

Supporting information

Synthesis procedures

All chemicals were obtained from Sigma-Aldrich except for dimethyl-formamid (DMF) and dichloromethane which were obtained from Carl-Roth and were used without further purification.

(Salen@)NH₂-MIL101(Al)

270 mg of amino- terephthalic acid was dissolved in 60ml of DMF, when encapsulating the salen complex 50 mg of (R,R)-(-)-N,N'-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamino-manganese(III) chloride (Jacobsen's salen complex) was added to this solution, which resulted in a deep-brown color. This solution was heated to 110°C and 730 AlCl₃.6H₂O was added in 6 equal portions, one each 15 minutes, solid material starts to form after about 30 minutes. After adding the last portion, the mixture was left stirring for three hours. In a last step the mixture was left under heating without stirring for 16 hours. The resulting solid was filtered of and washed several time with DMF after which a soxhlet extraction with acetone was performed for 6 hours in order to remove any free linkers, AlCl₃ and salen complex.

Homogeneous catalytic test

4 mg of (R,R)-(-)-N,N'-Bis(3,5-di-tert-butylsalicylidene)-1,2-cyclohexanediamino-manganese(III) chloride was dissolved in 5 ml of dichloromethane. 20 µl of dihydronaphthalene and 90 mg N-Methylmorpholine N-oxide was added together with 62 µl toluene as internal standard. The mixture was left to stir at room temperature while 52 mg of meta-chloroperoxybenzoic acid was added in 3 equal portions spread over 10 minutes. After two hours the solution was analyzed with HPLC to determine the conversion and selectivity.

Heterogeneous catalytic test

330 mg of salen@NH₂-MIL101(Al) was added to 5 ml dichloromethane. 20 µl of dihydronaphthalene and 90 mg N-Methylmorpholine N-oxide was added together with 62 µl toluene as internal standard. The mixture was left to stir at room temperature while 52 mg of meta-chloroperoxybenzoic acid was added in 3 equal portions spread over 10 minutes. After two hours the catalyst was filtered of and the filtrate was analyzed with HPLC. The solid was washed 3 times with dichloromethane and reused for the next run with the same conditions.

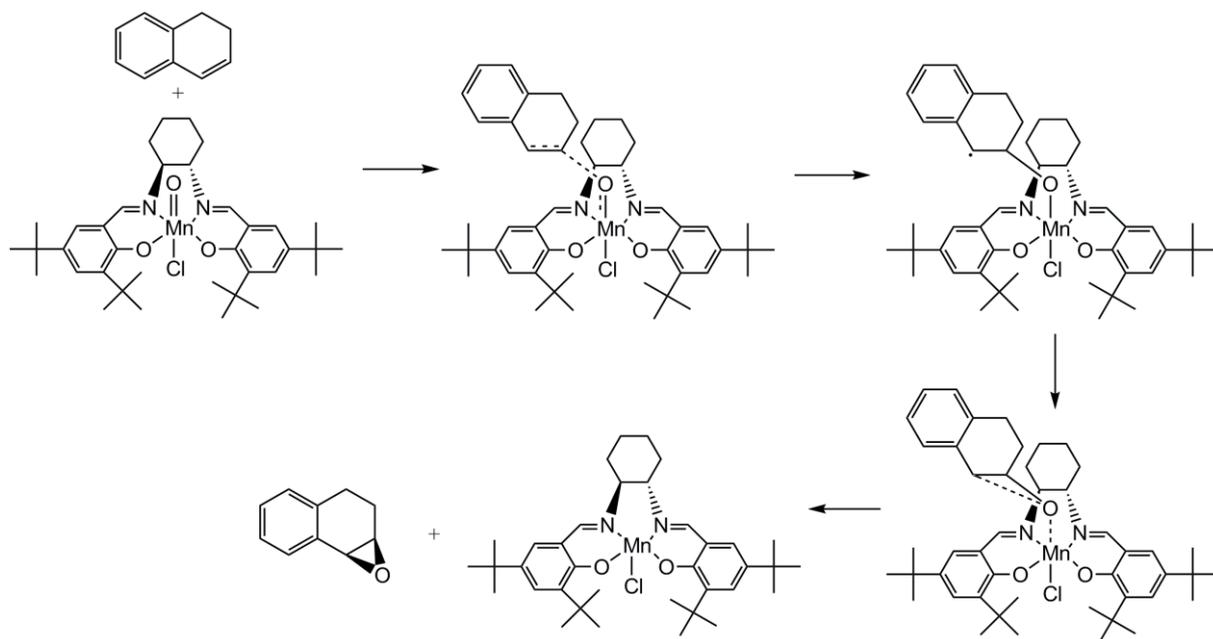
Blank test

For blank tests, the same mixture of 20 µl dihydronaphthalene, 90 mg N-Methylmorpholine N-oxide and 62 µl toluene in 5 ml dichloromethane was made. For the test with the empty NH₂-MIL101(Al) 330mg of MOF was added. The mixture was left to stir at room temperature while 52 mg of meta-chloroperoxybenzoic acid was added in 3 equal portions spread over 10 minutes. In the mixture without the MOF a slight precipitation was observed probably due to the reaction between N-Methylmorpholine N-oxide and meta-chloroperoxybenzoic acid. Both systems resulted in less than 5% conversion.

Characterization

Nitrogen sorption measurements were done with a Belsorp mini II gas analyzer at a temperature of -196°C . Powder XRD measurements were done with an ARL X'TRA X-ray diffractometer using K- α radiation of copper with a wavelength of 0.15418 nm and a solid state detector. X-ray fluorescence (XRF) spectroscopy measurements were performed on Rigaku NexCG, Energy Dispersive X-ray Fluorescence (EDXRF) apparatus. DRIFT-spectra were measured on a Nicolet 6700 FT-IR spectrometer from ThermoScientific. HPLC analysis was done with a Waters 2690 separation module and a UV detector of 220 nm. The column was a Daicel AD-H type chiral column. The mobile phase was a 98/2 vol% mixture of hexane/isopropanol with a flowrate of 0.900 ml/min.

Mechanism



Scheme S1. Generally accepted two-step mechanism for the epoxidation of olefins. The selectivity of the reaction is determined in the first step since the side of the oxygen addition is fixed there.

N₂-sorption

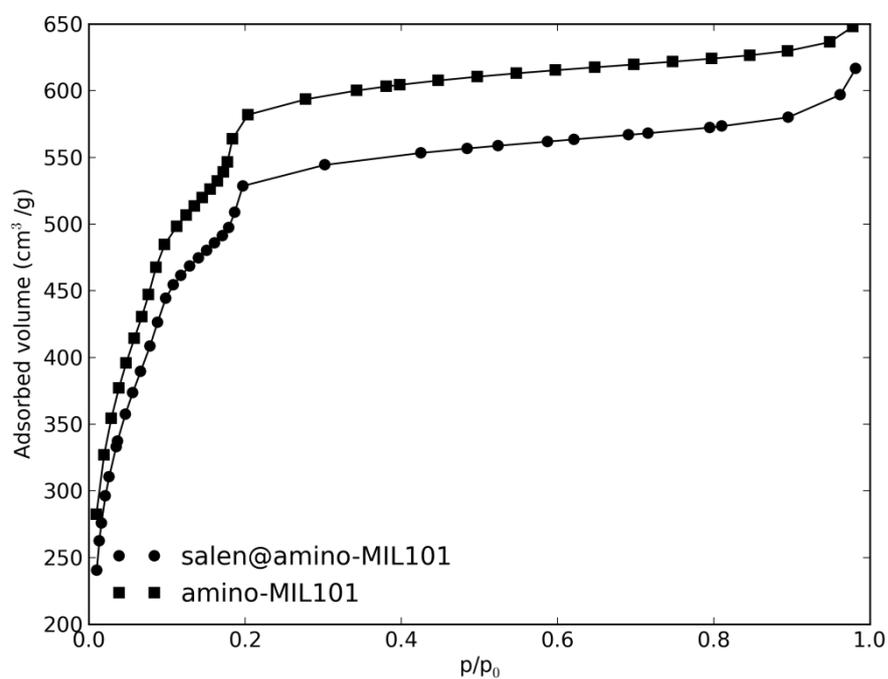


Figure S1. N₂-sorption experiment for both materials

Drifts measurement

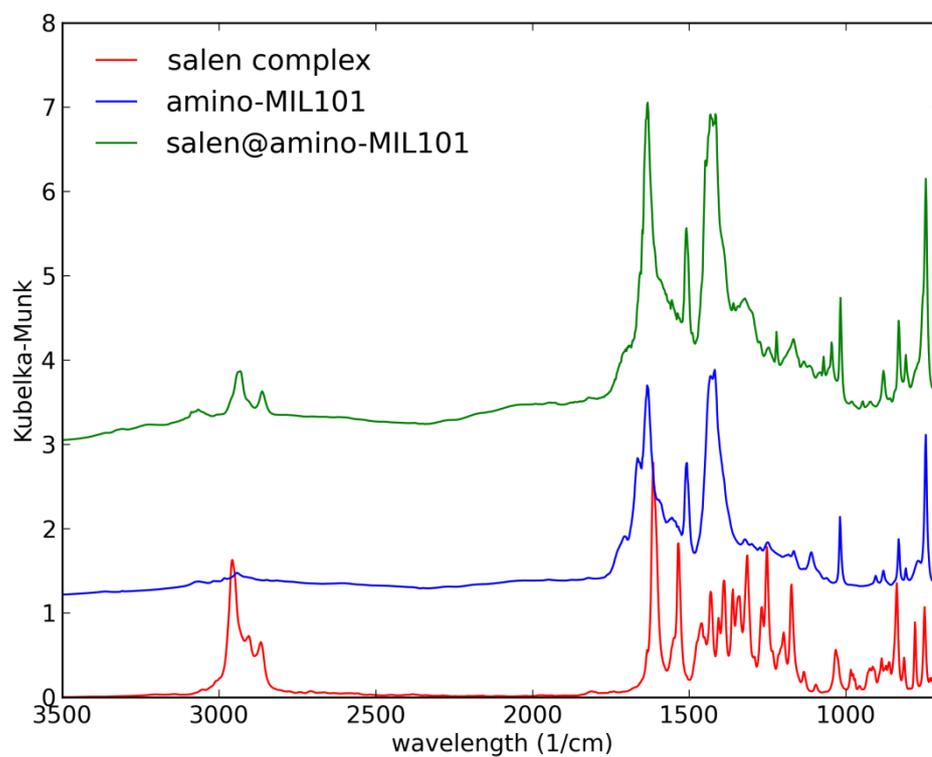


Figure S2. DRIFT spectra of the pure salen complex, NH₂-MIL101(Al) and salen@NH₂-MIL101(Al).

Influence of the MOF cage

In order to assess the influence of the surroundings we isolated a cluster model for a single cage from the cif file of MIL101(Cr) and saturated the removed linkers with a formiate moiety. The amine moieties were omitted. In order to optimize this cage we replaced the Cr atoms with Co, we didn't use aluminium for this optimization since there are no parameters for hexagonal aluminium in the UFF-forcefield¹. The cage was optimized with UFF holding the saturating moieties and the metal atoms in place.

After optimization Co was replaced by aluminium again for the single point calculation, here we placed both transition states in the center of the cage with the same orientation. We applied an ONIOM-scheme using UFF for the MOF-cage and the OPBE DFT functional for the salen complex with the same LOT as we used for optimization. The electronic energy difference between the two transition states is 12,1 kJ/mol which is very similar to what we found without embedding, this further shows that the support has no influence on the selectivity behaviour

1. A. K. Rappe, C. J. Casewit, K. S. Colwell, W. A. Goddard and W. M. Skiff, *J. Am. Chem. Soc.*, 1992, **114**, 10024-10035.