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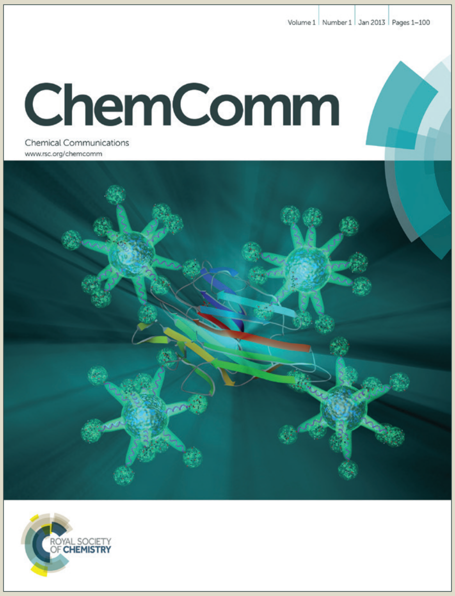

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"Click" Post-Functionalization of Metal-Organic Framework for Engineering Active Single-Site Heterogeneous Ru(III) Catalysts

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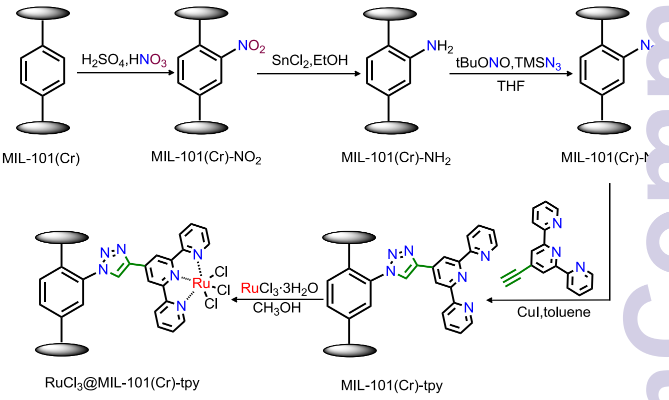
We present a general strategy for incorporating π-conjugated NNN-chelators (e.g., terpyridyl moiety) into a porous metal-organic framework (MOF) MIL-101(Cr) by using the "click" post-functionalization. The functionalized MOF could be used a platform for metalation to yield highly active and stable single-site heterogeneous metal (e.g., Ru(III)) catalysts.

Chelating ligands containing pyridyl moieties such as bipyridines, phenanthrolines, and terpyridines, have been extensively employed in coordination chemistry and homogeneous catalysis.[1-3] Owing to their robust redox stability, strong coordinating ability with metal ions, and easy functionalization, these ligands have offered a useful platform to alter the catalytic activity of the anchored metal ions.[4,5] However, these homogeneous catalysts based on nitrogen donor ligands are prone to deactivation via intermolecular pathways.[6] Thus, the immobilization of these metal-pyridine homogeneous catalysts on a solid support (e.g., zeolites, mesoporous aluminosilicates, and other porous inorganic or organic materials) has been developed as an efficient way to isolate each catalytic site to enhance the stability and catalytic activity.[7-9]

Metal-organic frameworks (MOFs) have emerged as a new type of functional materials owing to their high surface areas, porosity, and chemical tunability.[10-12] The modification of the pore surfaces with desired functional groups could provide various anchoring sites for the immobilization of metal ions on MOFs to develop novel single-site heterogeneous catalysts for a variety of organic transformations.[13,14]

Currently, the modification of MOF pore surface is mostly based on the use of pre-designed ligands with specific functional groups. But this pre-synthesis method still remains relatively limited by the complicated multi-step preparation of bridging ligands, and the unpredictable framework caused by potential coordination of the functional groups to the metal ions during MOFs formation.[15-17] In this regard, postsynthetic modification (PSM) represents a powerful tool to incorporate functional groups in a MOF backbone for the preparation of supported organometallics.[18-20] Among the developed PSM methods, the "click" chemistry has been discovered as a useful methodology for post-functionalization of MOFs, which would largely enrich the chemical diversity of MOFs.[21-23] More recently, homogeneous catalysts based on simple bipyridyl and phenanthryl ligands have been successfully incorporated on MOFs to elicit significantly enhanced catalytic activity over their homogeneous counterparts. Considering the extensive use of terpyridyl ligands in coordinating with many transition metal ions (e.g., Ru, Pd, Ni, and Cu) to construct stable complexes with interesting catalytic, photovoltaic, and electrochemical properties, it is highly desirable if such terpyridyl ligands could be immobilized on MOFs and reused.[24-27] However, up to date, the incorporation of terpyridyl ligands on MOFs has never been explored.



Scheme 1 Schematic representation of the post-synthesis modification of MIL-101(Cr) and the synthesis of a single-site heterogeneous Ru(III) catalyst.

In this work, we report the successful incorporation of 2,2′:6′,2′′-terpyridine (tpy), a tridentate oligopyridine σ-donor chelator, onto a new azides-tagged MIL-101(Cr)-N_3 through a

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click PSM method. Transition metal species, e.g., $RuCl_3$, could be then easily immobilized on the tridentate chelator to afford single-site heterogeneous catalysts. The as-synthesized Ru catalyst is demonstrated to be highly active and selective in the oxidation of benzyl alcohols, which is much superior to the homogeneous counterpart (i.e., $RuCl_3$). Furthermore, metal leaching is inhibited because of the strong interaction between Ru(III) ions and the chelators in the MOF network. To the best of our knowledge, this work represents the first example of successful incorporation of terpyridyl ligands on MOFs.

MIL-101(Cr)-NH_2 was prepared from the nitration of MIL-101(Cr) to MIL-101(Cr)–NO_2 and the subsequent reduction by using $SnCl_2 \cdot 2H_2O$ and ethanol (Scheme 1).[28,29] Powder X-ray diffraction (PXRD) measurements confirmed that MIL-101(Cr)-NH_2 was isostructural to MIL-101(Cr) (Fig. S1).[30] ^{1}H-NMR spectroscopy of the digested MIL-101(Cr)-NH_2 material in deuterated dimethyl sulphoxide (DMSO-d_6) showed the same signals as that of 2-aminoterephthalic acid (H_2BDC-NH_2). This result demonstrated that all the terephthalate ligands in the MIL-101(Cr) were converted to 2-aminoterephthalate in the as-prepared MIL-101(Cr)-NH_2.

Using the similar procedures for the functionalization of IRMOF-3,[31] MIL-101(Cr)-NH_2 was treated with tBuONO and $TMSN_3$ in THF overnight at room temperature to give a new azido functionalized MOF material MIL-101(Cr)-N_3 (Scheme 1). From XRD, no significant loss of the framework integrity was observed after the transformation of -NH_2 to azido (-N_3) group. FT-IR spectroscopy verified the presence of azido group on the MIL-101(Cr)-N_3, showing a peak at ca. 2123 cm^{-1} that can be ascribed to the -N_3 asymmetric stretching vibration (Fig. 1). ^{1}H-NMR spectroscopy of the digested MIL-101(Cr)-N_3 showed totally new aromatic signals at 7.74-7.83 ppm, demonstrating the complete conversion of the amino groups into the corresponding azido groups (Fig. S2). HRMS provided additional proof to this modification. The negative mode spectrogram of digested MIL-101(Cr)-N_3 gave values of m/z around 206 and 413 (Fig. S3), corresponding to $[(N_3\text{-BDC})\text{-H}]^-$ and $[2(N_3\text{-BDC})\text{-H}]^-$, respectively ($N_3$-BDC: 2-azido-1,4-benzenedicarboxlate).

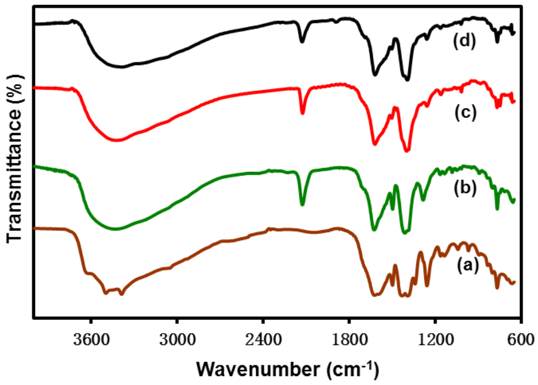

Fig. 1 Infrared spectra of MIL-101(Cr)-NH_2 (a), MIL-101(Cr)-N_3 (b), MIL-101(Cr)-tpy (c), and $RuCl_3$@MIL-101(Cr)-tpy (d).

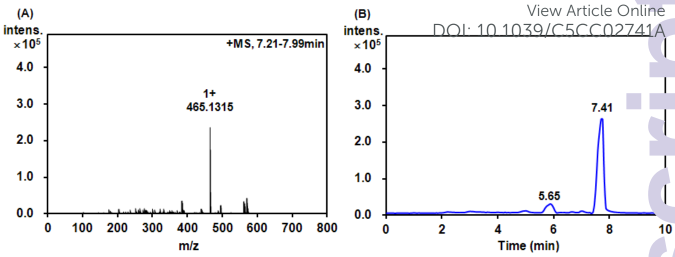

Fig. 2 LC-HRMS spectrogram (A) and TIC chromatogram (B) of the linker molecule of the digested MIL-101(Cr)-tpy (positive mode).

The presence of azido groups on the MIL-101(Cr)-N_3 could allow for covalent attachment of tridentate ligands through post-synthetic modifications (Scheme 1). We next modified the MIL-101(Cr)-N_3 employing the efficient azide-alkyne cycloaddition protocol (CuAAC) with 4′-ethynyl-2,2′:6′,2″-terpyridine. The obtained material was denoted as MIL-101(Cr)-tpy. FT-IR data indicated that the intensity of the characteristic peak of the azido group at 2123 cm^{-1} decreased after this modification (Fig. 1). Using the positive mode, LC-HRMS spectrogram of the MIL-101(Cr)-tpy showed that a base peak at m/z ca. 465 ($[M+H]^+$) was appeared as the major species, which could be attributed to the triazole product of the cycloaddition (Fig. 2). These results indicated that the azide MOF crystals had been successfully modified by the alkyne derivatives in the click reaction. PXRD confirmed the modified MOF had identical crystallinity to the MIL-101(Cr)-NH_2, demonstrating the maintenance of the framework structure (Fig. S1).

It should be note that due to the large size of the chelating terpyridyl unit, only one part of the azido groups in the MIL-101(Cr)-N_3 could be transformed into the triazole groups (about 14.8% based on the elemental analysis). The occupancy of the pore volume by the large terpyridyl moiety was evident from N_2 adsorption isotherms and pore-size distribution (Fig. S4), which showed a remarkable decrease in N_2 adsorption capacity and pore diameter for MIL-101(Cr)-tpy as compared to MIL-101(Cr)-N_3.

The open terpyridyl groups in the MIL-101(Cr)-tpy would offer an excellent platform for the chelation of transition metal complexes. Taking Ru as an example, we used the as-synthesized MIL-101(Cr)-tpy to bind the ruthenium trichloride in methanol to obtain $RuCl_3$@MIL-101(Cr)-tpy (Scheme 1). PXRD and TEM results showed that the crystalline structure of the parent MIL-101(Cr) was mostly retained after the doping of $RuCl_3$ (Fig. S1 and Fig. S5).[32] N_2 adsorption isotherms also confirmed the porous structure of the framework (Fig. S4). The Ru content in the $RuCl_3$@MIL-101(Cr)-tpy was ca. 1.0 wt%, determined by atomic absorption spectroscopy (AAS). To confirm that the Ru(III) ions were coordinated to the 2,2′:6′,2″-terpyridine chelating groups, we performed X-ray photoelectron spectroscopy (XPS) analysis on $RuCl_3$, MIL-101(Cr)-tpy, and $RuCl_3$@MIL-101(Cr)-tpy. Accordingly, both $RuCl_3$@MIL-101(Cr)-tpy and $RuCl_3$ exhibited Ru $3p_{3/2}$ and $3p_{1/2}$ bands at around 464 eV and 486 eV (Fig. 3A). However, the Ru 3p lines of $RuCl_3$@MIL-101(Cr)-tpy were shifted by ca. 0.5 eV

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toward lower binding energies, as compared to the pristine $RuCl_3$. Such shifts suggested that a strong coordination interaction between the terpyridine chelating groups and the Ru atoms in $RuCl_3$@MIL-101(Cr)-tpy.

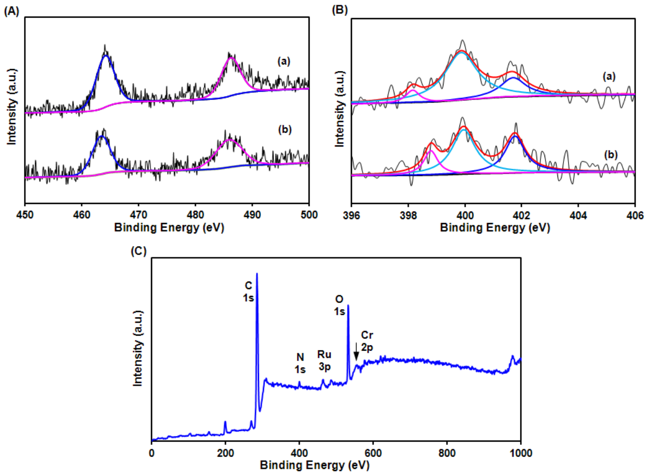
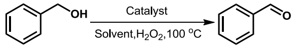


Fig. 3 (A) XPS spectra of the Ru 3p region for $RuCl_3$ (a), and $RuCl_3$@MIL-101(Cr)-tpy (b). (B) XPS spectra of the N 1s region for MIL-101(Cr)-tpy (a), and $RuCl_3$@MIL-101(Cr)-tpy (b). (C) XPS survey spectra of $RuCl_3$@MIL-101(Cr)-tpy.

The N 1s spectra indicated three types of chemical environments for nitrogen in the materials (Fig. 3B). The peak at 401.7 eV was attributed to the three nitrogen atoms of the triazole ring.[33] Another peak at around 398.1 eV could be ascribed to the three nitrogen atoms of the terpyridine in the parent MIL-101(Cr)-tpy. Because of the strong interaction between the terpyridine and $RuCl_3$ in the $RuCl_3$@MIL-101(Cr)-tpy, this peak was observed to shift toward higher binding energy by ca. 0.6 eV. The peak at 399.9 eV may be assigned to the residual azide groups, which showed a lower binding energy compared to the triazole ring.[34]

Table 1 Results of the oxidation of benzyl alcohol[a]

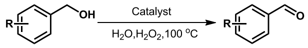


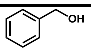
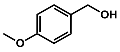
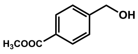
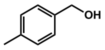
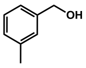
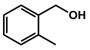
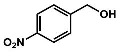
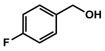
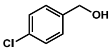
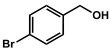
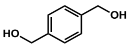
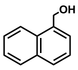
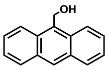
Entry	Catalyst	Solvent	Conv. /sel. (%)
1	$RuCl_3$@MIL-101(Cr)-tpy	DCE	41/92
2	$RuCl_3$@MIL-101(Cr)-tpy	Toluene	64/>99
3	$RuCl_3$@MIL-101(Cr)-tpy	DCM	25/>99
4	$RuCl_3$@MIL-101(Cr)-tpy	THF	31/>99
5	$RuCl_3$@MIL-101(Cr)-tpy	CH_3CN	82/91
6	$RuCl_3$@MIL-101(Cr)-tpy	H_2O	>99/>99
7	$RuCl_3·3H_2O$	H_2O	49/98
8	MIL-101(Cr)-tpy	H_2O	11/>99
9[b]	$RuCl_3$@MIL-101(Cr)-tpy	H_2O	99/>99

[a] Reaction conditions: benzyl alcohol (0.5 mmol), catalyst (Ru 1 mol%), solvent (5 mL), 100 °C, H_2O_2 (0.75 mmol), 6 h. [b] Fifth run to test the reusability of $RuCl_3$@MIL-101(Cr)-tpy under the conditions of entry 6.

Selective oxidation of alcohols is a significant process in organic synthesis and industrial manufacture.[35-37] The synthesized $RuCl_3$@MIL-101(Cr)-tpy material was investigated as catalyst for the oxidation of various alcohols with H_2O_2. A preliminary study using benzyl alcohol as the model substrate was performed for optimizing the reaction conditions, and the results are summarized in Table 1. First, the effect of solvent on the oxidation reaction was investigated. It was observed that water was the best among the examined solvents with respect to both conversion and selectivity (Table 1, entries 1-6), achieving almost quantitative yield of benzyl aldehyde within 6 h. For comparison, we also carried out the oxidation reaction using the parent MIL-101(Cr)-tpy or homogeneous $RuCl_3·3H_2O$ as catalyst under the same reaction conditions. Much lower activities were obtained for both the MIL-101(Cr)-tpy and $RuCl_3$ as compared to $RuCl_3$@MIL-101(Cr)-tpy (Table 1, entries 7-8). The observation indicated that the excellent catalytic performance of $RuCl_3$@MIL-101(Cr)-tpy compared to its homogeneous counterpart could be related to the difference in the electron configuration and σ-donor ligands of the tpy moiety in the MOF.

Table 2 Oxidation of various alcohols catalyzed by $RuCl_3$@MIL-101(Cr)-tpy [a]



Entry	Substrate	Time (h)	Yield (%)
1		6	99
2		6	99
3		6	97
4		6	99
5		6.5	99
6		8	98
7		6	99
8		5.5	99
9		6	99
10		7	99
11[b]		5.5	99
12		6	99
13		9	95[c]

[a] Reaction conditions: alcohol (0.5 mmol), $RuCl_3$@MIL-101(Cr)-tpy (Ru 1 mol%), H_2O (5 mL), 100 °C, H_2O_2 (0.75 mmol). [b] H_2O_2 (1.25 mmol). [c] Isolated yield.

Various aromatic alcohols were further employed in the reaction to investigate the range of alcohols that can be tolerated in the reaction over this novel $RuCl_3$@MIL-101(Cr)-tpy catalyst. Substituted benzyl alcohols containing both

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electron-donating and electron-withdrawing groups underwent the oxidation smoothly, affording the desired oxidation products in almost quantitative yields (Table 2, entries 1-10). With the presence of more amount of H_2O_2, 1,4-benzenedimethanol was selectively oxidized to 1,4-phthalaldehyde in 99% yield (Table 2, entry 11). 1-Naphthalenemethanol and 9-anthracenemethanol also reacted well to provide the desired aldehydes in excellent yields (Table 2, entries 12-13). It was noteworthy that the reaction of 9-anthracenemethanol took more time to complete, probably due to the space steric hindrance.

The heterogeneous nature of $RuCl_3$@MIL-101(Cr)-tpy was investigated by using a hot filtration experiment. At ca. 30% conversion, the reaction solution was quickly filtrated at the reaction temperature in order to avoid re-deposition of dissolved Ru upon cooling. The content of Ru in the filtrate was below the detection limit of the AAS analysis. The isolated solution was allowed to further react for 8 h. It was observed the reaction was essentially stopped after the removal of the catalyst (Fig. S6). This result strongly suggested that the reaction would proceed mostly on the heterogeneous surface. Moreover, the Ru content of the recycled catalyst was almost identical to the fresh one. These studies indicated that the leaching of Ru active sites was negligible, which could account for the preservation of the catalytic activity of this catalytic system after being reused for at least 5 times (Table 1, entry 9).

In summary, we have successfully incorporated terpyridyl moiety into a new azido-functionalized MOF, MIL-101(Cr)-N_3, by using the CuAAC click reaction. The as-prepared MOF with open terpyridyl unit may be used as a useful platform to synthesize various single-site heterogeneous metal catalysts. Preliminary metalation investigation demonstrated the synthetic utilization of MIL-101(Cr)-tpy for the construction of highly active single-site Ru(III) catalyst. Moreover, the catalyst was easily recoverable and reusable for at least five times without any apparent loss of catalytic efficiency. The proposed PSM methodology starting from the aromatic rings that are contained in the majority of MOFs, is believed to be applicable to a wide range of MOFs that might bring new opportunities in the development of highly active heterogeneous single-site metal catalysts.

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