3080.658O10.0000.3620.343O20.0000.2550.750O30.1770.3630.503O40.1800.2870.250O50.7500.7500.500O60.5000.3290.524O71.0000.5450.554O8-0.2560.5350.427O9 | x $y$ $z$ Atom $x$ 0.0000.3240.250Si10.0000.2090.2710.750Si20.2110.2960.3120.546Si30.3030.0000.3860.450Si40.0000.1310.5000.500Si50.1320.2630.3080.658O10.2470.0000.2550.750O30.0000.1770.3630.503O40.1820.1800.2870.250O50.1820.7500.7500.500O60.7500.5000.3290.524O70.5001.0000.5450.554O81.000-0.2560.5350.427O9-0.255 | x $y$ $z$ Atom $x$ $y$ 0.0000.3240.250Si10.0000.3280.2090.2710.750Si20.2110.2700.2960.3120.546Si30.3030.3110.0000.3860.450Si40.0000.3850.1310.5000.500Si50.1320.5000.2630.3080.658O10.2470.3070.0000.3620.343O20.0000.3700.0000.2550.750O30.0000.2500.1770.3630.503O40.1820.3600.1800.2870.250O50.1820.2890.7500.7500.500O60.7500.7500.5000.3290.524O70.5000.3341.0000.5450.554O81.0000.547-0.2560.5350.427O9-0.2550.532 | x $y$ $z$ Atom $x$ $y$ $z$ 0.0000.3240.250Si10.0000.3280.2500.2090.2710.750Si20.2110.2700.7500.2960.3120.546Si30.3030.3110.5440.0000.3860.450Si40.0000.3850.4510.1310.5000.500Si50.1320.5000.5000.2630.3080.658O10.2470.3070.6570.0000.3620.343O20.0000.3700.3390.0000.2550.750O30.0000.2500.7500.1770.3630.503O40.1820.3600.4930.1800.2870.250O50.1820.2890.2500.7500.7500.500O60.7500.7500.5000.5000.3290.524O70.5000.3340.5461.0000.5450.554O81.0000.5470.550-0.2560.5350.427O9-0.2550.5320.422 |

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



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.