ChemComm

COMMUNICATION

Surface functionalization of metal–organic polyhedron for homogeneous cyclopropanation catalysis[†]

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Received 3rd January 2011, Accepted 8th March 2011 DOI: 10.1039/c1cc00030f

A super-paddlewheel (comprised of two paddlewheels) metalorganic polyhedron (MOP) containing surface hydroxyl groups was synthesized and characterized. Condensation reactions with linear alkyl anhydrides lead to new MOPs with enhanced solubility. As a result, the surface-modified MOP 4 was demonstrated as a homogeneous Lewis-acid catalyst.

Emerged as an exciting new branch of supramolecular chemistry, metal–organic polyhedra (MOPs, also known as molecular polyhedra, nanoballs, nanocontainers, or nanocages) have attracted a great deal of attention in the past decade because of their aesthetically pleasing structures, and intriguing application potential in chemical sensing, catalysis, gas storage, drug delivery, and separation.¹ Further studies of MOPs have been largely focused on functionalization of the inner or outer surfaces for various applications.²

Dicopper paddlewheel structural unit is a commonly used building block in the construction of MOPs.³ It occurs to us that these MOPs can serve as potential Lewis-acid catalysts when the axial ligands on the copper atoms are removed. They can be used as homogeneous catalysts if soluble in noncoordinating solvent. To the best of our knowledge, of all the MOPs based on dicopper paddlewheel structural units, those that are soluble in non-coordinating solvents are very rare.⁴ MOPs that are not soluble tend to aggregate. Unlike uniformly constructed MOFs (metal-organic frameworks),⁵ whose interconnected channels and cavities allow reactants and products to shuttle, MOP aggregation is detrimental to catalysis⁶ because most of the active sites will be blocked and inaccessible. Dicopper paddlewheel MOFs were used as Lewis-acid heterogeneous catalysts due to the presence of copper atoms with open coordination sites once the coordinating solvents were removed.⁷ However, utilization of dicopper paddlewheel MOPs as homogeneous catalysts in non-coordinating solvent has rarely been explored, presumably due to the lack of such MOPs. In addition, the self-assembly process of MOPs depends on many factors and may not lead to desired MOPs exclusively.8

Therefore, the synthesis of novel MOPs becomes a difficult task; appropriate reaction conditions have to be found for each novel linker.

To take on the solubility and synthetic challenges, we developed a general surface-functionalization strategy of pre-assembled MOPs as an alternative synthetic route to the *de novo* self-assembly. Modifying MOFs has grown substantially in the past few years;⁹ however, modifying pre-assembled MOPs has rarely been studied. First, a super-paddlewheel (comprised of two paddlewheels) MOP (MOP 1) with four hydroxyl groups was synthesized and characterized. Reactions between MOP 1 and a series of alkyl anhydride have led to MOPs containing the same core structure, with carbon chains of different lengths on the exterior (Fig. 1). Solubility has been fine-tuned by such a surface-functionalization strategy. As a result, MOP 4 becomes soluble in non-coordinating solvents after surface modification, ideal for homogeneous Lewis-acid catalysis.

MOP 1 was formed spontaneously when H₂L was mixed with copper nitrate in the presence of 2,6-lutidine in an appropriate solvent mixture. Interestingly, two different types of inter-MOP interaction have been observed when different solvent systems were used. In crystals of MOP 1a, adjacent MOPs connect to each other through coordination bonds between hydroxyl groups from one MOP and copper atoms of the other MOP; in crystals of MOP 1b, however, MOPs pack *via* π - π stacking, with dimethyl sulfoxide (DMSO) molecules bound to the copper atoms on the exterior of each MOP (Fig. 1).

Preliminary N₂ sorption studies of the activated MOP 1, in which terminal ligands were removed, revealed a Langmuir surface area of 181 m² g⁻¹ (BET 160 m² g⁻¹) (Fig. 2). Both N₂ and H₂ uptakes are relatively low with respect to the calculated accessible surface area, presumably because of the blockage of the open windows of the MOPs with random orientations in the activated sample, which is typically amorphous.^{3c} Although the possibility of structural disintegration cannot be completely ruled out, given the fact that the activated MOP 1 and MOPs 1a as well as 1b are interconvertible, it is safe to assume that the polyhedron intactness of MOP 1 on the molecular level and its porosity should be maintained.¹⁰

It is foreseeable that a reaction of a MOP is much more difficult than that of its precursor ligand for the following reasons: (1) solubility: as a large molecule, MOP is usually not soluble in conventional solvents; (2) stability: dicopper paddlewheel is a delicate building unit, the reaction condition

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[†] Electronic supplementary information (ESI) available: Experimental details, crystallographic data, TGA, PXRD, IR, HPLC data, extra gas sorption isotherms. CCDC 797901–797905. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc00030f.





Fig. 1 Reaction scheme for the self-assembly of super-paddlewheels MOP 1a and MOP 1b; interconversion of MOP 1a, MOP 1b, and activated MOP 1; reaction scheme of surface modification of MOP 1 with linear alkyl anhydrides. Hydrogen atoms were omitted for clarity.



Fig. 2 N_2 and H_2 sorption isotherms of activated MOP 1 at 77 K.

has to be mild; (3) separation: conventional methods such as flash chromatography and recrystallization are not applicable.

Fortunately after a few attempts, a suitable combination of reaction conditions and separation procedures was developed. When treated with alkyl anhydride in *N*,*N*-dimethylformamide (DMF) in the presence of 4-dimethylaminopyridine (DMAP) at room temperature overnight, MOP 1 was quantitatively converted into MOP 2, MOP 3, or MOP 4, respectively.

The right amount of DMAP was crucial to this reaction, normal catalytic amount of DMAP (<10%) led to an incomplete reaction, probably due to DMAP preferentially coordinating to copper sites; excessive amount of DMAP led to collapse of the dicopper paddlewheel unit, accompanied by a color change from blue to brown. Approximately, 1.2 equivalents of DMAP were needed for this reaction.

To verify the products, we obtained crystals of all three surface-modified MOPs with sufficient quality for single crystal X-ray analysis (see ESI[†]).

NMR was employed to verify bulk product purity and the completion of the surface modification. As-synthesized MOP 2, 3, or 4 was dissolved with 1 mol L^{-1} HCl to release their respective ligand, which was extracted with ethyl acetate. The

recovered diacids were checked with ¹H-NMR (Fig. 3). No detectable amount of unreacted H_2L (Fig. 3 black) in any of the recovered ligands (Fig. 3 red, blue, and green) was found, which was indicative of the completion of the condensation reactions.

Given the crystal structure and solubility in a non-coordinating solvent of MOP 4, the catalytic reactivity of activated MOP 4 was tested for cyclopropanation reaction of styrene with ethyl diazoacetate (EDA). Compared to other copper catalysts, such as a representative homogeneous catalyst (Cu–H), copper complexes supported on ultrastable Zeolite Y (Cu–USY) or MCM-41 mesoporous silica (Cu–MCM-41),¹¹ as well as a metal–organic framework [Cu₃(BTC)₂],⁷⁷ MOP 4 displays similar or better activity and selectivity (Table 1).

For comparison, the activated MOP 1 was also tested with the same reaction, and showed almost no catalytic activity (entry 7, Table 1). An additional observation is that the



Fig. 3 ¹H-NMR (DMSO-d₆): black, R = H (H₂L); red, $R = CH_3$ (extract from HCl decomposed MOP 2); blue, $R = C_5H_{11}$ (extract from HCl decomposed MOP 3), green, $R = C_{11}H_{23}$ (extract from HCl decomposed MOP 4).

 Table 1
 Catalytic data of cyclopropanation reactions of styrene with EDA



1	MOP 4^c (1 mol%) ^d	1	89	2.7^{e}
2	MOP 4^{c} (1 mol%) ^d	2	81	2.7^{e}
3	Cu-H (5 mol%)	1	74	2.0
4	Cu–USY (5 mol%)	1	32	1.9
5	Cu-MCM-41(5 mol%)	1	60	2.0
6	$[Cu_3(BTC)_2]$ (5 mol%)	1	98	2.3
7	MOP 1^c (1 mol%)	1	n.a. ^f	n.a. ^f

^{*a*} Catalyst loading. ^{*b*} Yield of cyclopropane, based on EDA. ^{*c*} Preactived (methanol exchange 3 times, dynamic vacuum at 120 °C overnight). ^{*d*} Reaction condition: catalyst/EDA/styrene = 1/100/200, CH₂Cl₂, 25 °C, 10 h addition of EDA and then stirring for 10 h. ^{*e*} Determined by HPLC. ^{*f*} Catalyst decomposed (color changed from blue to brown).

dicopper paddlewheel units decompose within 30 min upon addition of EDA, presumably due to the aggregation of MOP 1 in dichloromethane, which blocked most of the copper sites leading to slow EDA consumption. Excessive EDA decomposes dicopper paddlewheel in all of our experiments.

Besides the reusability experiment (entry 2, Table 1), absorption spectra also demonstrate the stability of MOP 4 in dichloromethane solution during catalysis. The absorption band around 700 nm is characteristic of the dicopper paddle-wheel structural unit.¹² After the reaction, the 700 nm absorption band barely changes, indicating the intactness of the dicopper paddlewheel units (Fig. S11, ESI†).

In summary, a super-paddlewheel MOP containing four hydroxyl groups has been synthesized and characterized. Surface functionalization *via* condensation reactions between the hydroxyl groups and liner alkyl anhydrides has proven to be an efficient strategy to tune the solubility of a MOP. MOP 4 has been surface-functionalized using such a strategy and becomes soluble in non-coordinating solvents. It has subsequently been utilized as a highly efficient homogeneous Lewis-acid catalyst for cyclopropanation reactions.

The US Department of Energy (DOE DE-SC0001015, DE-FC36-07GO17033, and DE-AR0000073), the National Science Foundation (NSF CBET-0930079 and CHE-0911207), and the Welch Foundation (A-1725) supported this work. The microcrystal diffraction of MOP 4 was carried out with the assistance of Yu-Sheng Chen at the Advanced Photon Source on beamline 15ID-B at ChemMatCARS Sector 15, which is principally supported by the NSF/DOE under grant number CHE-0535644. Use of the Advanced Photon Source was supported by the U. S. DOE, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

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