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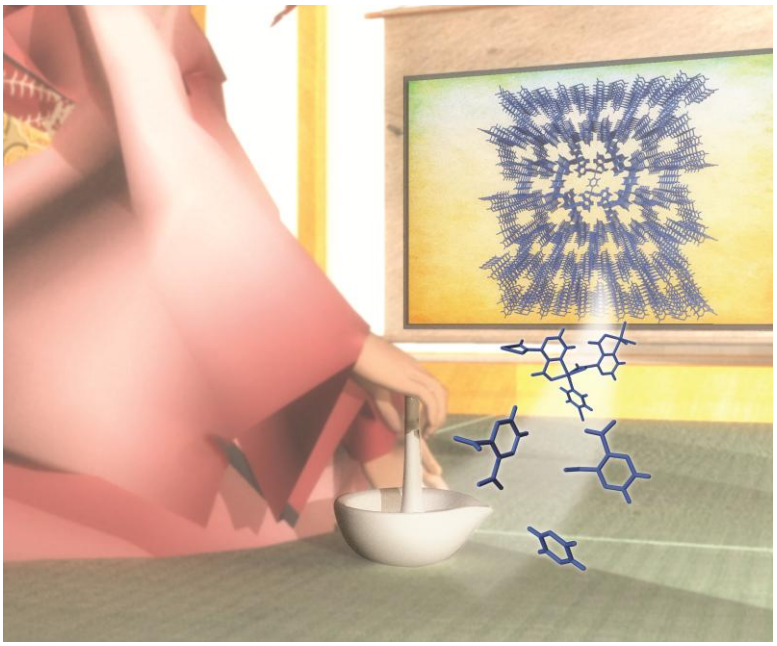

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COMMUNICATION

Tailoring metal–organic framework catalysts by click chemistry†

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We successively introduce new catalytic centers through click reaction into MOFs and modify their environment by addition of lipophilic groups. The resulting bifunctionalized MOF provides an optimized balance between basicity and lipophilicity and shows outstanding performance for the transesterification reaction.

Metal–organic frameworks (MOFs) are porous crystalline materials composed of cationic metal systems that behave like nodes with polytopic organic ligands acting as spacers.[1–10] These materials are often viewed as a new class of zeolites due to their porous structure. MOFs of the most recent generation present molecular recognition properties[11–13] originating from their considerable dynamic flexibility,[14–16] which is usually under the control of host–guest interactions. It is acknowledged that MOFs could ultimately mimic enzymes using a "locking" concept favoring high chemo-, regio- and enantioselectivity.[17–22] MOFs could indeed be viewed as potential "artificial enzymes" combining several properties in a concerted fashion at the nanometre scale. Fairly few MOFs bear more than one reactive function, however. MOFs have already been reported to catalyze a broad range of organic transformations involving their Lewis acid nodes as well as their Brønsted acid–base properties.[17–18,23] For example, inorganic clusters with unsaturated coordination (such as HKUST-1) or bridging hydroxyl groups (such as MIL-53) have been shown to perform Lewis[24–26] and Brønsted type catalysis,[27] respectively.

One solution for synthesizing advanced MOFs suitable for specialized and sophisticated applications is the controlled addition of more complex functionalities into the porous network. Through this functionalization, if the physical environment of the pores and the cavities within the MOFs can be modified, the interactions with guest species can in turn be adapted, thereby fine-tuning the chemical reactivity.[28] However, the introduction of reactive chemical functions by self-assembly methods is not a trivial task and cannot be generalized to all MOFs.[29,30] Various synthetic strategies have been employed with the aim of achieving MOF post-functionalization, as detailed in extensive reviews by Cohen *et al.*[31–40] Post-synthetic modification (PSM) using covalent-type grafting methods has undergone outstanding progress during the last five years.[41–47] We have recently reported an original PSM method starting from amino derived MOFs (Fig. 1).[48–52]

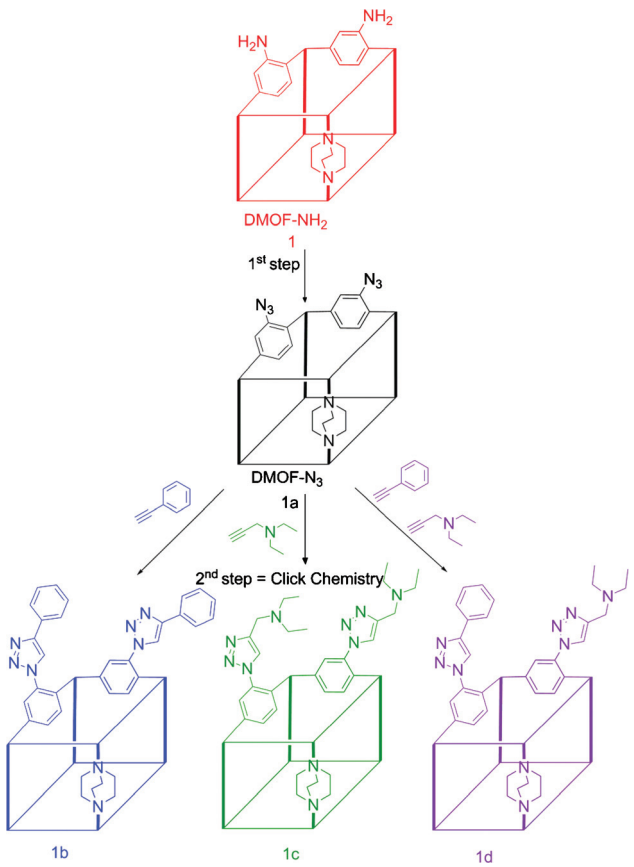

Fig. 1 Synthesis of MOF catalysts by "click chemistry".

The first step consists in converting the amino groups on the framework walls into their analogous azido (N_3). Without isolation nor purification, the desired triazolyl functionalized MOF materials are obtained by grafting the corresponding alkyne using "click chemistry". Using two different MOFs templates, the DMOF [Zn_2(2-amino-terephthalate)$_2$(dabco)] (dabco = 1,4-diazabicyclo[2.2.2]octane) and the IHM-2 [In(OH)(2-amino-terephthalate)], we showed that this novel PSM method presents key benefits for the engineering of MOF: (i) the softness of the method allows no restriction on the choice of starting amino-

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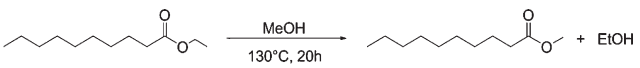
MOFs and (ii) the grafting yield can be controlled by adjusting the MOF : alkyne ratio.

Despite intensive efforts to develop new efficient, selective and recyclable solid base catalysts such as Layered Double Hydroxides (LDH),[53–55] hydrotalcite, KF and amine supported compounds, the development of green processes involving basic catalysts remains a challenge.[56–59]

In this contribution, we demonstrate that PSM by "click chemistry" enables the engineering of MOFs for application in base catalysis. The controlled post-modification of the frameworks introducing basic and/or lipophilic, *i.e.* with an affinity towards fatty molecules, features allows a rational design of catalytic MOFs for the transesterification reaction.[60,61] We show for the first time that outstanding cooperative catalytic effect can be obtained by an optimal formulation of our functionalized material. The base-catalyzed model reaction considered here is the transesterification of ethyldecanoate, a fatty ester, in methanol (Scheme 1).



Scheme 1 Transesterification of ethyldecanoate in methanol.

For this reaction to proceed efficiently, both substrates must be co-adsorbed into the MOF and MeOH should be activated by a base in order to favour the nucleophilic attack on the carbonyl group. The DMOF parent structure was selected as the starting platform since it contains neither Lewis nor Brønsted acid groups, which could have a catalytic effect, and only slightly basic amino groups. Two different functional groups were selected for the post-modification: a 1,2,3-triazolyl substituted with phenyl, corresponding to b compounds, or tertiary amine at the 4-position, corresponding to c compounds (Fig. 1). They are obtained by reacting the DMOF-N_3 (**1a**) with phenylacetylene to give **1b** and with propargylamine to give **1c**. The former **1b** presents moderate basicity originating from the triazolyle group ($pK_b \approx 9.4$) as well as strong lipophilicity, whereas the latter **1c** is a much stronger base ($pK_b \approx 3$ for trialkylamines).

A bifunctionalized MOF modified with b groups (phenyl) and then subsequently modified with c groups (tertiary amine) on the remaining azido sites was obtained and hereafter denoted as **1d**. The degree of modification of the MOF catalysts is given in Table 1.

Table 1 Transesterification yield using functionalized MOFs and reference catalysts[a]

Entry	Catalyst	b (%)	c (%)	Yield (%)
1	none	—	—	10
2	**1**	—	—	10
3	**1a**	—	—	10
4	**1b-40**	40	—	48
5	**1b-40**[b]	40	—	10
6	**1b-80**	80	—	80
7	**1c-40**	—	40	21
8	**1c-85**	—	85	28
9	**1d**	30	30	84

[a] Conditions: ethyldecanoate (2.5 mL) is allowed to react in methanol (10 mL) using 20 mg of DMOF catalyst (~0.03 mmol of MOF, *c.a.* 0.06 mmol of $-NH_2$) at 130 °C for 20 h [b] 2-ethyl-1-butanol is used instead of methanol.

Clear proof of the azide formation and of the subsequent full (3 + 2) cycloaddition can be characterized by liquid ^{1}H NMR on a quantitative manner (Fig. 2). After the cycloaddition step, new aromatic shifts of the post-modified compounds **1b** and **1c** confirm that the corresponding triazole derivative is formed as the sole product. The post-digestion ^{1}H NMR spectrum of **1d** shows contributions of both **b** and **c** and also of the remaining azide in a 30 : 30 : 40 ratio. Despite solvent effects on DMOF crystallinity,[48,62] the powder XRD patterns indicate that long-range order is preserved for all samples (Fig. S4†).

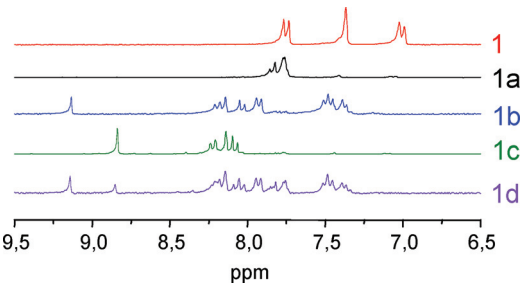


Fig. 2 Liquid ^{1}H NMR of digested MOF samples.

Following similar methodology, samples with a variable degree of modification were prepared. They are obtained by adjusting the amount of alkyne reactants, phenylacetylene or diethylpropargylamine, with respect to **1a**. There are denoted hereafter **1b-15**, **1b-40** and **1b-80** for degrees of modification with b groups (phenyl) of 15%, 40% and 80%, respectively, and **1c-40** and **1c-85** for degrees of modification with c groups (tertiary amine) of 40% and 85%, respectively.

These DMOF catalysts were involved in the transesterification of ethyldecanoate in methanol and the catalytic results are summarized in Table 1. It is worthy to note that the transesterification conversion obtained using the unmodified DMOF-NH_2 (**1**) as catalyst is not higher than that obtained without catalyst (*c.a.* 10%, entries 1 and 2).

Fig. 3 illustrates also how the degree of modification affects ethyldecanoate conversion in the case of the monofunctionalized materials. It appears that the activity of these DMOF materials increases linearly with the degree of modification. The syntheses and tests were performed twice for **1b-80** in order to verify

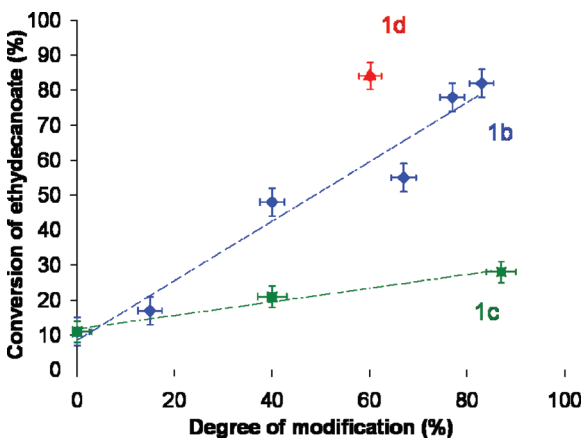


Fig. 3 The effect of the degree of modification for **1b** (◆), **1c** (■) and **1d** (▲) on ethyldecanoate conversion at 130 °C after 20 h.

experimental reproducibility; both times the ethyldecanoate conversion was approximately 80%.

The DMOF grafted with **c** groups could have been expected to show better activity based on the higher basic strength of the trialkylamine compared to that of the phenyl substituent. Surprisingly, the introduction of lipophilic functions *via* **b** exhibits a more beneficial effect on the catalytic activity. Furthermore, the corresponding organic linkers found in **1b** and **1c**, respectively, **linker b** (dimethyl-2-(4-phenyl-1*H*-1,2,3-triazol-1-yl)-terephthalate) and **linker c** (dimethyl-2-(4-diethylaminomethyl-1*H*-1,2,3-triazol-1-yl)-terephthalate), were synthesized. The **linker b** and the **linker c** were tested in the transesterification reaction under homogeneous conditions and show moderate activity compared to the corresponding grafted MOFs (Table S1†). These results confirm the moderate activity of the triazolyl group itself.

In contrast, the tandem post-modified **1d** shows outstanding performances compared to the monofunctionalized DMOF samples. Although **1d** contains only 30% of **b** and 30% of **c**, 84% conversion was achieved (entry 9). Under similar reaction conditions, using **1b-40** and **1c-40** with a similar degree of modification, the conversion only reached 48% and 21%, respectively (entries 4 and 7). The superior activity of **1d** is not the simple addition of the activities of both **1b-40** and **1c-40** but can be attributed to a cooperative effect resulting from the combination of both basic and lipophilic groups at a molecular level (Fig. 4). A high degree of functionalization (≥ 80% in **1b-80** and **1c-85**) with lipophilic or basic groups is not necessarily required but a combination of low modification degrees (30% in **1d**) with both basic and lipophilic groups allows the maximum activity to be reached.

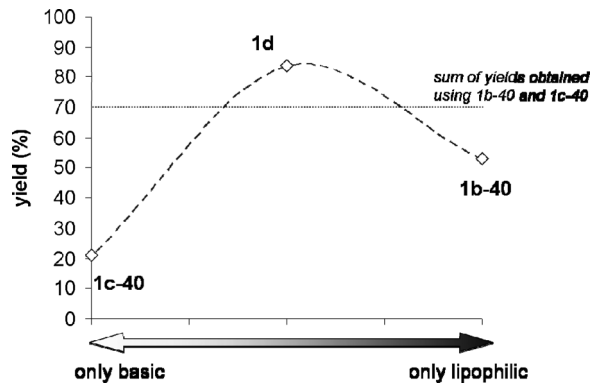
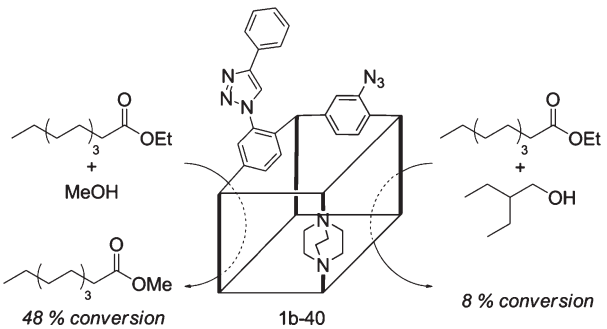


Fig. 4 The effect of the basic/lipophilic functionalization of MOF catalysts on ethyldecanoate transesterification yield.

In order to assess our hypothesis of a cooperative basic-lipophilic effect, liquid adsorption isotherms with an ethyldecanoate/isooctane mixture were investigated for **1** and for **1b-40**, containing 40% of 4-phenyl-1,2,3-triazolyl functions (Fig. S5†). These adsorption measurements confirm the stronger lipophilicity of the latter material. Consequently, we suggest that the higher apparent activity of **1b** compared to **1c** should be due to a more appropriate co-adsorption ratio of both substrates inside the pores on the more lipophilic MOF. Hence, **1d** with a tandem functionalization reaches an optimal basic/lipophilic balance to perform the reaction.

Moreover, the use of a bulky primary alcohol in the transesterification reaction has been also used to confirm that the reaction takes place in the porous system and not only at the surface.[61] The transesterification with 2-ethyl-1-butanol, which is a much bulkier substrate than methanol, was carried out using the MOF **1b-40** (Scheme 2). As shown in the Table 1, only a low percentage of conversion was obtained in 2-ethyl-1-butanol against 48% in MeOH (entry 5). This indicates that the reaction proceeds in the porous framework using MeOH, whereas the reaction does not take place in the pores in the case of a bulky alcohol due to the molecular sieving property of the MOF. However, even if uptake experiments conducted with the two alcohols would give additional information about the sieving effect, the already reported solvent-dependent flexibility of the DMOF framework[48] undermines the reliability of alcohol uptake as a characterization method.



Scheme 2 Molecular sieving effect of the catalysts **1b-40**.

Powder XRD shows that the DMOF materials remain mostly crystalline after catalysis although peak broadening is observed (Fig. S9†). As discussed previously, it may arise from the intrinsic flexibility of the DMOF structure.[48,62] Most important, under catalytic conditions the robustness of the solid towards leaching was investigated. When the catalyst is filtered off, the reaction still slightly proceeds but the trend follows that of a reaction performed without catalyst.

As the elemental analyses performed on our samples show the presence of 1 to 2 wt% of Cu in the solids, we investigated the effect of copper on our catalytic system. According to the molecular formula of the functionalized MOFs and to the catalyst quantity used in the reaction, the amount of copper present in our tests corresponds to 0.002–0.004 mmol. Although the exact nature and oxidation state of the copper is not known, it might be possible that some of the copper remains as $Cu^{I}(ACN)_4PF_6$ in the pore after the click chemistry and may act as a catalyst.[63] Control experiments carried out with 0.3 mmol of $Cu(ACN)_4PF_6$ or $Cu(OAc)_2$, corresponding to 100 times more Cu than is really contained in our MOFs, showed conversion of 32 and 40% respectively, lower than that obtained using our functionalized DMOF.

In conclusion, we were able, in a single framework, to successively introduce new basic catalytic centers (amino groups) and lipophilic groups (phenyl groups) in order to enhance the catalytic activity of our solid. Thanks to the strict control of the synthetic conditions, the precise optimization of these parameters can be achieved. The resulting bifunctionalized MOF, involving a low degree of modification at each functionalization step,

provides an optimized balance between catalytic activity and substrates co-adsorption for the transesterification reaction. More generally, this post-functionalization methodology enables the engineering of MOF catalysts in a rational manner, considering multiple independent factors and starting from an initial MOF structure that is appropriate in terms of pore size or intrinsic functionalities.[64] This opens a new perspective for the rational design of multifunctional solid catalysts.

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