Electronic supporting information

Evaluation of two- and three-dimensional electrode platforms for the electrochemical characterization of organometallic catalysts incorporated in non-conducting metal-organic frameworks

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Materials and methods

Multi-walled carbon nanotubes (**MWCNT**, carbon >95%, produced by catalytic chemical deposition, outer diameter 10-15 nm, inner diameter 2-6 nm, length 0.1-10 mm), 1-Pyreneacetic acid (**PAA**, >97%), and mesoporous carbon (nanopowder, < 500 nm particle size) were purchased from Sigma-Aldrich and used as received. n-Bu_4NPF_6 for electrochemical analysis (>99%) acquired from Sigma-Aldrich was recrystallized three times from absolute ethanol and dried at 85 ˚C under vacuum for 72 h prior to use. Acetonitrile anhydrous (99.8%), also obtained from Sigma-Aldrich, was degassed by freeze-pump-thaw and kept over activated 3Å molecular sieves for 72 h before use. Glassy carbon rods (**GC**, Carbon-Vitreous-3000C Rod, 7.0 mm diameter) were purchased from Goodfellow, divided in 2 cm long segments, covered with a polytetrafluoroethylene jacket (exposing only the 0.38 cm^2 disk area) and used as working electrodes. UiO66 and UiO-66-[FeFe] were synthetized using previously reported methods.[1, 2] Detailed characterization of UiO-66-[FeFe] has been reported earlier.[2]

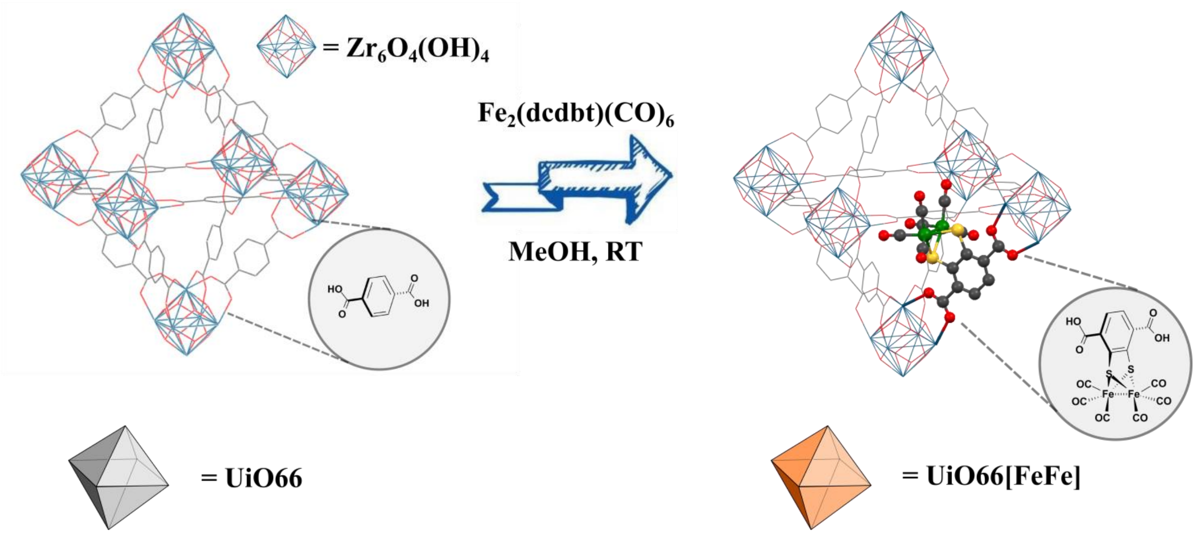

Figure S1. Scheme for incorporation of the molecular catalyst, [Fe_2(dcbdt)$(CO)_6$], into the UiO66 framework by post-synthetic exchange (PSE)

Scanning electron microscope (SEM)

Glassy carbon modified electrodes were transferred to conductive carbon tape on a sample holder disk, and coated using Pd-Ir-sputter coating for 30 s. A high resolution FEG-SEM/EDS Zeiss 1550 instrument was used for acquiring images at 5 KV under vacuum.

Electrochemical measurements

All electrochemical measurements were carried out under argon atmosphere in an anaerobic glovebox (MBraun, maintained at < 0.1 ppm O_2 and < 0.1 ppm H_2O), using a Metrohm Autolab potentiostat/galvanostat (PGSTAT302) with a GPES electrochemical interface. A 0.1 M solution of *n*-Bu_4NPF_6 in MeCN was used as supporting electrolyte (**SE**). A three-electrode electrochemical cell was used with a glassy carbon rod counter electrode and Ag/$AgNO_3$ (10 mM in MeCN) reference electrode and all potentials reported here are against $Ag^{+/0}$. $E_{1/2}$ of ferrocene against Ag/$AgNO_3$ (10 mM) reference electrode was determined to +60 mV. Both, the counter electrode and the reference electrode were kept separate from the main solution by salt bridges with glass frit tip filled with supporting electrolyte. 7 mm diameter glassy carbon disks (geometrical area 0.38 cm^2) were used as working electrodes and were carefully polished with successively smaller alumina particles down to 0.05 μm for 3 min, rinsed thoroughly and then sonicated for 3 min before any coating was applied. Prior to any measurement, all modified electrodes where dipped in supporting electrolyte and stirred for 5 min to remove all non-adsorbed material on the surface. Ohmic drop was compensated using a positive feedback compensation implemented in the instrument.

Electrode preparations

GC-UiO66 and GC-UiO66[FeFe] modified electrodes. A dispersion of UiO66 or UiO66[FeFe] (2 mg mL^{-1}) was prepared by sonicating the respective MOF in a sealed vial with MeCN under Ar atmosphere for 30 min, then it was centrifuged for 5 min at 5000 rpm and re-suspended in MeCN. This cycle was repeated 5 times to help to eliminate oxygen inside the MOF. A 20 μL aliquot of a freshly suspended MOF dispersion was placed on the surface of a glassy carbon electrode (geometrical area 0.38 cm^2) and allowed to dry overnight while covered with a test tube (to promote a homogeneous coating during the evaporation process). Afterwards it was allowed to stand uncovered for 72 h before any measurement to eliminate residual traces of oxygen. All samples were prepared and measured under argon atmosphere inside of the glovebox.

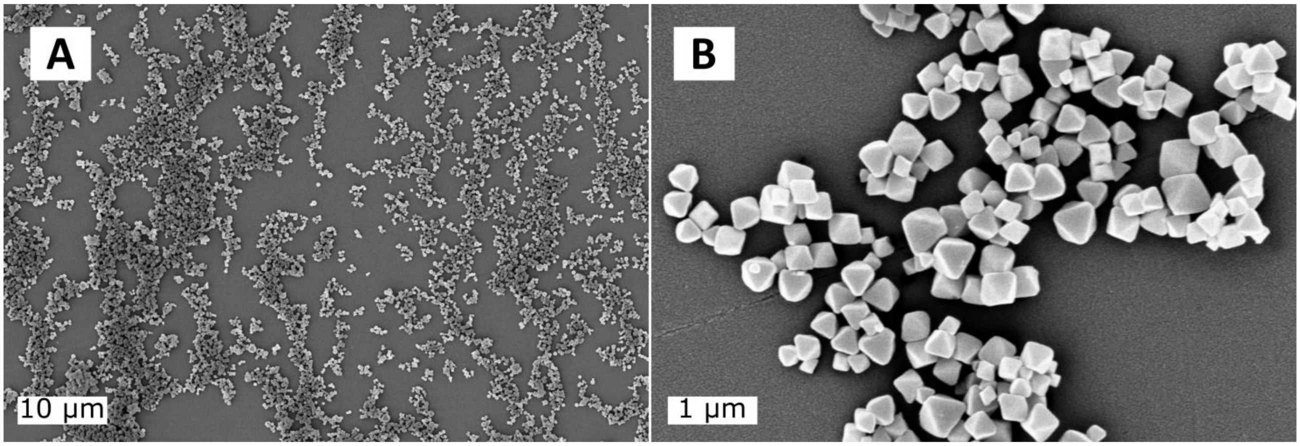

Figure S2. Top-view SEM image of UiO-66 modified GC-electrodes at (A) 5,000 x and (B) 50,000 x magnification. The electrodes were prepared by drop-casting MOF suspension on bare glassy carbon electrode.

GC-PAA-UiO66[FeFe] modified electrodes. The procedure for preparing GC-PAA-UiO66[FeFe] electrodes was similar to that described above for GC-UiO66[FeFe] modified electrodes. Here, a solution of 1-pyreneacetic acid (1 mg mL^{-1} in MeCN) was added to 2 mg of the respective MOF in a sealed vial and sonicated for 30 min. The suspension was kept overnight to leave PAA enough time for anchoring onto the surface of the MOF particles. After this, non-linked PAA was washed out by 5 continuous cycles of centrifugation and re-suspension in degassed MeCN. 20 μL of a freshly suspended PAA-MOF dispersion (2 mg mL^{-1}) was deposited by drop casting on a GC electrode and allowed to dry as described above.

GC-MWCNT-PAA-UiO66[FeFe] modified electrodes. As described for GC-PPA-UiO66[FeFe] electrodes, a dispersion of PAA-MOF (2 mg mL^{-1}) was prepared after which 1 mg of MWCNT (per mL of dispersion) was added. This new mixture was placed in a sealed vial and sonicated for 10 min every hour for ten hours and allowed to stand overnight to get a strong π-stacked MWCNT-PAA-MOF assembly.[3, 4] 20 μL of a freshly suspended MWCNT-PAA-MOF dispersion (2 mg mL^{-1}) was deposited onto a GC electrode by drop casting and allowed to dry as described for GC-UiO66[FeFe] modified electrodes.

GC-CB-UiO66[FeFe]$^{4:1}$ modified electrodes. The MOF (1 mg) and carbon black (4 mg) was mixed in an aliquot (0.5 mL) of the 2-propanol solution which contains 0.5% v/v of Nafion® 117. The suspension was homogenized by ultra-sound sonication for 1 h to form a stable ink. The ink was (20 µL) was drop-casted on a polished glassy carbon electrode (geometrical surface area 0.38 cm^2) and dried in air for 24 h.

GC-CB-UiO66[FeFe]$^{1:2}$ modified electrodes. 1 mg MOF was mixed with 0.5 mg carbon black in 0.5 mL 2-propanol to prepare the ink. Next steps are similar to that for GC-CB-UiO66[FeFe]$^{4:1}$.

Surface coverage and average particle size.

The surface area coverage of the films was determined by digital analysis of the SEM images using ImageJ. ImageJ is a public domain Java image processing program that can calculate area and pixel value statistics, such as distribution and particle size. The images are first transform into a high contrast black and white format, and then they are processed to determine the surface coverage and the particle size.

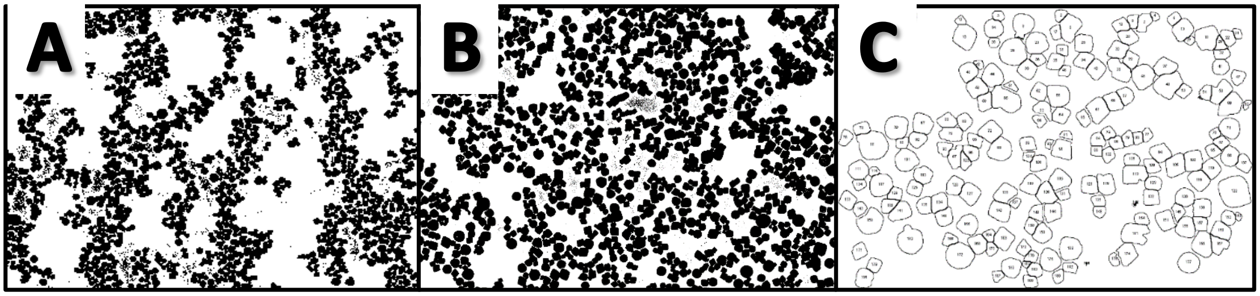

Figure S3. Examples of high contrast digitalized SEM images of (**A**) GC-UiO66[FeFe] (**B**) GC-PAA-UiO66[FeFe] modified electrodes, giving an average surface coverage value of 33.5 % and 46.9 %, respectively. (**C**) Example of a GC-PAA-UiO66[FeFe] SEM image processed to determine the average particle size of ca. 250 nm.

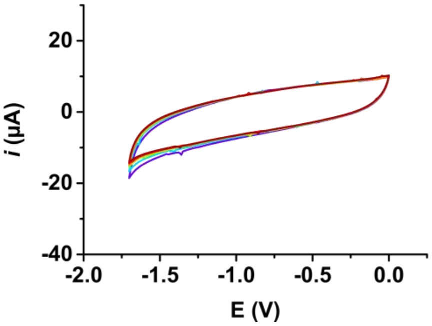

Figure S4. Progressive cyclic voltammograms of GC-UiO66 in acetonitrile (0.1 M n-Bu$_4$NPF$_6$) at ν = 100 mVs^{-1} under Ar atmosphere.

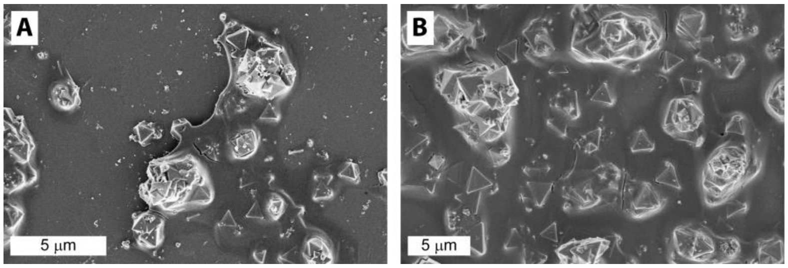

Figure S 5. Top-view SEM images of UiO-66-[FeFe] modified glassy carbon electrodes at (A) 9,000 x and (B) 11,000 x magnification recorded after performing cyclic voltammetry (20 scans) in acetonitrile. After electrochemical measurements, the electrodes were dried without washing and SEM images were recorded. The images therefore show that the MOF crystals are coated in electrolytes.

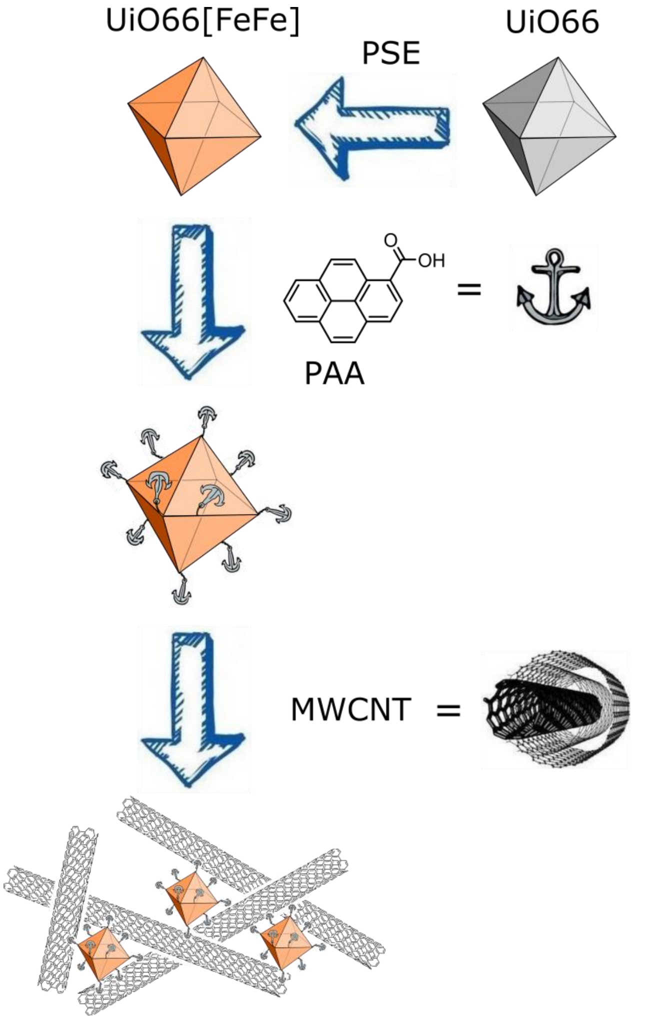

Figure S6. Schematic representation of fabrication of MWCNT-PAA-UiO66[FeFe] materials prior to drop-casting on glassy carbon electrodes.

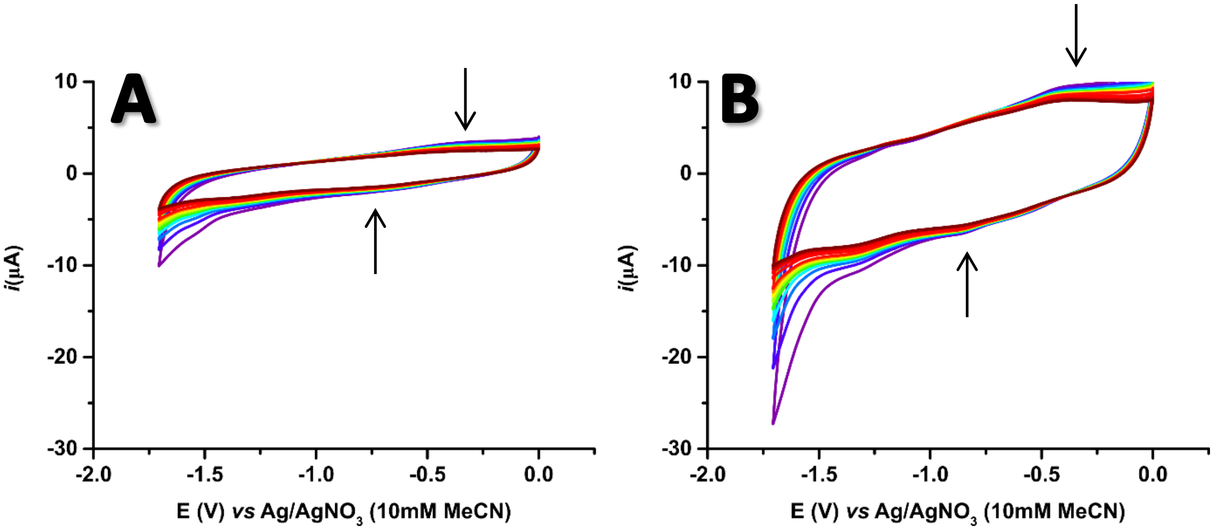

Figure S7. Cyclic voltammograms of (**A**) PAA on a bare GC electrode in acetonitrile solution and (**B**) GC-PAA-UiO66[FeFe] modified electrodes. Solvent MeCN (n-Bu_4NPF_6 0.1 M) at ν= 100 mVs^{-1} under Ar atmosphere.

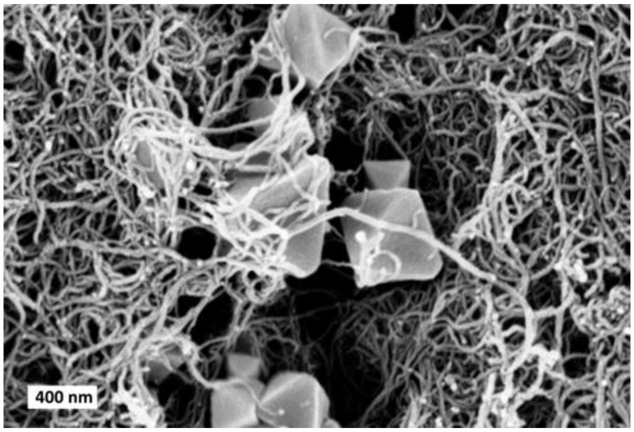

Figure S8. Top-view SEM image of a GC-MWCNT-PAA-UiO-66-[FeFe] electrode at 100,000 x magnification.

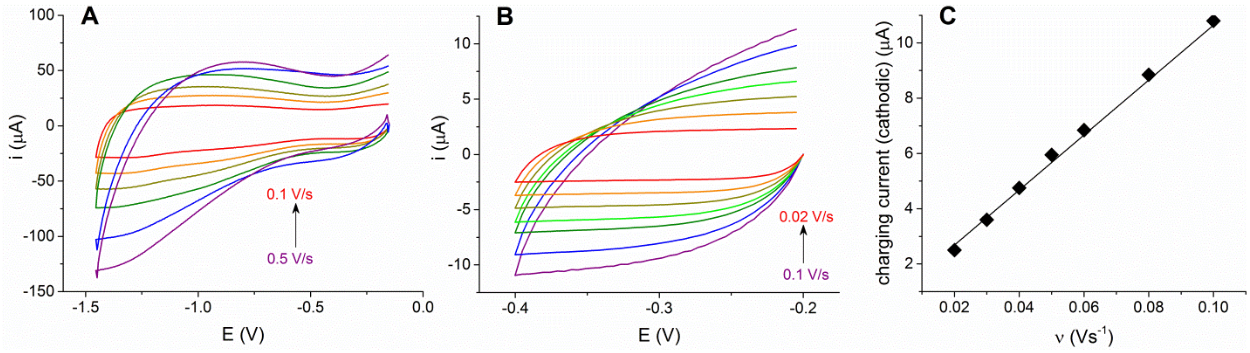

Figure S9. (A) Scan-rate dependent cyclic voltammograms of CB-UiO-66 modified glassy carbon electrodes (purple: 0.5 V s^{-1}; blue: 0.4 V s^{-1}; olive: 0.25 V s^{-1}; dark yellow: 0.2 V s^{-1}; orange: 0.15 V s^{-1}; red:

0. V s^{-1}). As expected, the reductive peak for the [FeFe]-complex at ca. -1.2 V is absent for these electrodes. (B) Cyclic voltammograms measured in a non-Faradaic region (close to the open circuit potential) at the following scan rate: (purple) 0.1, (blue) 0.08, (olive) 0.06, (green) 0.05, (dark yellow) 0.04, (orange) 0.03, and (red) 0.02 V/s. The capacitive current is associated with double-layer charging. (C) Linear dependence of cathodic charging currents measured at -0.35 V on the scan rates.

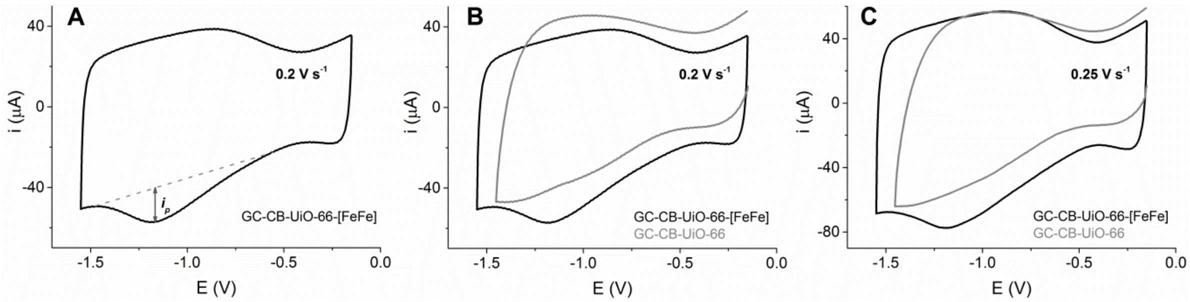

Figure S10. (A) Illustration to show the calculation for reductive peak currents (i_p) from the cyclic voltammograms of CB-UiO-66-[FeFe] modified glassy carbon electrodes. Peak currents were determined using GPES software (Metrohm Autolab) and these i_p values were plotted against scan rate to obtain Figure 3B (manuscript). (B and C) Comparison of the cyclic voltammograms of GC-CB-UiO-66-[FeFe] (black traces) and GC-CB-UiO-66 (grey traces) recorded at 0.2 V s^{-1} (B) and 0.25 V s^{-1} (C).

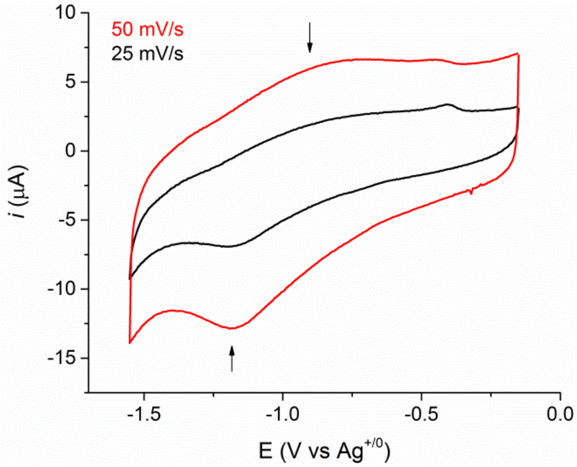

Figure S 11. Cyclic voltammograms of GC-CB-UiO-66-[FeFe]$^{4:1}$ recorded at slow scan rates (25 and 50 mV/s) in acetonitrile.

References

1. J. Hafizovic Cavka, S. Jakobsen, U. Olsbye, N. Guillou, C. Lamberti, S. Bordiga and K. P. Lillerud, *J. Am. Chem. Soc.*, 2008, **130**, 13850-13851.
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