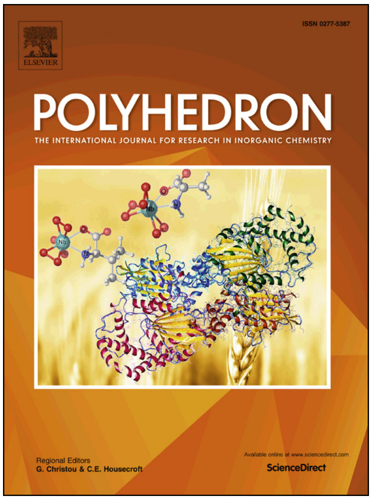

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A bifunctional metal-organic framework platform for catalytic applications

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Abstract

DUT-71 (DUT - Dresden University of Technology), a copper paddle wheel based framework, was used as a platform for postsynthetic modification to introduce specific catalytically active sites and to enhance the catalytic activity for fine chemicals production using bifunctional N-donor ligands such as dabco (1,4-diazabicyclo[2.2.2]octan) and 3,5-bis(1*H*-imidazol-1-yl)arene derivatives resulting in the corresponding networks DUT-72 and DUT-90. The intact network structure after functionalisation was confirmed by powder X-ray diffraction, the degree of functionalization was analysed by ^{1}H NMR, thermal and elemental analysis. As model reaction, the C-C coupling reaction of Henry type catalysed by Lewis acids in presence of organic base was chosen. The influence of the functionalisation degree, solvent, and reaction temperature on the catalytic activities was studied. Finally, yields up to 77% of 2-nitro-1-(4-nitrophenyl)ethan-1-ol in the reaction of 4-nitrobenzaldeyde with nitromethane were achieved using a dabco functionalised network DUT-72.

Keywords: coordination polymer; Henry reaction; copper paddle wheel; post synthetic modification

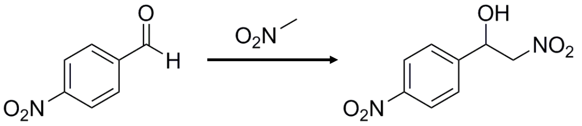
Introduction

The crystalline character combined with a high pore volume accessible for guest molecules make metal-organic frameworks suitable for catalytic applications.[1–3] Because of the easy integration of active centres of interest into the cluster or the ligand, a catalyst can be designed in a modular way. It is the main reason for the wide applicability of this type of materials in a broad range of catalytic reactions, including C-C or C-X (X = N, O, S) coupling reactions.[4]

Depending on the network composition and functional groups presented, various kinds of reactions are feasible.[5] By introduction of active palladium species into the cluster, ligand or as guest species in the pore system, the catalytic conversion in Suzuki-Miyaura,[6] Sonogashira[7] or Mizoroki-Heck[8,9] coupling were successful. Also transformations catalysed by copper were often reported, since the copper-based paddle wheel cluster is the most prominent node in MOF chemistry, offering catalytically active open metal sites. Amongst others, C-C coupling reactions[10,11] or various types of condensation[12] or addition[13] reactions can be catalysed by copper paddle wheel based MOFs.

Recently, we reported a DUT-71 ($Cu_4(m\text{pbatb})_2(H_2O)_4$) MOF, based on copper paddle wheels and a tetratopic 1,3-phenylebis(azanetriyl)tetrabenzoate (*m*pbatb) ligand, as a platform for introducing various active molecular building blocks post synthetically.[14,15] As an example, the integration of 1,3-bis(1*H*-imidazol-1-yl)benzene (1,3-bib) or 3,6-bis(pyridine-4-yl)1,2,4,5-tetrazine (bpta) in combination with 1,4-diazabicyclo[2.2.2]octane (dabco) ligands increases the robustness of the network for desolvation and enables to use DUT-71 based materials for sensing[14] and gas adsorption.[15] In particular, the functionalised structures facilitate the detection of alcohols in the ppm range or the identification of the solvents of different polarity.[14] The disposition for functionalisation renders DUT-71 as an ideal candidate for the integration of predefined catalytically active centres. Post-synthetic modification is nowadays recognized as a powerful tool in MOF chemistry[16,17] to create new catalysts.[18,19]

The Henry reaction is one example of a C-C coupling reaction catalysed by copper under the addition of a base such as dabco.[20] In the course of the reaction the α-carbon of an aliphatic nitro compound reacts with a carbonyl compound to a β–nitro alcohol under the formation of a C-C bond. Products of the Henry reaction are useful intermediates for the synthesis of complex organic molecules. The resulting nitro alcohol can act as functionalised starting material for subsequent transformations such as oxidation or reduction.



Scheme 1: Model catalytic reaction investigated.

The structure of DUT-71 contains two crystallographically independent paddle wheel clusters. The paddle wheels arranged along *c*-axis have alternating inter-paddle wheel distances of 8.0 and 13.8 Å (Figure 1a). The accessible metal sites of remaining paddle wheels point into the pores. DUT-71 is ideal to bind dabco in a way, that only one nitrogen atom is coordinated to the paddle wheel (monodentate). The non-coordinating nitrogen can consequently participate in the Henry reaction, making use of the bifunctionality: the copper open site and the pending nitrogen of the organic base dabco. To evaluate this concept, the Henry reaction of 4-nitrobenzaldehyde with nitromethane to 2-nitro-1-(4-nitrophenyl)ethan-1-ol was chosen as a test reaction (Scheme 1).

Experimental

1. MOFs synthesis

DUT-71, DUT-72 and DUT-90 MOFs were synthetized as reported elsewhere[14,15] (for more details see ESI.

2. Catalysis

For a typical experiment the MOF catalyst was transferred into a GC vial and the vial was placed in a Pyrex or Schlenk tube (Fig. S11 ESI). 4-Nitrobenzaldehyde (102.7 mg, 0.679 mmol) dissolved in 6.500 mL nitromethane or in 6.500 mL ethanol/nitromethane mixture (mixture composition: 0.364 mL (414 mg, 10 eq) nitromethane and 6.136 mL ethanol) was added and the reaction mixture was heated to the desired temperature, indicated in the Table S1 of ESI.

To identify and characterise the products of the reactions, they were isolated after defined reaction time periods and analysed by high performance liquid chromatography (HPLC). HPLC measurements were performed on ELITE LACHROM System from VWR/HITACHI using a UV L2400 detector. For data evaluation EZCHROM ELITE software from AGILENT TECHNOLOGIES was applied. The chiral column CHIRALPAK ID (diameter 4.6 mm, length 250 mm, particle size 5 μm) was used with following parameters for baseline separation: wavelength 220 nm; composition of the mobile phase: n-hexane/isopropanol (85/15); flow: 1 ml min^{-1}. Retention times for enantiomers: 20.8 and 26.8 min, respectively.

The 2-nitro-1-(4-nitrophenyl)ethan-1-ol (**1**) was synthetized, purified and used for the HPLC calibration. The yields of **1** in the reaction was determined using obtained calibration curve. If 1-(diethoxymethyl)-4-nitrobenzene (**2**) or 1-nitro-4-(2-nitrovinyl)benzene (**3**) appeared as a side products, they could be detected as additional signals in the chromatogram. Moreover, the ^{1}H and ^{13}C NMR analysis was performed to identify the compounds. The yield of **2** and **3** was not determined.

Results and discussion

To create bifunctional, copper/base containing catalyst, DUT-71 (Fig. 1a) crystals were soaked in a dabco solution at 80 °C for 7 days resulting in the formation of DUT-72 (Figs. 1b and 2a).

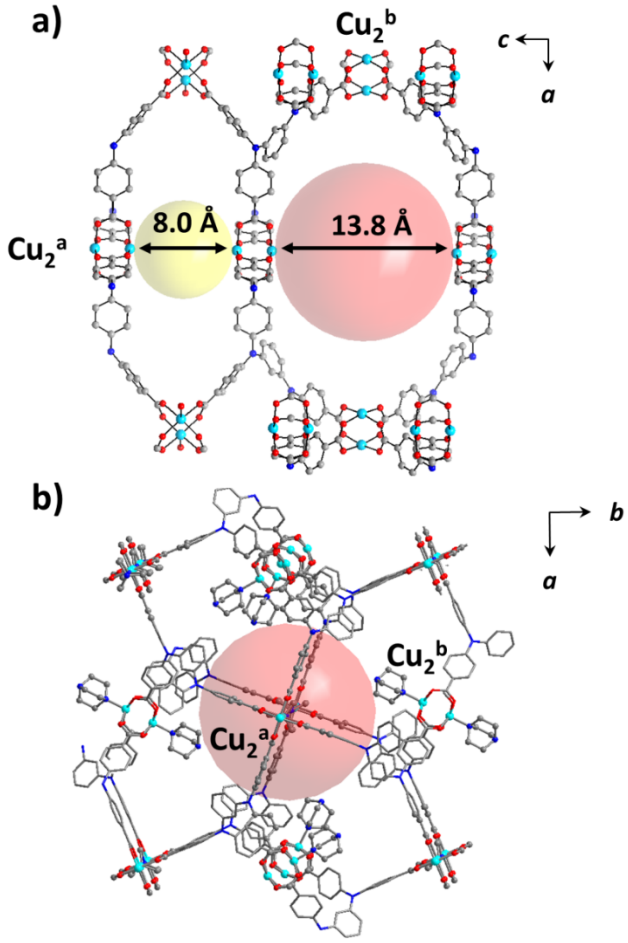


Figure 1: a) Crystal structure of DUT-71 along *b* axis. b) Crystal structure of DUT-72 along *c* axis. [14,15]

Since the structure of the DUT-71 derivatives contains two independent paddle wheel clusters (paddle wheel Cu_2^a consists of Cu2 and Cu1 atoms; paddle wheel Cu_2^b consists of two symmetry equivalent Cu3 atoms, Figs. 1, S12), dabco can be distributed between four Cu atoms inside the MOF upon post synthetic modification. The maximal, theoretically possible loading (coordination ability) of the available Cu sites with dabco in DUT-71 (Cu_4(*m*pbatb)$_2$) is 3.5 molecules per 4 Cu atoms (ideal composition Cu_4(*m*pbatb)$_2$(dabco)$_{3.5}$ or [Cu_2^a(dabco)$_{1.5}$][Cu_2^b(dabco)$_2$](*m*pbatb)$_2$).
In DUT-72 and DUT-90 we expect a full occupancy of the small Cu - Cu gap (8 Å gap in Fig. 1a, Figs. 2a, S12) by dabco first, because of favourable two-fold coordination mode. The remaining dabco should be coordinated in a monodentate fashion to the paddle wheels (Table 1, column 3) pointing into the pores (Fig. 2a, S12) and can potentially act as base in the catalysis.
The real compositions of MOFs obtained after post-synthetic modification (content of dabco and 1,3-bib derivatives) were determined on the basis of elemental and thermogravimetric analysis results (Table 1, Figs. S8 – S9 ESI). The real composition of DUT-72 was estimated to be Cu_4(*m*pbatb)$_2$(dabco)$_{1.45}$, pointing on some dabco deficit in the structure and some Cu sites left unoccupied by dabco (Table 1, column 2). Accordingly, the 2.05 cooper atoms per formula unit still accessible (linker free) and potentially available as Lewis acidic catalytic sites. So, the ratio between the Lewis acidic catalytic sites and base (dabco coordinated in a monodentate fashion)

amounts to 2.15 in DUT-72 (Table 1, column 4), pointing on the excess of Cu sites in respect to dabco amount.

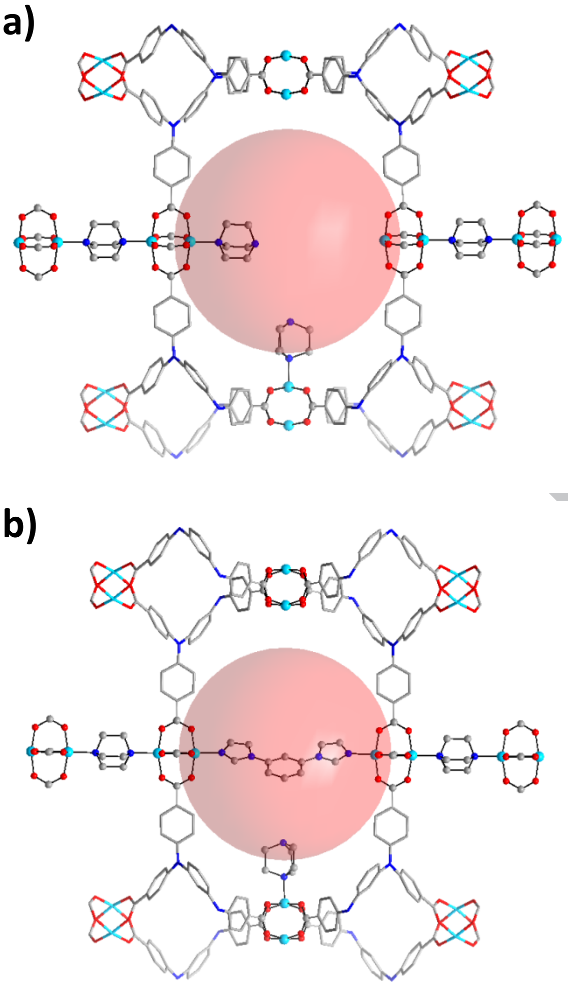


Figure 2: Part of the crystal structure of: a) DUT-72; b) DUT-90 along *b* axis.

Table 1: Analysis of Cu and dabco contents in the investigated MOFs given per formula unit.

	Open (linker free) copper sites (a)	**Monodentate coordinated dabco (b)**	**ratio (a) to (b)**
DUT-71 $Cu_4(m\text{pbatb})_2$	4	0	n.a.
DUT-72 $Cu_4(m\text{pbatb})_2(\text{dabco})_{1.45}$	2.05	0.95	2.15
DUT-90 $Cu_4(m\text{pbatb})_2(\text{1,3-bib})_{0.5}(\text{dabco})_{1.85}$	0.65	1.35	0.48

In DUT-90, the large gap (13.8 Å, Fig. 1a) is occupied by additional, nitrogen containing ligand (1,3-bib) (Fig. 2b), making it possible to encircle more precisely the position of possible catalytic sites in this compound in comparison to DUT-72, because all Cu_2^a paddle wheels are involved into the coordination of two-fold coordinating ligands (dabco in small gape, 1,3-bib in large gape). In this compound, catalytically active sites as well as monodentate coordinated dabco molecules should more probably come from Cu_2^b paddle wheels only (Fig. 2b). In case of DUT-90, lager amount of dabco coordinated in a monodentate fashion should be present according to the elemental analysis (Tab. 1).

To evaluate the impact of crystallographically different Cu sites (regarding the coordination and chemical environment) as well as dabco in the catalytic reaction, the obtained materials were applied as catalyst in a model Henry reaction (Scheme 1).
Initially, catalytic tests were performed in nitromethane (at 100 °C), acting as solvent and as reactant at the same time. The reaction was terminated after 72 h. The products were isolated and analysed by HPLC (for more details see experimental section).
The DUT-72 and DUT-90 turned out to be more active catalysts then DUT-71, producing 43% and 45% of 2-nitro-1-(4-nitrophenyl)ethan-1-ol (**1**, Scheme 2),respectively. The DUT-71 yields only 14% (Fig. 3). For DUT-71 and DUT-90 a stepwise increase in yield after 30 h of reaction was observed, pointing on some induction period.

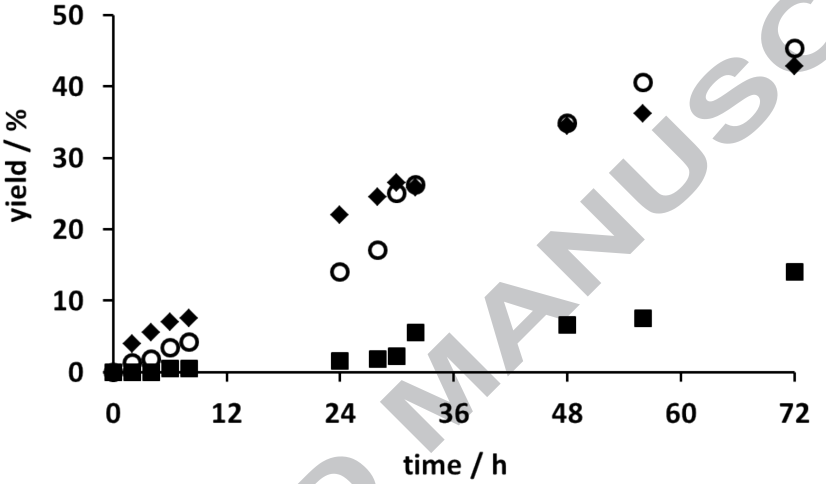
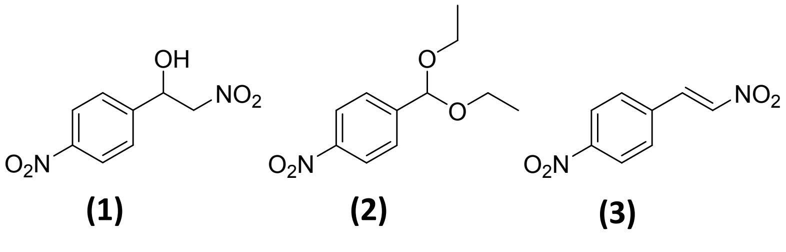


Figure 3: MOF-catalysed production of 2-nitro-1-(4-nitrophenyl)ethan-1-ol using DUT-71 (■), DUT-72 (♦) and DUT-90 (○) as catalyst in nitromethane at 100 °C.

DUT-71 has the highest concentration of accessible Cu sites (Table 1), but the absence of dabco leads to the low yield in comparison to DUT-72 and DUT-90. In case of DUT-71, the activation of the nitromethane takes place, obviously, only by a thermal treatment, since the reaction was performed at high temperature (100 °C). In DUT-72 the amount of potentially accessible Cu-sites is almost three times higher than in DUT-90 at comparable dabco amount (Table 1), so we conclude that slightly higher loading of manodentate coordinated dabco in DUT-90 leads to the slightly better performance in the catalytic reaction.
Thus, the positive influence of dabco, post-synthetically introduced into DUT-72 and DUT-90 could be clearly identified.



Scheme 2: Products formed in the catalytic tests.

To evaluate the effect of solvent, ethanol was added to the reaction system in the next trials. Utilizing DUT-71 at room temperature (RT), the formation of 1-(diethoxymethyl)-4-nitrobenzene (**2,** Scheme 2) was observed. The same reaction product was detected in small amounts in a control reaction, when only 4-nitrobenzaldehyde and nitromethane were stirred in ethanol at RT without catalyst, pointing on low activity of the Cu sites of MOFs under such conditions.

For further test the temperature was increased to 80 °C. For DUT-72 and DUT-90 a yield of **1** up to 50% was detected after 8 h of reaction (Fig. 4). Interestingly, longer reaction time leads to decrease in the amount of **1** formed (Fig. 4). After isolation of the products, 1-nitro-4-(2-nitrovinyl)benzene (**3**, Scheme 2) as a side product was detected. Obviously, ethanol accelerates the reaction of 4-nitrobenzaldehyde to 2-nitro-1-(4-nitrophenyl)ethan-1-ol (**1**) and facilitates a secondary elimination reaction of 2-nitro-1-(4-nitrophenyl)ethan-1-ol (**1**) to 1-nitro-4-(2-nitrovinyl)benzene (**3**). The reason for the side reaction is the protic character of ethanol as solvent, which is able to act as proton donor interacting with OH group of **1** to form water. Such elimination was not observed if the reaction was performed in aprotic nitromethane.

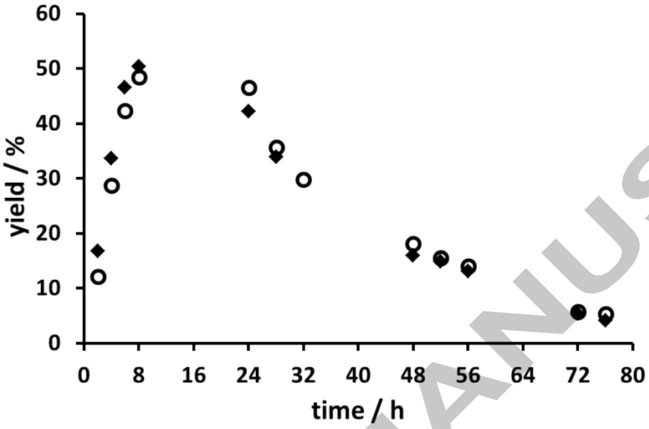


Figure 4: Formation of 2-nitro-1-(4-nitrophenyl)ethan-1-ol using DUT-72 (♦) and DUT-90 (○) as catalyst in ethanol at 80 °C.

To evaluate temperature dependence for the formation of **3**, the reaction temperature was decreased stepwise. If the temperature was decreased to 50 °C, 74% yield of **1** for DUT-90 and 77% of **1** for DUT-72 were obtained.

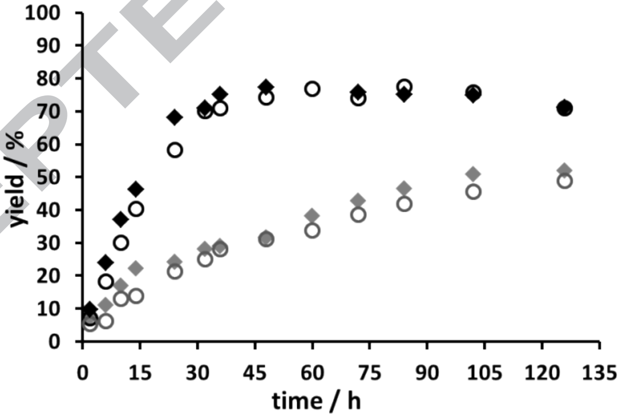


Figure 5: Formation of 2-nitro-1-(4-nitrophenyl)ethan-1-ol (**1**) in ethanol for DUT-72 (♦) and DUT-90 (○) at 50 °C (black) and at 25 °C (grey).

Longer reaction times (up to 126 h) show no significant improvement in the yields (Fig. 5). Obviously, lowering the reaction temperature suppresses the secondary reaction of **1**.

At 25 °C a maximal 2-nitro-1-(4-nitrophenyl)ethan-1-ol **1** yield of 47% for DUT-72 and 45% for DUT-90 were observed after 126 h of reaction (Fig. 5). Also no side products were detected.

Interestingly, the type of catalyst critically influences the products formed in the reaction, giving, to some extent, the possibility to design the catalyst. For example amines immobilized on silica-alumina are able to convert an aldehyde with nitromethane to a 1,3-dinitroalkane species.[21] Such a product was not observed in our studies. Also MOFs are able to catalyse the reaction to different products, depending on the nature of the catalyst applied. For example amine functionalised MIL-101(Cr) and amine functionalised UiO-66 (Zr based MOF) guide the reaction to elimination, forming product **3** (Scheme 2).[22-25] Interestingly, a reaction catalysed by UiO-67 (isoreticular to UiO-66) functionalised with an urea group stops at alcohol formation step (yield 67%).[26] Dabco containing Zn-MOF[27] (yield 60%) or pyridine containing Cu-MOF[28] (yield 85%) were reported to produce the alcohol derivatives.

To analyse the stability of DUT-72 and DUT-90 during the catalysis, recycling tests were performed for reactions at 25 °C and 50 °C.

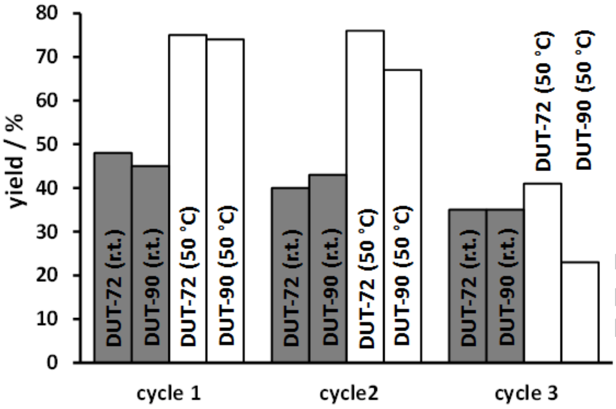


Figure 6: Recycling tests for DUT-72 and DUT-90 at RT and 50 °C after 96 h reaction time.

At 25 °C, a certain decrease in yield of **1** was observed during three catalytic cycles for both catalysts (from 48 % to 35 % for DUT-72 and from 45% to 35% for DUT-90). At 50 °C the yield decreases more drastically in the third cycle (from 76 to 41% for DUT-72) than in the second cycle (Fig. 6), although PXRD analysis of the reused catalysts reveals the retained crystallinity after 3 runs (Figs. S1 - S6).

Thus, the results obtained in this study indicate a high sensitivity of the MOF catalysed reaction towards solvent nature and temperature. Advantageous opportunity to terminate the reaction selectively at the alcohol formation stage opens the possibility to use it as starting material for further oxidation of the hydroxyl group to a ketone[29] or for the reduction of the nitro group to an amine.[30]

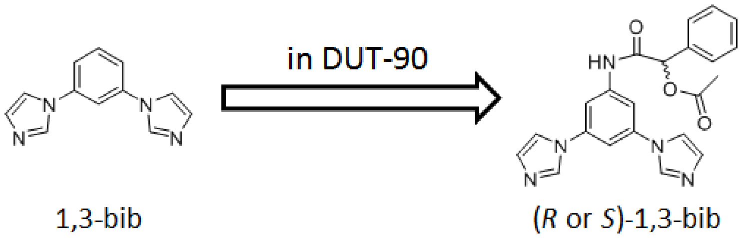


Figure 7: Introducing of the chiral information into the DUT-90 framework by ligand functionalisation.

Since examples of enantioselective Henry reaction catalysed by MOFs are not reported in the literature yet, chirality was introduced into the DUT-90 by replacing the 1,3-bib ligand by a chiral analogue (Fig. 7) to form *chir*-DUT-90 ($[Cu_4(m\text{pbatb})_2(chir\text{-1,3-bib})_{0.5}(\text{dabco})_{1.7})$ according to PXRD analysis (Fig. S7) and NMR data (Fig. S10). Only few reports about preferable formation of diastereomers by coupling with e.g. nitroethane are published.[31-34]

Catalytic tests using *chir*-DUT-90 were carried out in ethanol at 0 °C, 25 °C, and 50 °C. After three days yields of 34%, 37%, and 40% of **1**, respectively, were obtained. However no enantiomeric excess was observed for the desired product. A possible explanation could be the wide gap in-between chiral information and the catalytic active sites within the network.

Conclusions

Post synthetic modification is a versatile tool for the introduction of desired functionalities into MOF structures containing open metal sites. The crystallinity of MOFs allows precise crystal engineering as well as prediction of molecules suitable for introduction into a certain MOF. In this work we could show that the intrinsic catalytic activity of MOFs can be enhanced by post synthetic modification. The introduction of dabco gives a bifunctional catalyst and leads to the yield of 2-nitro-1-(4-nitrophenyl)ethan-1-ol up to 77% in Henry reaction. By deliberately choosing the right solvent and temperature, the selectivity of the reaction product could be controlled.

Acknowledgements

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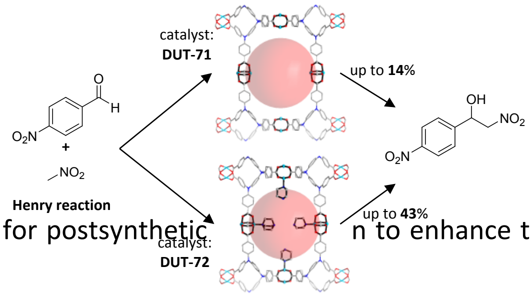

DUT-71 was used as a platform for postsynthetic n to enhance the catalytic activity of MOF in Hanry reaction.