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[NaCu(2,4-HPdc)(2,4-Pdc)] Mixed Metal–Organic Framework as a Heterogeneous Catalyst

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The synthesis of a new mixed metal–organic framework (M'MOF) has been accomplished by the metalloligand approach. [NaCu(2,4-HPdc)(2,4-Pdc)] (2,4-H₂Pdc = pyridine-2,4-dicarboxylic acid) has been obtained from the hydrothermal reaction of the metalloligand [Cu(2,4-HPdc)₂(H₂O)₂] NaOH, and a transition metal salt. [NaCu(2,4-HPdc)(2,4-Pdc)] is isostructural to [CuMn(2,4-Pdc)₂] and crystallizes in the triclinic space group *P* $\bar{1}$. The 3D structure is built up from [Cu(2,4-HPdc)₂(H₂O)₂] metalloligands and

[NaO₆] octahedra in a pcu α -Po-like uninodal six-connected net. The compound is stable to 290 °C, and its crystal structure undergoes a 3% volume expansion between room temperature and thermal decomposition. The unsaturated Cu^{II} centers at the surface act as a heterogeneous Lewis acid catalyst for the cyanosilylation of aldehydes and Knoevenagel C–C bond-forming reactions. The catalytic activity has been compared with those of other copper(II) porous metal–organic frameworks such as HKUST-1 and MOF-74.

Introduction

Coordination polymers or metal–organic frameworks (MOFs) have experienced a rapid emergence in the last two decades.^[1,2] It is no coincidence that many researchers have devoted their efforts to obtain such materials. The properties that they may present range from gas storage and separation^[3–8] to highly selective sensing.^[9–12] They have also shown interesting activity as heterogeneous catalysts.^[13–19]

In this sense, incompletely coordinated metal cations, also known as unsaturated metal centers (UMC),^[20] can be used as Lewis acid sites in catalytic reactions that are important for organic synthesis. The presence of UMCs greatly favors catalysis as well as adsorption, as the direct interaction between the metal center and the substrates is strongly favored. The use of metalloligands as linkers for the construction of MOFs is a promising approach to obtain unsaturated metal sites.^[21] Through the combination of UMCs with a second metal center, which acts as framework node, mixed metal–organic frameworks (M'MOFs) can be obtained in a “two-step self-assembly” synthesis.^[22]

In spite of the advantages of this synthetic approach, the use of metalloligands is still not very extensive, and reports on M'MOFs are still scarce in comparison with the great amount of papers on MOFs. A possible reason for this is that these ligands are more difficult to stabilize into a framework because of their size and flexibility.

Nonetheless, since this synthetic approach was introduced at the beginning of the last decade,^[23–26] important advances have been made. Several M'MOFs have been synthesized,^[27–36] and the properties of some of them have been studied. Chen and co-workers^[37–40] have synthesized a mixed zinc/copper metal–organic framework, named M'MOF **1**,^[37] with selective adsorption properties for D₂ and H₂. M'MOFs **2** and **3** have been used for the chiral recognition of 1-phenylethanol and are selective for the separation of ethylene and acetylene.^[38] Other M'MOFs such as M'MOFs **4–7**^[39] and M'MOF **20**^[40] have been described for the selective separation of small molecules and gas adsorption. Salen-type metal complexes have been used as metalloligands and immobilized into M'MOFs owing to their catalytic properties. This way, heterogeneous catalysts have been obtained for olefin epoxidation^[41] and the cycloaddition of CO₂ to epoxides.^[42,43] Song et al.^[44] have also recently synthesized a family of isorecticular chiral MOFs with Mn–salen catalysts incorporated as metalloligands. These M'MOFs are highly active catalysts for enantioselective alkene epoxidation reactions.

For the present work, to obtain copper(II) UMCs as Lewis acid sites, a metalloligand with pyridine-2,4-dicarboxylic acid (2,4-H₂Pdc) has been used. Pyridinedicarboxylates are very versatile linkers owing to their large number of potential combination modes with metal ions^[45,46] and

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have been used widely for the preparation of monometallic and dimetallic MOFs.^[27,28,47–53]

Bis(pyridine-2,4-dicarboxylato)copper(II) dihydrate $\{[\text{Cu}(\text{2,4-HPdc})_2(\text{H}_2\text{O})_2]\}^{[54]}$ is a mononuclear coordination complex with the Cu^{II} center coordinated by the two N atoms and two O atoms of two 2,4-HPdc ligands. In this configuration, the Cu^{II} cations form a distorted planar four-coordinate geometry in the equatorial plane and establish weak interactions with two water molecules in the axial plane of the octahedron. The 2,4-HPdc molecules in the complex have a free reactive carboxylate group. All of these features make it an appropriate candidate to form a M' MOF with copper(II) UMCs that is likely to present catalytic or adsorption properties.

Herein, we report the synthesis and characterization of $[\text{NaCu}(\text{2,4-HPdc})(\text{2,4-Pdc})]$, a new M' MOF based on $[\text{Cu}(\text{2,4-HPdc})_2(\text{H}_2\text{O})_2]$ metalloligands with copper(II) UMCs in its structure. The catalytic properties of the material were tested, and it is an active heterogeneous catalyst for the cyanosilylation of aldehydes and the Knoevenagel C–C bond-forming reaction.

Results and Discussion

Synthesis of $[\text{NaCu}(\text{2,4-HPdc})(\text{2,4-Pdc})]$

The aim of the study was to obtain M' MOFs including the complex $[\text{Cu}(\text{2,4-HPdc})_2(\text{H}_2\text{O})_2]$ by the metalloligand synthetic approach (Scheme 1). Therefore, this complex was used as the starting reagent with various transition metals to form frameworks with higher dimensionality. Hydrothermal and diffusion techniques were used.

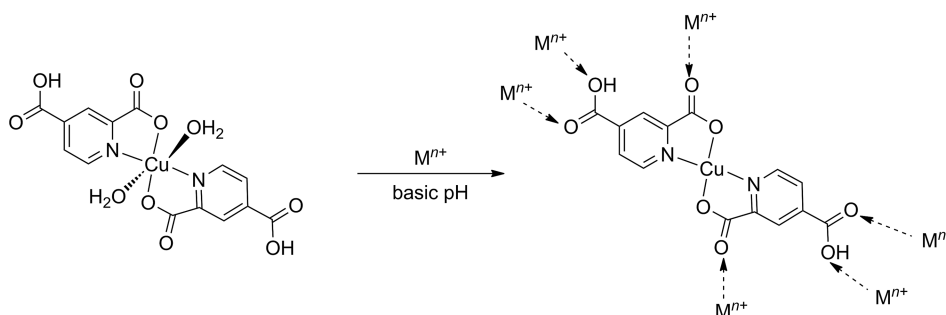
Different M' MOFs have been obtained with the initial complex structure in their framework, some of which have been reported previously. For instance, the isostructural

compounds $\text{MnCu}(\text{Pdc})_2(\text{H}_2\text{O})_4$ ^[27] and $\text{CoCu}(\text{Pdc})_2(\text{H}_2\text{O})_4$ ^[28] were obtained, the first one by the diffusion of Mn^{II} ions into a gel containing the metalloligand, and the second by the hydrothermal reaction of the metalloligand with Co^{II} ions. These compounds crystallize in the triclinic $P\bar{1}$ space group. Their structures consist of equatorially hydrated $\text{M}(\text{H}_2\text{O})_4$ units ($\text{M} = \text{Mn}, \text{Co}$) that bridge $\text{Co}(\text{2,4-Pdc})_2$ metalloligands at the apical positions through the uncoordinated oxygen atom of the carboxylate group at the 2-position of the 2,4-Pdc ligand to produce sheets stacked along the [011] direction. Crystals of $\text{CoCu}(\text{Pdc})_2(\text{H}_2\text{O})_6$ and $\text{ZnCu}(\text{Pdc})_2(\text{H}_2\text{O})_6$ ^[27] were also obtained by diffusion methods. These compounds are also isostructural and crystallize in the monoclinic $P2_1/a$ space group. In their structures, the metalloligand acts as a bridge between the secondary metal centers (Co or Zn) to produce chains along the [10–2] direction.

The compound $[\text{NaCu}(\text{2,4-HPdc})(\text{2,4-Pdc})]$ was obtained by a hydrothermal reaction. It appears as a minority phase if a Co^{II} salt is used and a majority phase if an Fe^{II} or Fe^{III} salt is used (Figure 1). The Fe^{II} salt was selected to reproduce the compound because of the improved yield (ca. 43%) and cleanness of the crystals with this metal ion. Several trials were made to obtain the compound in the absence of these metal ions or with the addition of sodium salts instead. However, the title compound was not obtained. This suggests a possible synergetic effect of the transition metals during the synthesis that favors the formation of $[\text{NaCu}(\text{2,4-HPdc})(\text{2,4-Pdc})]$ in preference to other phases.

Structure of $[\text{NaCu}(\text{2,4-HPdc})(\text{2,4-Pdc})]$

$[\text{NaCu}(\text{2,4-HPdc})(\text{2,4-Pdc})]$ is isostructural to $[\text{CuMn}(\text{2,4-Pdc})_2]$ (Figure S1 in the Supporting Information)^[28]



Scheme 1. Representation of the metalloligand synthetic approach.

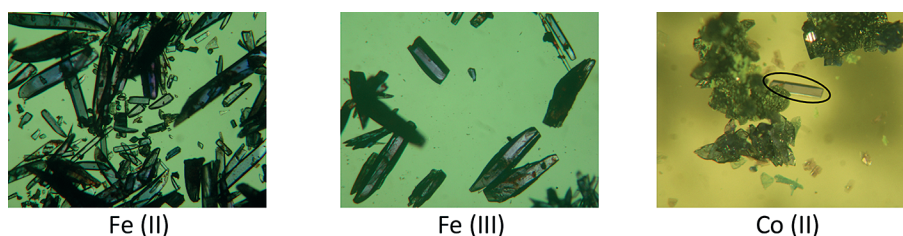


Figure 1. Pictures of crystals of $[\text{NaCu}(\text{2,4-HPdc})(\text{2,4-Pdc})]$ obtained when different transition metal salts were used in the synthesis.

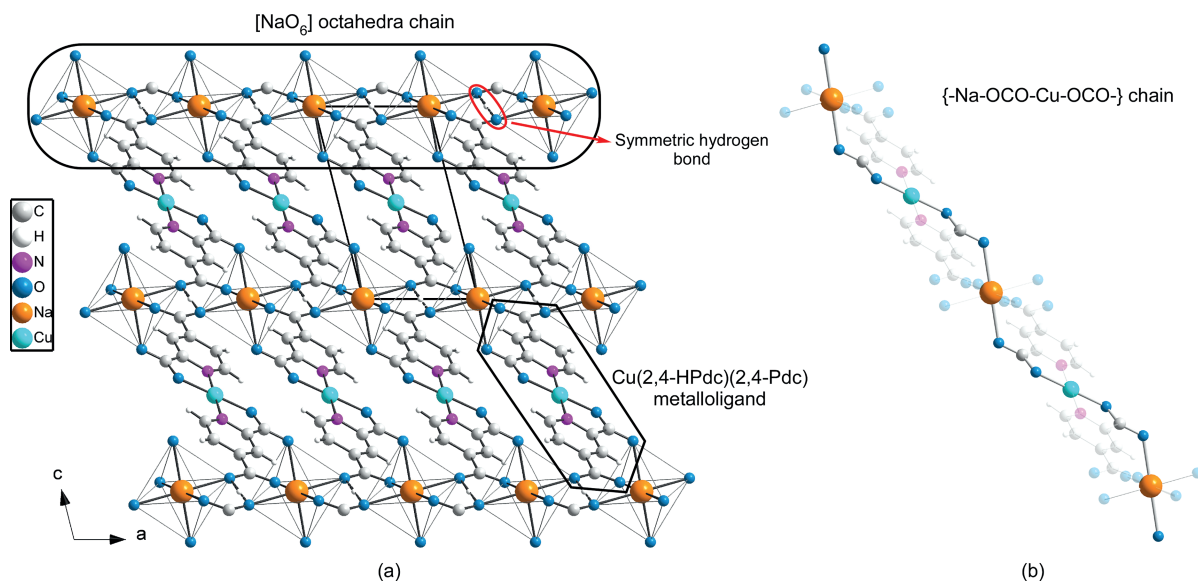


Figure 2. (a) View of the structure of [NaCu(2,4-HPdc)(2,4-Pdc)] along the *b* axis. (b) Detail of the undulating {-Na-OCO-Cu-OCO-} chains.

and crystallizes in the triclinic space group $P\bar{1}$. The structure is built up from [Cu(2,4-HPdc)(2,4-Pdc)] metalloligands and [NaO₆] octahedra. The main difference between these two compounds is the replacement of Na⁺ ions with Mn²⁺ ions. The charge difference between the Mn²⁺ and Na⁺ ions is compensated by the presence of one proton that is bonded equally to two 2,4-Pdc ligands to establish a symmetric hydrogen bond.

The [NaO₆] octahedra are linked to each other through carboxylic bridges at the 4-position of 2,4-Pdc molecules to produce chains along the *a* axis. In addition, the metalloligand acts as a bridge between these chains and links them through the free oxygen atoms of the carboxylate groups at the 2-position of the 2,4-Pdc molecule. This results in undulating chains of {-Na-OCO-Cu-OCO-} repeat units that form the 3D network shown in Figure 2.

The O(1) oxygen atoms in the equatorial plane of the [NaO₆] octahedra are bonded by a symmetric hydrogen bond with an O(1)–H(4) distance of 1.22 Å and an O(1)–H(4)–O(1)^v angle of 180° (symmetry transformation *v*: $-x + 1, -y, -z$). This hydrogen atom, H(4), is at a special position and equally bonded to both 2,4-Pdc molecules of the formula (Tables S1 and S2).

Both metal ions, Cu and Na, are also located at special positions of the cell over inversion sites. The metalloligand Cu^{II} ions are in a square-planar environment and chelated by two 2,4-Pdc molecules. This coordination involves one oxygen atom of the carboxylate groups at the 2-position and the pyridinic nitrogen atoms of two 2,4-Pdc molecules, and these five atoms are in the same plane. The bond lengths in the square-planar Cu environment are very similar: 1.945(2) Å for Cu–O(3) and 1.959(1) Å for Cu–N. The *trans* bond angles are 180°, whereas the *cis* ones are 83.87(6)° for the O(3)ⁱ–Cu–N and O(3)–Cu–Nⁱ bonds and 96.13(6)° for the O(3)–Cu–N and O(3)ⁱ–Cu–Nⁱ bonds; the lowest value corresponds to the bite angle, and the highest

one corresponds to the angle formed by the atoms from different 2,4-Pdc molecules (symmetry transformation *i*: $-x + 1, -y, -z + 1$).

As stated above, pyridinedicarboxylates are very versatile linkers. In particular, 2,4-Pdc has been observed in 18 different coordination modes (Figure S2). In [NaCu(2,4-HPdc)(2,4-Pdc)], each 2,4-Pdc molecule establishes interactions with four different metal centers, one copper(II) ion and three sodium ions. Among the 83 structures reported in the Cambridge Structural Database, six have the same coordination mode for 2,4-Pdc.

Continuous shape measures of the metal coordination environments were performed with the Shape v2.1 program.^[55] As expected, the values obtained for the copper(II) environment are very near to the square-planar geometry, $S(D_{4h}) = 0.29$ and $S(T_d) = 33.52$. If this pair of values is situated in a shape map for four coordination environments,^[56] a little deviation from the spread curve to the scissoring line can be observed, and the symmetry of the polyhedra is D_{2h} owing to the difference between the *cis* angles. The sodium environment is very close to an ideal octahedron, and the continuous shape measure values are $S(O_h) = 0.56$ and $S(D_{3h}) = 16.02$. These values imply very little distortion from the ideal octahedron to a compressed trigonal antiprism.^[57]

To characterize the structure topologically, the framework was simplified. The Na and Cu atoms were taken as nodes of the net, and the 2,4-Pdc molecules were taken as connectors. The topological analysis gives rise to a pcu α -Po-like uninodal six-connected net with the $\{4^{12}.6^3\}$ point symbol (Figure S3).

Thermal Behavior of [NaCu(2,4-HPdc)(2,4-Pdc)]

The thermogravimetric decomposition curve shows a unique mass loss process from approximately 290 °C to al-

most 340 °C. The differential scanning calorimetry (DSC) curve shows that it is an exothermic process. The total weight loss is approximately 67.6%, which is very close to the theoretic percentage for the organic molecules (68.0%, Figure S4).

The thermal stability of [NaCu(2,4-HPdc)(2,4-Pdc)] was also studied by time-resolved X-ray thermodiffractometry under an air atmosphere (Figure S5). The thermodiffractogram shows that the phase is stable until 290 °C. Above this temperature, some unidentified maxima appear and coexist with the most intense maxima of [NaCu(2,4-HPdc)(2,4-Pdc)] until 350 °C. At this point, the crystallization of the main calcination product CuO ($C2/c$, $a = 4.6833 \text{ \AA}$, $b = 3.4208 \text{ \AA}$, $c = 5.1294 \text{ \AA}$, $\beta = 99.5670^\circ$) starts.^[58]

In the thermal stability range of the phases, an angular variation of the diffraction maxima can be observed, owing to the thermal expansion of the unit-cell parameters. The evolution of the cell parameters with increasing temperature was studied by cyclic refinements of the X-ray patterns. The a , b , c , and γ cell parameters increase with increasing temperature, whereas α remains almost unchanged and β decreases (Figure S6). Such cell-parameter evolution is due to slight reorientation of the structural units during the heating process. The decrease of the β angle indicates that the chains of [NaO₆] octahedra shift in opposite directions. The total effect of these shifts and reorientations is a 3% increase of the unit-cell volume between room temperature and 290 °C.

Catalytic Activity Study

[NaCu(2,4-HPdc)(2,4-Pdc)] has coordinatively unsaturated Cu^{II} ions in its crystal structure. Thus, although the structure is not porous, the copper(II) ions at the surface could act as catalytic centers. Therefore, the material was tested as a catalyst for the cyanosilylation of aldehydes and the Knoevenagel reaction. Both reactions are important C–C bond-forming reactions within the drug industry.^[59,60] In both cases, the activation of carbonyl groups by a Lewis acid occurs.

Cyanosilylation of Aldehydes

The aldehyde cyanosilylations were performed with trimethylsilyl cyanide (TMSCN) at room temperature in the absence of solvent. The results are shown in Figure 3 and Table 1. For aromatic aldehydes, the conversion decreases in the order 4-methylbenzaldehyde > 4-chlorobenzaldehyde > benzaldehyde. The aliphatic aldehyde heptanal reacts quantitatively in 210 min. In all cases, an induction period was observed and corresponds to the formation of the active species. No size selectivity was observed; therefore, the reaction mainly occurs on the surface, as expected from the crystal structure. Blank experiments without catalyst were performed, and only traces of the product were observed by GC–MS.

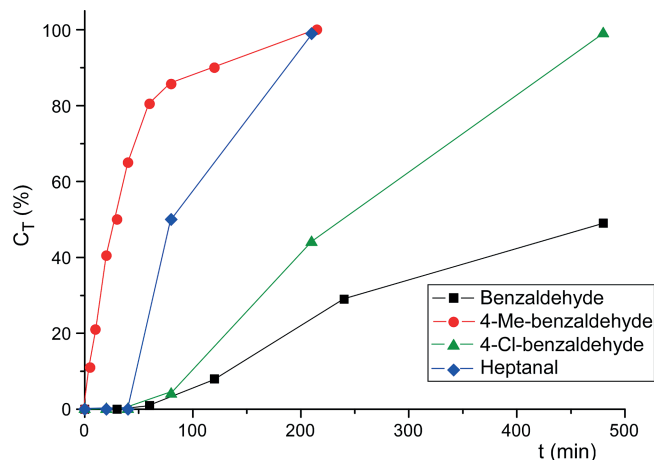


Figure 3. Kinetic profiles of the cyanosilylation reactions of aldehydes.

Table 1. Scope of the [NaCu(2,4-HPdc)(2,4-Pdc)]-catalyzed cyanosilylation of aldehydes.^[a]

Substrate	Time [h]	Yield [%]	TOF [h ⁻¹]
Benzaldehyde	24	85	10.5
4-Methylbenzaldehyde	3	100	132
4-Chlorobenzaldehyde	8	100	19.2
Heptanal	3	99	36

[a] Reaction conditions: room temp., 0.5% catalyst, without solvent.

At the end of the reactions, the solid catalyst was recovered by centrifugation and washed with dichloromethane and acetone and then characterized by powder X-ray diffraction and IR spectroscopy. The powder diffraction patterns of the recovered catalyst are the same as that of the as-synthesized catalyst. Some weak extra peaks were observed only for the reaction with heptanal (Figure S7). The IR spectra of the recovered catalyst do not show significant changes with respect to that of the as-synthesized [NaCu(2,4-HPdc)(2,4-Pdc)] (Figure S8).

Recycling Test

Reutilization is one of the greatest advantages of heterogeneous catalysts and can also provide useful information about the anchoring process and catalyst stability along the catalytic cycle. Recycling tests were performed over [NaCu(2,4-HPdc)(2,4-Pdc)] for the cyanosilylation of benzaldehyde. The catalyst was recycled for five runs with no activity decrease (Figure 4).

The recovered catalyst was washed with dichloromethane and acetone and characterized by IR spectroscopy (Figure S9). The amount of catalyst recovered after the fifth run was insufficient for X-ray powder diffraction characterization. On the other hand, the IR spectrum shows the bands of the as-synthesized compound and, therefore, indicates that the material has not changed chemically during the catalytic process. The IR spectrum did not show bands corresponding to the cyanide group, in contrast to the previously studied catalyst $[\{CoNi(H_2O)_2(Bpe)_2\}(V_4O_{12})]$.

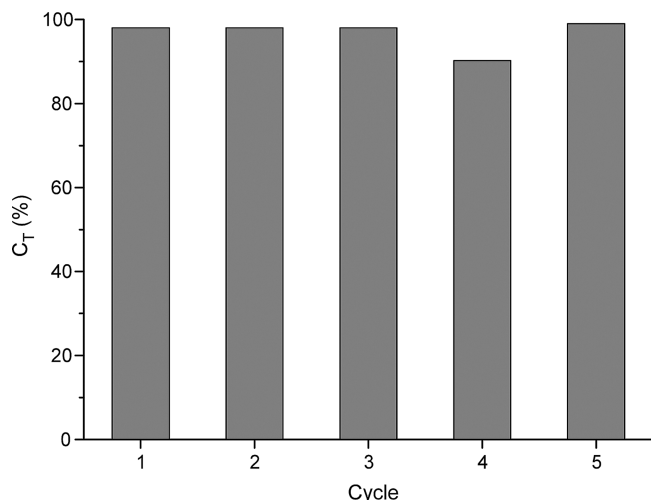
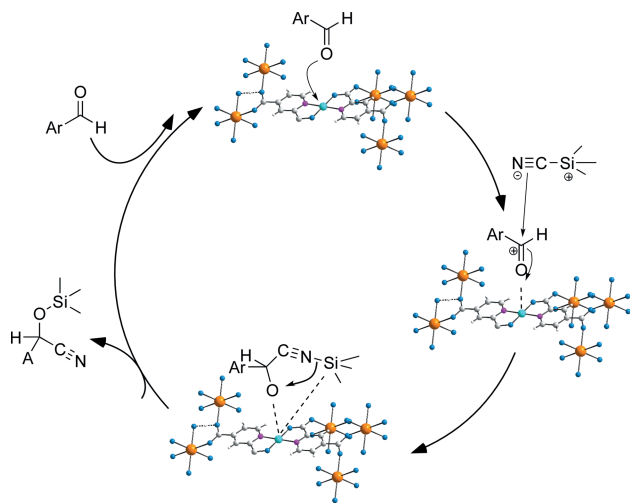


Figure 4. Recycling of catalyst for the cyanosilylation of benzaldehyde (50 °C, 5% catalyst, without solvent).

4H₂O·Bpe [Bpe = 1,2-di(4-pyridyl)ethylene].^[61] In this case, the mechanism should occur through the external coordination sphere, and the copper center acts only as a carbonyl activator (Scheme 2).



Scheme 2. Proposed mechanism for cyanosilylation reactions over [NaCu(2,4-HPdc)(2,4-Pdc)].

These results are comparable with those reported by Han et al. for a polyoxometalate-based metal–organic framework, {[Cu₂(bipy)(H₂O)_{5.5}]₂[H₂W₁₁O₃₉]·3H₂O·0.5CH₃CN} (bipy = 4,4'-bipyridine).^[62] This compound has an accessible pore volume of 429 Å³ (14% of the unit-cell volume), as calculated from PLATON analysis. In this case, the reaction with benzaldehyde was performed at room temperature with 8% of catalyst (calculated with respect to the Cu^{II} content) in acetonitrile. The conversion achieved after 24 h of reaction was 98.1%.

On the other hand, other porous Cu^{II} metal–organic frameworks show lower catalytic activity for the cyanosilylation reaction of benzaldehyde.^[63–65] Schlichte et al. reported the catalytic properties of Cu₃(BTC)₂ (BTC = benzene-1,3,5-tricarboxylate), formed from the dehydration of

Cu₃(BTC)₂(H₂O)₃·xH₂O.^[63] The crystal structure of this compound has channels of 9.5 × 13.3 Å perpendicular to the [100] direction.^[66] The nanochannels intersect to provide a 3D connected network of pores. The cyanosilylation reactions were performed with benzaldehyde in three solvents, namely, pentane, heptane, and toluene. The conversions achieved with 15% of catalyst at 40 °C were 57% after 72 h in pentane, 55% after 48 h in heptane, and 20% after 24 h in toluene. For comparison, we performed a test with commercial Cu₃(BTC)₂ under the same conditions as those used for our other experiments. The conversion reached in this case was 48% in 24 h (Table S3).

From these data, the presence of structural pores seems not to be a determining factor for catalytic activity in cyanosilylation reactions. The catalytic activity of [NaCu(2,4-HPdc)(2,4-Pdc)] must be a result of the concentration of unsaturated Cu^{II} centers at the surface.

Knoevenagel Condensation

Knoevenagel reactions were performed between benzaldehyde and malononitrile (pK_a = 11.1) or ethyl cyanoacetate (pK_a = 13.1, Table 2) at 100 °C with 5 mol-% of catalyst. A yield of 61% was obtained after 24 h for the reaction with malononitrile. Under the same conditions, the reaction with ethyl cyanoacetate gave a yield of 37%.

Table 2. Scope of [NaCu(2,4-HPdc)(2,4-Pdc)]-catalyzed Knoevenagel condensations.^[a]

Substrate	Donor	Conv. [%] (after 2 h)	Conv. [%] (after 24 h)
Benzaldehyde	malononitrile	27	64
Benzaldehyde	ethyl cyanoacetate	19	37
4-Methylbenzaldehyde	malononitrile	74	86
4-Methoxybenzaldehyde	malononitrile	25	50
4-Fluorobenzaldehyde	malononitrile	23	48
4-Nitrobenzaldehyde	malononitrile	49	87
Heptanal	malononitrile	50	96
Cyclohexanone	malononitrile	2	39
Cyclopentanone	malononitrile	0	20
Acetophenone	malononitrile	0	1.5

[a] Reaction conditions: 100 °C, 5 mol-% catalyst, in toluene.

The scope of the reaction was studied with different aldehydes and ketones with malononitrile (Table 2). The presence of a methyl substituent at the carbonyl group, as in acetophenone, involves a drastic decrease in the conversion rate, probably owing to steric hindrance. On the other hand, cyclic ketones reach conversion rates higher than that for aromatic acetophenone but lower than those of aldehydes. If substituents are introduced to the aromatic ring of benzaldehyde, the conversion rates differ with regard to electronic effects, and the reactivity order is 4-methylbenzaldehyde ≈ 4-nitrobenzaldehyde > benzaldehyde > 4-methoxybenzaldehyde ≈ 4-fluorobenzaldehyde (Figure 5). With an aliphatic aldehyde such as heptanal, a conversion of 50% was reached after 2 h, and the reaction was complete after 24 h.

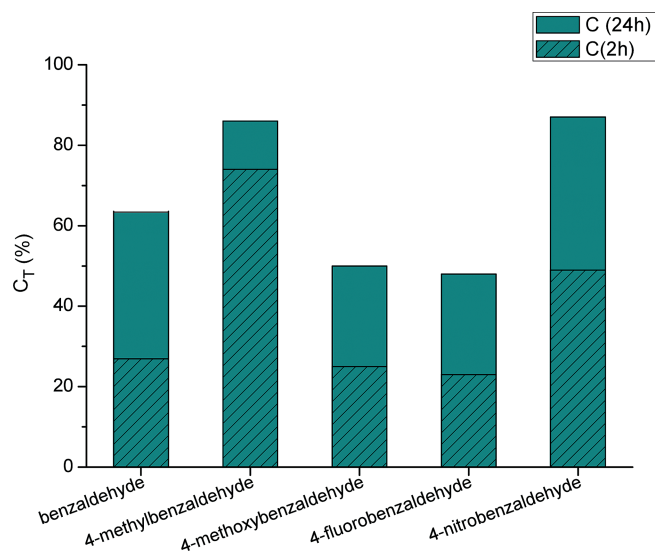


Figure 5. Knoevenagel condensations between different aldehydes and malononitrile.

After the reactions, the solid catalyst was recovered by centrifugation and washed with dichloromethane and acetone. Once dried, it was characterized by powder X-ray diffraction and IR spectroscopy (KBr pellet). The powder diffraction patterns of the recovered catalyst are very similar to that of the as-synthesized catalyst. Some of the diffraction patterns present an increased intensity for the (−101) reflection, probably because of a slight reorganization of the atoms in the structure (Figure S10). The IR spectra of the recovered catalyst do not show significant changes with respect to that of the as-synthesized [NaCu(2,4-HPdc)(2,4-Pdc)] (Figure S11).

Recycling Test

Recycling tests were performed with [NaCu(2,4-HPdc)(2,4-Pdc)] as the catalyst for the Knoevenagel condensation of benzaldehyde and malononitrile. The catalyst was used for five runs with no significant activity loss (Figure 6).

The recovered catalyst was characterized by powder X-ray diffraction and IR spectroscopy (Figures S12 and S13). The powder X-ray diffraction pattern also shows an intensity increase for the (−101) reflection, which indicates a slight reorganization of the structure. The IR spectrum shows the bands of the as-synthesized compound and an additional band at $\tilde{\nu} = 2960 \text{ cm}^{-1}$, which may correspond to a small amount of adsorbed condensation products.

Owing to the proximity of the active sites, a mechanism involving two-site adsorption of the donor molecule could be proposed.^[67] The shortest distance between two Cu^{II} ions is 5.310(1) Å; however, there are pairs of Cu^{II} ions at 7.324(1) Å, a distance that allows the cyanide groups of malononitrile to establish the geometrically most favorable interactions with the copper active centers.

The Knoevenagel condensation of benzaldehyde and malononitrile is employed as a classic test reaction to analyze the activity of solid catalysts. Therefore, several studies of

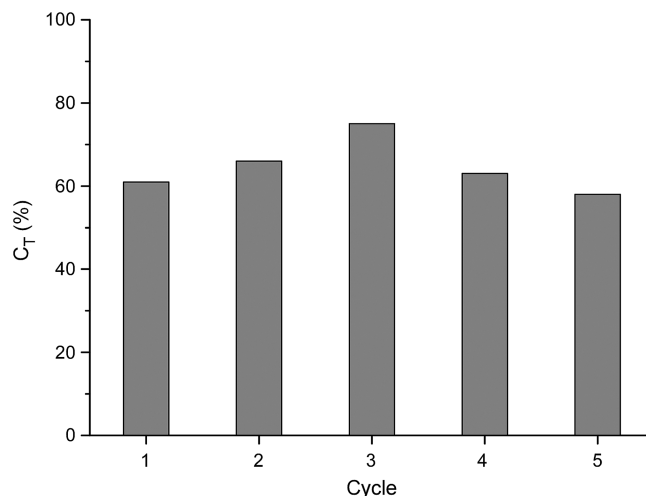


Figure 6. Recycling experiments for the Knoevenagel condensation of benzaldehyde with malononitrile (100 °C, 5 mol-% catalyst, 24 h, in toluene).

metal–organic frameworks have been performed with this reaction.^[60,68] However, the studies of this reaction catalyzed by Cu^{II} MOFs are not numerous.^[69–72]

The catalytic activity of Cu₃(BTC)₂ MOF in Knoevenagel condensation reactions has also been studied.^[71] It showed very good results compared with those for zeolites BEA and TS-1. With a catalyst/substrate ratio of 16.5% (with respect to the Cu^{II} content of the catalyst), the conversion reached 88% after 6 h of reaction at 60 °C. However, with the catalyst amount reduced to 4%, the yield of the reaction was 14% under the same reaction conditions (60 °C in *p*-xylene).

Likewise, Valvekens et al.^[72] studied the catalytic activity of M₂dobdc (dobdc^{4−} = 2,5-dioxidoterephthalate, M²⁺ = Mg²⁺, Co²⁺, Ni²⁺, Cu²⁺, and Zn²⁺), also known as MOF-74. The structure presents coordinatively unsaturated metal sites in a honeycomb structure with large, one-dimensional hexagonal pores with diameters of 11–12 Å. In addition, the base sites that are potentially available in the framework could ensure that the deprotonation of the donor molecule is favored. The reactions were performed in toluene at 70 °C and with a catalyst/benzaldehyde ratio of 20%. The condensation of benzaldehyde and malononitrile over Cu₂dobdc yielded 39% after 2 h and 69% after 24 h. This results are very similar to those observed for [NaCu(2,4-HPdc)(2,4-Pdc)].

To allow a better comparison, tests of the Knoevenagel reaction of benzaldehyde and malonitrile over commercial Cu₃(BTC)₂ under the same conditions as those for the studied catalyst have been performed. After 24 h, the reaction was complete. The same test over the metalloligand [Cu(2,4-HPdc)₂(H₂O)₂] was performed, and a conversion of 48% was achieved after 24 h (Table S3).

A hot filtration test was performed to corroborate the heterogeneous nature of the catalysis process. The reaction was performed under the typical conditions, and the mixture was filtered after 2 h. The liquid was allowed to react

for 24 h. The reaction conversion after this time had not increased with respect to that reached after 2 h. The inductively coupled plasma MS (ICP-MS) analysis of the filtrate after the reaction indicated that only 0.01 % of the Cu from the catalyst was leached into the solution, which is a negligible amount.

On the other hand, the cyanosilylation and Knoevenagel condensation reactions were also tested over [MnCu(2,4-Pdc)₂]. The results obtained are very similar to those obtained for the isostructural [NaCu(2,4-HPdc)(2,4-Pdc)] (Table S4) and confirm that the Cu^{II} metal centers are involved in the catalytic processes.

Conclusions

The metalloligand synthetic approach has been used to obtain the new M' MOF [NaCu(2,4-HPdc)(2,4-Pdc)] with unsaturated copper(II) centers. The crystal structure of [NaCu(2,4-HPdc)(2,4-Pdc)] is built up from [Cu(2,4-HPdc)(2,4-Pdc)] metalloligands with Cu^{II} ions in a square-planar geometry and [NaO₆] octahedra. The presence of unsaturated Cu^{II} centers favors the catalytic activity at the surface of the material. The compound is an active heterogeneous catalyst for the cyanosilylation of different aldehydes and Knoevenagel reaction and can be reused at least five times with no activity loss in the successive cycles. The activity of this compound is comparable with the activity of other Cu^{II} MOFs with structural pores.

Experimental Section

Materials and Methods: All chemicals are commercially available and were used without further purification. [Cu(2,4-HPdc)₂(H₂O)₂] was prepared by the literature method.^[73] Syntheses of the title compound were performed in 50 mL Parr Teflon-lined acid digestion bombs, and the [Cu(2,4-HPdc)₂(H₂O)₂] metalloligand was synthesized under microwave radiation in a CEM Mars 5 microwave oven.

[Cu(2,4-HPdc)₂(H₂O)₂]: A mixture of Cu(NO₃)₂·2.5H₂O (0.560 g, 2.4 mmol), 2,4-H₂Pdc·H₂O (0.217 g, 1.17 mmol), and H₂O (50 mL, 2.78 mol) was placed in a 100 mL Teflon vessel and heated at 120 °C for 2 h under microwave radiation. The use of microwave radiation allowed the reduction of the synthesis temperature and time. Blue crystals of [Cu(2,4-HPdc)₂(H₂O)₂] were collected by filtration and washed with water and acetone. Once dried, the crystals were pulverized for later use and characterized by powder X-ray diffraction.

[NaCu(2,4-HPdc)(2,4-Pdc)]: In a typical synthesis, [Cu(2,4-HPdc)₂(H₂O)₂] (0.35 mmol, 0.150 g) was dissolved in H₂O (20 mL), and 1 M NaOH solution was added dropwise until the pH was 10.5. A solution of FeCl₂·4H₂O (0.037 mg, 0.18 mmol) in H₂O (10 mL) was added, and the mixture was placed in a 50-mL Parr Teflon-lined autoclave. The autoclave was sealed and heated for 2 d at 120 °C. After the reaction, purple tabular crystals of the title compound were obtained with a brown powder that can be removed readily by washing with water. The yield of the purple compound after the washing process was ca. 43 %. C₁₄H₇CuN₂NaO₈ (417.75): calcd. C 40.25, H 1.69, Cu 15.21, N 6.71, Na 5.50; found C 40.3(1), H 1.69(2), Cu 15.98(1), N 6.7(1), Na 5.18(1). The density of the crys-

tals was determined by the flotation method^[74] with a mixture of bromoform and bromobenzene [2.04(2) g/cm³].

X-ray Structure Determination of [NaCu(2,4-HPdc)(2,4-Pdc)]: A needlelike crystal with dimensions 0.12 × 0.02 × 0.02 mm was carefully selected under a polarizing microscope and glued on a glass fiber. The diffraction data were collected with an Agilent Supernova single-source diffractometer with Mo-K_α radiation. Details of crystal data, intensity collection, and some features of the structural refinement are reported in Table 3. First of all, a standard short program was used to obtain the crystal lattice and to confirm the quality of the crystal from a few diffraction images. Once the unit cell and the quality of the single crystal were determined, the data collection was performed with consideration of the triclinic symmetry. A total of 2162 reflections were measured in the range 2.32 ≤ 2θ ≤ 28.22°. The number of independent reflections was 1481 (R_{int} = 0.0157) with the criterion I > 2σ(I) applied. The diffraction data were corrected for Lorentz and polarization effects^[75] as well as for the absorption with consideration of the crystal shape and size. The structure was solved by direct methods (SHELXS97^[76]) and refined by the full-matrix least-squares procedure on F² with the SHELXL 97^[76] computer program within the WINGX software package.^[77] The scattering factors were taken from the International Tables for Crystallography.^[78] Anisotropic thermal parameters were assigned to the non-H atoms. H atoms were located in Fourier maps and refined with their isotropic thermal parameter fixed by assuming that their isotropic U value is 1.20 times the U_{eq} value of the atom to which the hydrogen atom is bound. The final R factors were R₁ = 0.0247 and wR₂ = 0.0603 with I > 2σ(I). The maximum and minimum peaks in the final difference synthesis were 0.514 and -0.483 e Å⁻³. Atomic coordinates and selected bond lengths and angles are shown in Tables S1 and S2 in Supporting Information. CCDC-1012869 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

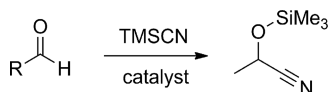
Table 3. Crystal data and structure refinement for [NaCu(2,4-HPdc)(2,4-Pdc)].

Empirical formula	C ₁₄ H ₇ CuN ₂ NaO ₈	
Formula weight	417.75	
Temperature [K]	100.0(1)	
Wavelength [Å]	0.71073	
Crystal system	triclinic	
Space group (No.)	P $\bar{1}$ (2)	
Unit-cell dimensions	<i>a</i> = 5.3102(5) Å	<i>a</i> = 98.022(7)°
	<i>b</i> = 7.3237(7) Å	<i>β</i> = 102.847(7)°
	<i>c</i> = 9.1508(8) Å	<i>γ</i> = 98.015(7)°
Volume [Å ³]	338.18(5)	
Z	1	
ρ _{calcd.} , ρ _{obs} [g/cm ³]	2.051, 2.04(2)	
μ [mm ⁻¹]	1.703	
F(000)	209	
Crystal size [mm]	0.12 × 0.02 × 0.02	
θ range for data collection [°]	2.32 to 28.22	
Index ranges	-7 ≤ <i>h</i> ≤ 6, -9 ≤ <i>k</i> ≤ 4, <i>l</i> = ±11	
Reflections collected	2162	
Independent reflections	1481 [R(int) = 0.0157]	
Completeness to θ = 25.00° [%]	99.0	
Refinement method	Full-matrix least-squares on F ²	
Data/restraints/parameters	1481/0/130	
Goodness-of-fit on F ²	1.044	
Final R indices [I > 2σ(I)]	R ₁ = 0.0247, wR ₂ = 0.0603	
R indices (all data)	R ₁ = 0.0256, wR ₂ = 0.0609	
Largest diff. peak and hole [e Å ⁻³]	0.514 and -0.483	

Physical Measurements: The IR spectra (KBr pellets) were obtained with a Jasco FTIR 6100 spectrometer in the 400–4000 cm⁻¹ wave-number range. Thermogravimetric analysis (TGA) was performed under synthetic air with a NETZSCH STA 449F3 DSC–TGA instrument. A crucible containing the sample (ca. 10 mg) was heated at 5 °C min⁻¹ in the temperature range 30–800 °C. Thermodiffraction analysis was performed with a Bruker D8 Advance Vantec diffractometer equipped with an Anton Parr HTK2000 variable-temperature stage and a Pt sample holder. The diffraction patterns were collected in 2θ steps of 0.03334° in the range of 8–38.5° for 0.36 s per step, and the temperature was increased at 20 °C min⁻¹ from 30 to 810 °C.

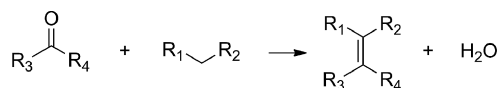
Catalytic Tests: [NaCu(2,4-HPdc)(2,4-Pdc)] was dried at 100 °C in vacuo to remove the possible humidity that could interfere with the reactions. [Cu(2,4-HPdc)₂(H₂O)₂] metalloligand and Cu₃(BTC)₂ metal–organic framework (Basolite® C300) were dried at 150 °C for 90 min in vacuum to remove the crystallization and coordination water molecules.

The cyanosilylation reactions of aldehydes (Scheme 3) were performed at 50 °C and room temperature in the absence of solvent. Into a screw cap vial with dried [NaCu(2,4-HPdc)(2,4-Pdc)] (10 mg, 0.024 mmol), the aldehyde was added at a catalyst/substrate ratio of 1:20 or 1:200. The reaction was initiated by the addition of excess TMSCN, and the mixture was stirred during the reaction. Recycling experiments for the cyanosilylation of benzaldehyde were performed at 50 °C with 5% of catalyst. After the completion of the reaction, the catalyst was recovered by centrifugation and washed with dichloromethane. The recovered powder was placed into a vial to repeat the reaction under the same conditions.



Scheme 3. General representation of the cyanosilylation of aldehydes.

Knoevenagel reactions (Scheme 4) were performed at 100 °C in toluene. Into a screw cap vial were placed dried [NaCu(2,4-HPdc)(2,4-Pdc)] (10 mg, 0.024 mmol), benzaldehyde (0.48 mmol), malononitrile (0.48 mmol), and toluene (500 μL), and the reaction mixture was stirred. Dodecane was used as an internal standard. Recycling experiments were performed for the condensation of benzaldehyde and malononitrile. The catalyst was recovered by centrifugation and washed with toluene between the consecutive runs.



Scheme 4. General representation of Knoevenagel condensation.

The progress of the reactions was monitored by GC–MS. Once the reaction was complete, the solid phase was separated from the liquid by centrifugation. The catalyst was then characterized by powder X-ray diffraction and IR spectroscopy.

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