Supporting Information:

Sub-micron pore size tailoring for efficient chiral discrimination

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Experimental

Synthesis of the MOPSs:

The stevensite $[Na_{0.47(3)}]^{inter}[Mg_{2.59(5)}Li_{0.17(3)}]^{oct}[Si_4]^{tet}O_{10}F_2$ used was synthesized via melt synthesis[1,2]. The high purity reagents (in total ~45 g) of SiO_2 (Merck, fine granular, calcined), MgF_2 (Chempur, 99.99%), MgO (Alfa Aesar 99.95%), Li_2SiO_3 (Alfa Aesar 99.95%), and $Na_2O–2SiO_2$-glass were weighed into a molybdenum crucible in an Ar atmosphere in accordance with a stoichiometric composition of $[Na_{0.6}]^{inter}[Mg_{2.6}Li_{0.2}\square]^{oct}[Si_4]^{tet}O_{10}F_2$ (target composition). $Na_2O–2SiO_2$-glass was produced by melting Na_2CO_3 (Aldrich, 99.9%) and SiO_2 (Merck, fine granular, calcined) in a 1:2 molar ratio at 1050 °C for 10 h to ensure complete release of carbon dioxide. The molybdenum crucible was sealed so as to be gas-tight using the procedure described elsewhere[3]. The crucible was heated in a graphite furnace (Graphit HT-1900, Linn High Therm) for the synthesis. To prevent inhomogeneity of the product owing to gravity segregation in the melt, the crucible was positioned horizontally in the furnace and rotated at 50 rpm. The crucible was heated from room temperature to 1750 °C (20 °C / min), left at 1750 °C for 1 h, then cooled to 1300 °C with a cooling rate of 50 °C / min, followed by a cooling rate of 10 °C / min from 1300 °C to 1050 °C, and finally it was quenched by switching off the power. The crucible was opened under an Ar atmosphere and the synthetic stevensite was stored in a Glovebox.

The charge density was reduced prior to pillaring by first ion-exchanging the stevensite with Mg^{2+}. The samples were then put in a quartz crucible and heated at 250 °C for 3 h, 6 h and 12 h for MOPS-2, MOPS-3 and MOPS-4, respectively. During annealing, part of the Mg^{2+} moves from the interlayer to octahedral vacancies, which causes the reduction of the negative charge density of the silicate layers[4] as reflected by continuously dropping cation exchange capacities (105, 94, 86 to 58 meq / 100g for MOPS 1-4, respectively, Fig. S5).

For pillaring, the stevensites (100 mg) were treated hydrothermally four times for 12 h at 60 °C with 18 mg of cobalt sepulchrate trichloride, (–)-$Co(sep)Cl_3$ or (+)-$Co(sep)Cl_3$ (sep = $C_{12}H_{30}N_8$ = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]-eicosane)[5] in 5 mL H_2O.

The *powder X-ray diffraction patterns* of the dry samples were recorded with a STOE Stadi P powder diffractometer (transmission geometry, $CuK_{\alpha 1}$ radiation (λ = 1.54056 Å), Ge monochromator, MYTHEN 1K detector).

The *scanning electron microscopy (SEM)* image was taken on a LEO 1530 FE-SEM at an operating voltage of 3 kV.

For *infrared spectra* a JASCO FT/IR-6100 Fourier transform infrared spectrometer with an attenuated total reflectance (ATR) unit was used.

Argon Adsorption Measurements were performed using a Quantachrome Autosorb 1 at Ar(l) temperature (87.35 K) with Ar employing samples pre-dried for 24 h at 100 °C in high vacuum. The pore sizes and volumes were calculated using a non-local DFT model (software version 2.11, Ar on zeolite/silica, cylindrical pores, equilibrium model)[6]. The volume-weighted mean micropore width corresponds to the point where the total pore volume in the micropore regime (< 2 nm) was half filled. The BET equation calculates the surface area of a monolayer adsorption and is applied to a linear part of the isotherm. This p/p_0 range is normally taken to lie between 0.1 and 0.3 but has to be adjusted to lower p/p_0 values for microporous materials. Recommendations suggested by Rouquerol were followed for choosing the appropriate range of the isotherm[7].

Adsorption experiments:

Adsorption of a mixture of 2-methyl-but-3-yn-2-ol and (±)-*but-3-yn-2-ol*.

The MOPSs MOPS-1(+) to MOPS-4(+) pillared with (+)-Co(sep)$^{3+}$ were heated at 100 °C under high vacuum (10^{-6} bar) for 24 h, cooled and transferred to an argon glove box. There, three 10 mg samples of each MOPS were weighed into open Eppendorf plastic vials (1.5 mL) which were placed in a horizontally adjusted 50 mL Schlenk tube together with an open glass weighing tube containing 300 µL of a mixture of 153 µL 2-methyl-but-3-yn-2-ol and 147 µL (*±)*-but-3-yn-2-ol to secure a saturated atmosphere with a molar ratio of 51.3:48.7. The Schlenk tube was stoppered and kept at 4 °C for 48 h. Then it was connected to an argon line and after removal of the 2-methyl-but-3-yn-2-ol / but-3-yn-2-ol source the sample vials were each treated with 500 µL of dry acetone p.a.. The vials were sealed, vortexed for 1 min, treated with a cooled ultrasonic bath for 30 min to desorb the alcohols from the inorganic material, and centrifuged.

The acetone extracts were analysed by GC-FID on a Shimadzu GC-2010 equipped with a chiral Lipodex E column (25 m) under the following conditions: 0.5 µL injection volume, split 1:100, T_{inj} 250 °C, constant flow of hydrogen carrier gas (1.2 mL/min = 40 cm/s), T_{det} 250 °C; column temperature initially 40 °C (3 min) then raised to 120 °C (10 °C/min). Quantities of but-3-yn-2-ol in the individual samples were determined by external calibration.

All experiments were repeated three times and the standard deviation was calculated.

Adsorption of (±)-*but-3-yn-2-ol*.

The MOPSs MOPS-1(+) to MOPS-4(+) pillared with (+)-Co(sep)$^{3+}$ and MOPS-1(-) to MOPS-4(-) pillared with (-)-Co(sep)$^{3+}$ were heated at 100 °C under high vacuum (10^{-6} bar) for 24 h, cooled and transferred to an argon glove box. Three 10 mg samples of each MOPS were weighed into open Eppendorf plastic vials (1.5 mL) which were placed in a horizontally adjusted 50 mL Schlenk tube together with an open glass weighing tube containing 300 µL of (±)-but-3-yn-2-ol to secure a saturated atmosphere. The Schlenk tube was stoppered and kept at 4 °C for 48 h. Then it was connected to an argon line and after removal of the but-3-yn-2-ol source the sample vials were each treated with 500 µL of dry acetone p.a.. The vials were sealed, vortexed for 1 min, treated with a cooled ultrasonic bath for 30 min to desorb the but-3-yn-2-ol from the inorganic material, and centrifuged.

The acetone extracts were analysed as described before whereby enantiomers were identified and assigned by chromatographic comparison with authentic pure (+)- and (–)-but-3-yn-2-ol.

All experiments were repeated three times and the standard deviation was calculated.

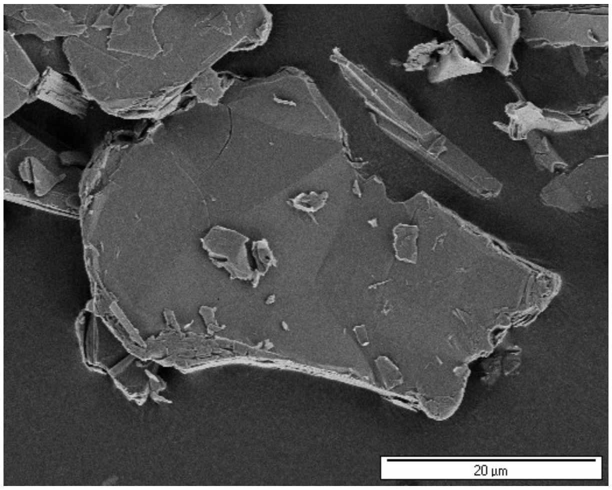

Figure S1. SEM image of MOPS-2(+).

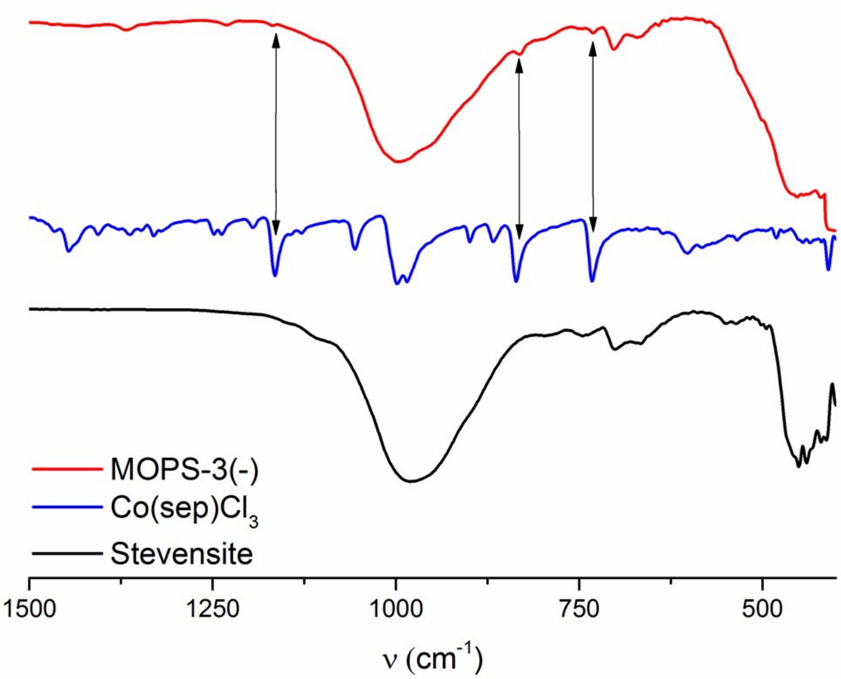

Figure S2. Infrared spectra before of Co(sep)Cl$_3$, MOPS-3(-) and synthetic stevensites proving preservation of integrity of pillars upon intercalation.

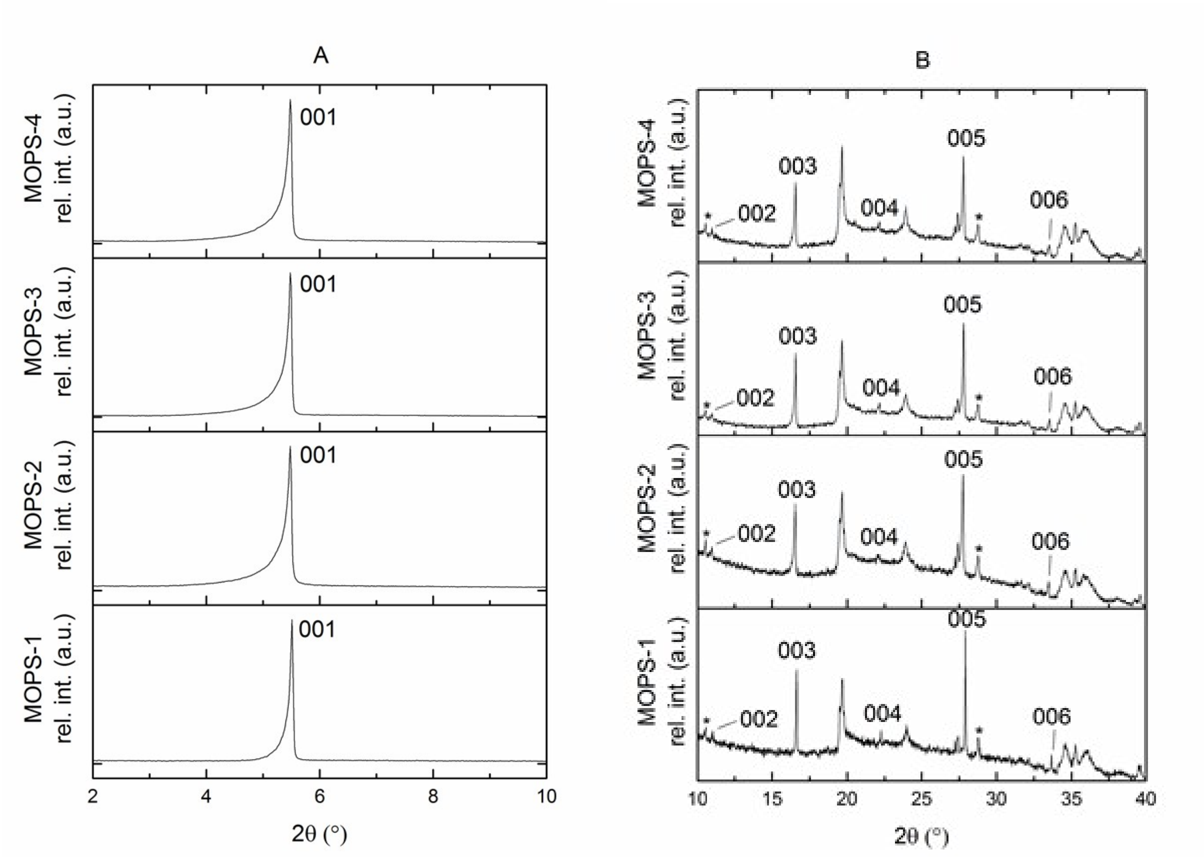

Figure S3. Powder X-ray diffraction pattern of MOPS-1 to MOPS-4 from (A) 2-10° 2θ and (B) 10-40° 2θ; asterisks mark a protoamphibole impurity phase.

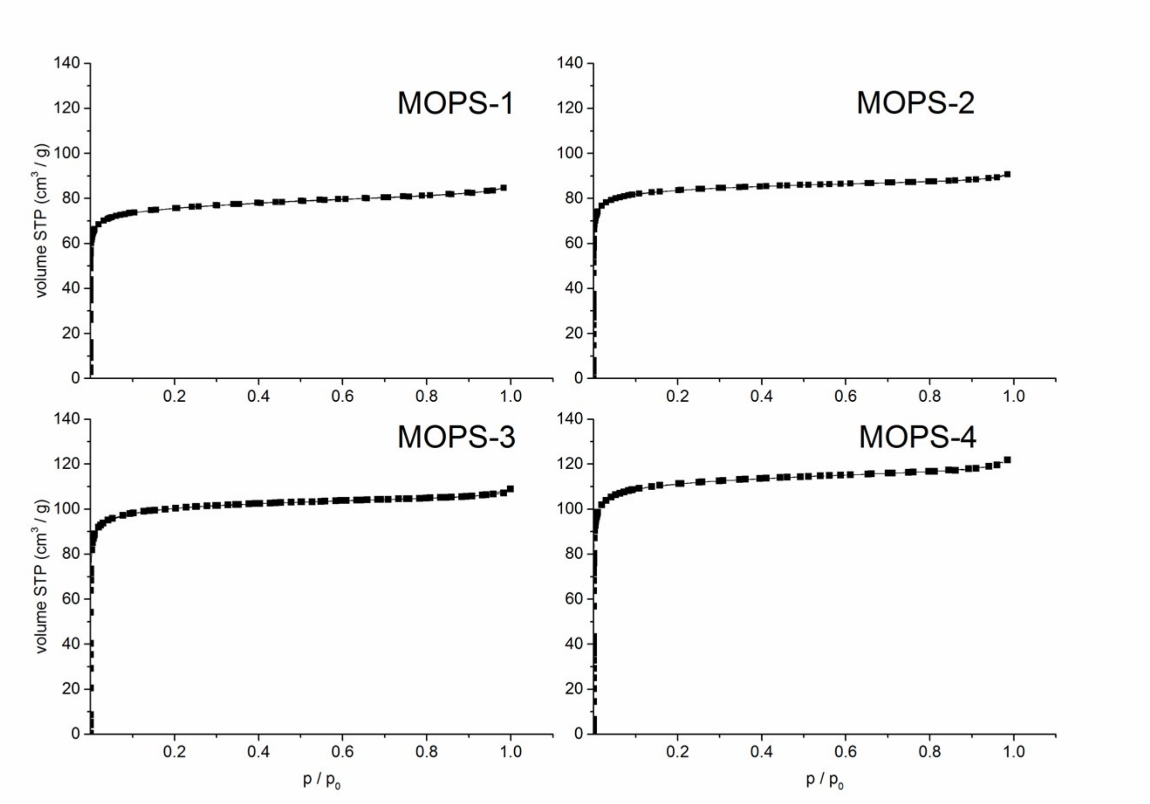

Figure S4. Physisorption isotherms Ar/Ar(l) at 87.35 K for MOPS-1 to MOPS-4 (linear scale).

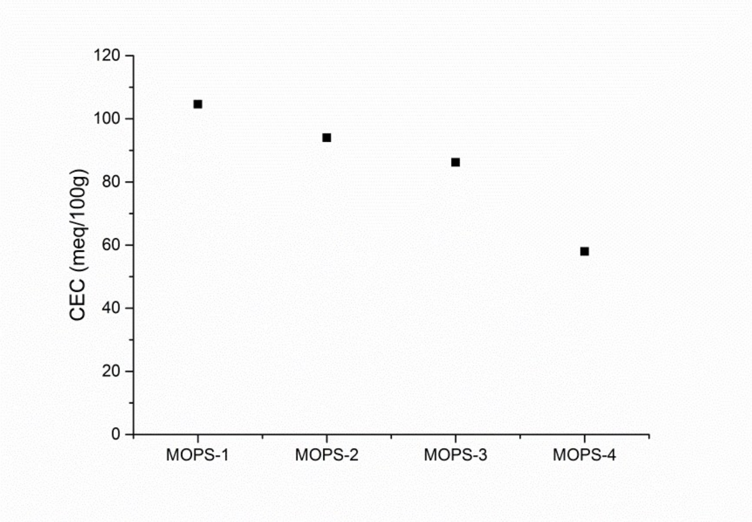

Figure S5. Stepwise reduction of the cation exchange capacity as function of the charge reduction time for MOPS-1 to MOPS-4.

Table S1. Measured values for Figure 3: Uptake of (±)-but-3-yn-2-ol and 2-methyl-but-3-yn-2-ol by MOPS-1 to MOPS-4.

	(±)-but-3-yn-2-ol (µL / 10 mg MOPS)	2-methyl-but-3-yn-2-ol (µL / 10 mg MOPS)	Molar Ratio *(rac)*-but-3-yn-2-ol / 2-methyl-but-3-yn-2-ol (%)
MOPS-1	1.24±0.05	0.55±0.06	73.7±0.5 / 26.3±0.5
MOPS-2	1.55±0.03	0.89±0.03	68.4±0.2 / 31.6±0.2
MOPS-3	1.50±0.02	0.93±0.04	66.7±0.3 / 33.3±0.3
MOPS-4	1.38±0.02	0.99±0.03	63.5±0.4 / 36.5±0.4
Gas Phase Composition			48.7±1.1 / 51.3±3.1

Table S2. Measured values for Figure 4: Uptake of (±)-but-3-yn-2-ol by stevensites pillared with (+)-Co(sep) (MOPS-1(+) to MOPS-4(+)) and enantiomeric excess.

	(±)-but-3-yn-2-ol (µL / 10 mg MOPS)	(*S*)-but-3-yn-2-ol (µL / 10 mg MOPS)	(*R*)-but-3-yn-2-ol (µL / 10 mg MOPS)	Enantiomeric excess (%)
MOPS-1(+)	1.73±0.01	0.80±0.01	0.94±0.02	7.45±0.45
MOPS-2(+)	2.24±0.02	1.11±0.02	1.13±0.02	0.54±0.31
MOPS-3(+)	2.46±0.05	1.22±0.05	1.24±0.05	-0.05±0.43
MOPS-4(+)	2.36±0.02	1.18±0.02	1.19±0.02	-0.31±0.31

Table S3. Measured values for Figure 4: Uptake of (±)-but-3-yn-2-ol by stevensites pillared with (-)-Co(sep) (MOPS-1(-) to MOPS-4(-)) and enantiomeric excess.

	(±)-but-3-yn-2-ol (µL / 10 mg MOPS)	(*S*)-but-3-yn-2-ol (µL / 10 mg MOPS)	(*R*)-but-3-yn-2-ol (µL / 10 mg MOPS)	Enantiomeric excess (%)
MOPS-1(-)	1.69±0.04	0.92±0.05	0.77±0.04	8.24±0.48
MOPS-2(-)	2.09±0.02	1.06±0.02	1.03±0.02	1.10±0.44
MOPS-3(-)	2.28±0.04	1.15±0.04	1.13±0.04	0.55±0.37
MOPS-4(-)	2.27±0.05	1.14±0.05	1.13±0.05	0.05±0.38

References

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