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FULL PAPER

In situ synthesis of metallophthalocyanines into pores of MIL-101: A novel and green strategy for preparation of host–guest catalysts

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A novel strategy is developed to encapsulate metallophthalocyanines (MPcs, M = Cu, Ni and Co) into MIL-101 to give MPcs@MIL-101 via *in situ* synthesis of MPcs from component fragments in 1-butyl-3-methylimidazolium bromide as an ionic liquid. This strategy overcomes some drawbacks of existing methods for encapsulation of MPcs into metal–organic frameworks. The chemical and structural properties of MPcs@MIL-101 were determined using scanning electron microscopy, powder X-ray diffraction, and Fourier transformation infrared and flame atomic absorption spectroscopies. The results showed that CuPc@MIL-101, which was used as a 'ship-in-a-bottle' catalyst, demonstrates excellent catalytic performance in the oxidative amidation of aldehydes with amine salts. It is confirmed that CuPc@MIL-101 can be reused up to five times without significant loss of its activity.

KEYWORDS

encapsulation, host–guest catalysts, metallophthalocyanines, MIL-101, oxidative amidation

1 | INTRODUCTION

Over the past decade, metal–organic frameworks (MOFs), as a new class of porous material, have been used in diverse fields, including separation, sensing, gas storage and catalysis.[1] Unique features of MOFs such as structure design ability, high specific surface area and ordered porous structure mean that they are excellent supports for immobilization of metal nanoparticles or catalytically active complexes.[2] This class of materials also can make a significant difference from catalyst recycling, selectivity and conversion value point of view.[3] Microporous and mesoporous MOFs in comparison to zeolites give better molecular accessibility when it comes to larger substrates and products through bigger windows and pores. Among the MOFs, MIL-101 shows good resistance to common solvents, water and temperature.[4] Due to the high stability of MIL-101 towards the leaching of Cr(III) to solution, non-carcinogenic and non-mutagenic Cr(III) compounds, it is an attractive compound as a support in heterogeneous catalysis.[5] Immobilization of Cu nanoparticles,[6] Pd,[7] PdAg alloy,[8] Au–Pd nanoparticles,[9] polyoxometalate,[10] organometallic complexes and organometallic compounds into MIL-101 provides efficient heterogeneous catalysts for a wide range of organic transformations.

Metallophthalocyanines (MPcs) are an important class of compounds that have attracted considerable attention due to their excellent properties and have many applications in dye-synthesized solar cells, photodynamic therapy, pigments, dyes and biomimetic catalysis.[11] Several methods have been developed for the immobilization of MPcs on organic and inorganic supports, including impregnation,[12] covalent grafting[13] and encapsulation.[14] Because of the low solubility of MPcs in common solvents, the use of the impregnation method is limited to using substituted and soluble MPcs such as $RuPcF_{16}$, $(FePctBu4)_2N$ and iron tetrasulfophthalocyanine.[15] Recently, Ma and co-workers developed a new strategy to encapsulate a metal-functionalized guest molecule such as CoPc into a bio-MOF-1 via metal-cation-directed *de novo* assembly.[16] Although this method is efficient for encapsulating guest molecules into MOFs, application of this strategy is limited because of the use of an anionic MOF, multiple steps and long reaction time for preparation of MPcs into MOF, and tedious work-up. Therefore, development of a simple, fast and green strategy to encapsulate MPcs into MOFs is in high demand.

The amide functional group is one of the most important in the structures of natural products, pharmaceuticals and polymers, and the development of benign and efficient methods for the formation of amide bonds has attracted considerable attention from both industry and academia.[17] The most frequently used methods for amide formations involve the reaction of activated carboxylic acid derivatives and amines.[18] These methodologies have some drawbacks, such as use of expensive and hazardous reagents, poor atom-efficiency and generation of a significant amount of waste.[18] To overcome these drawbacks, several innovative strategies such as catalytic acylation of amines with carboxylic acid,[19] hydrative coupling reaction of alkynes with azides[20] and direct oxidative amidation of aldehydes[21] or dehydrogenative amidation of alcohols with amines[22] have emerged. Among them, oxidative amidation of aldehydes with amines offers green and significant protocols for construction of amides due to the stability and availability of the starting materials.[23] A number of protocols have been developed for this transformation, which use heterogeneous or homogeneous catalysts based on Rh,[24] Ru,[25] Ag,[26] Au[27] and Cu.[28] Therefore, development of new methods for the facile construction of amides is highly desirable. To the best of our knowledge, there is no report on the use of MPcs@MIL-101 as a heterogeneous catalyst for oxidative amidation.

In continuation of our ongoing research on sustainable benign pathways for organic transformations and nanocatalysis,[29] we introduce a novel strategy for *in situ* synthesis of MPcs into MIL-101 and investigate the catalytic activity as heterogeneous catalysts for oxidative amidation of aldehydes with amines. Notable features of our work include (i) simple, fast and green approach to encapsulate MPcs into a three-dimensional MOF, (ii) using commercially available raw materials for preparation of MPcs@MIL-101, (iii) easy work-up of products and (iv) utilizing ionic liquids for the synthesis of catalyst and elimination of the use of organic solvents.

2 | EXPERIMENTAL

2.1 | Materials and methods

Fourier transform infrared (FT-IR) spectra were recorded with a Bomem MB-Series FT-IR spectrometer. Powder X-ray diffraction (XRD) patterns were recorded using a STOE diffractometer with Cu K_α radiation ($\lambda = 1.5418$ Å). Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) analyses were performed using a Philips XL-30 instrument. All samples for morphological studies were sputtered with gold before observation. ^{1}H NMR spectra were recorded with a Bruker DRX-300 Avance spectrometer using $CDCl_3$ and DMSO-d_6 as solvents and tetramethylsilane as internal standard. The melting points of the products were measured using an Electrothermal 9100 apparatus. The concentration of copper was estimated using a Shimadzu AA-680 flame atomic absorption spectrophotometer.

2.2 | General procedure for synthesis of MIL-101

MIL-101 was prepared by hydrothermal reaction according to a previous report.[30] Briefly, $Cr(NO_3)_3{\cdot}9H_2O$ (2.00 g, 5.00 mmol), terephthalic acid (0.82 g, 5.00 mmol) and deionized water (24 ml) were loaded in a hydrothermal chamber and heated at 220 °C for 18 h. The resulting pale green solid was collected and washed several times with deionized water, dimethylformamide (DMF) and hot ethanol and then soaked in 95% ethanol for 24 h. Finally, the powder was dried overnight at 150 °C.

2.3 | General procedure for preparation of Cu^{2+}@MIL-101

Cu^{2+}@MIL-101 was prepared via double solvents method according to pervious reports.[31] Typically, activated MIL-101 (0.200 g) was suspended in 50 ml of dry *n*-hexane as a hydrophobic solvent in a round-bottomed flask and the mixture was sonicated for 30 min until the sample was dispersed in the *n*-hexane. To this mixture 0.123 ml of a 1 M solution of dehydrated Cu(II) chloride as hydrophilic solvent was added dropwise under continuous vigorous stirring. The resulting mixture was stirred for 3 h and then the green powder was filtered and dried under vacuum at 150 °C. The Cu(II) content of Cu^{2+}@MIL-101 was determined using flame atomic absorption spectroscopy, it being found to be 3.0 wt%.

2.4 | General procedure for synthesis of CuPc@MIL-101

Cu^{2+}@MIL-101 (0.200 g) was suspended in 2 ml of ethanol and phthalonitrile (0.064 g, 0.500 mmol) was added to this suspension and stirring was continued for 1 h. Then the solvent was evaporated under vacuum. The residue and 1-butyl-3-methylimidazolium bromide ([Bmim]Br; 0.438 g, 2.00 mmol) were heated at 180 °C for 1 h to afford CuPc@MIL-101 as indicated by the change of colour of the mixture to deep blue. Upon completion and cooling the mixture to room temperature, the mixture was washed with distilled water three times and ethanol. Finally the solid was dried under vacuum at 150 °C. The amount of MPc in the cages of MIL-101 was analysed using inductively coupled plasma atomic emission spectroscopy, and a value of 18 wt% loading was obtained.

2.5 | General procedure for oxidative amidation of benzaldehyde with amine salts

A mixture of CuPc@MIL-101 (30.0 mg), benzaldehyde (1.00 mmol), amine hydrochloride salt (1.20 mmol), $CaCO_3$ (110 mg, 1.10 mmol) and *tert*-butyl hydroperoxide (TBHP; 70% in water, 0.16 ml, 1.10 mmol) in acetonitrile (2 ml) was added in a 25 ml round-bottom flask and the reaction mixture was stirred at room temperature for 4 h. Upon completion the reaction (TLC monitoring), the catalyst was filtered and the volatiles were removed under reduced pressure. The crude product was purified by column chromatography on silica gel (petroleum ether–ethyl acetate) to afford amide product.

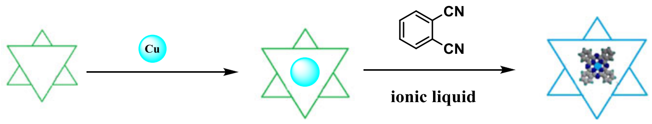
3 | RESULTS AND DISCUSSION

Our novel strategy for the preparation of CuPc@MIL-101 includes two steps (Scheme 1): (i) immobilizing Cu(II) ions inside the pores of MIL-101 prepared using the double solvent method[32] and (ii) preparation of MPcs by assembling of fragments under the direction of copper ions into the MIL-101 pores in the presence of ionic liquid.

Figure 1 shows the XRD patterns of MIL-101 and CuPc@MIL-101. The XRD pattern of MIL-101 does not change after the synthesis of the CuPc into the pores of MIL-101, which implies the structure of MIL-101 remains intact after reaction. Since CuPc is dispersed into the cavities of MIL-101, the characteristic reflections of CuPc are not observed in the XRD pattern of CuPc@MIL-101.

To confirm the assembly of phthalonitrile into Pc, FT-IR spectroscopy was used. Notably, the CN stretching vibration band at 2230 cm^{-1} is absent in the phthalonitrile-loaded Cu^{2+}@MIL-101 spectrum and the characteristic vibrations of CuPc at 721, 748, 1087, 1114, 1161 and 1712 cm^{-1} for CuPc@MIL-101 appear (Figure 2). These observations imply the successful formation of CuPc into MIL-101.

UV–visible absorption spectroscopy is an important technique for characterizing the optical properties of MPcs and identification of their chemical structures. Successful formation of the CuPc into the cavities of MIL-101 was confirmed using UV–visible spectroscopy. The UV–visible spectrum of CuPc@MIL-101 reveals two bands at 710 and 795 nm (Figure 3), which are characteristic bands of phthalocyanines.[5] In addition, CuPc@MIL-101 powder is blue, as compared to the green colour of MIL-101, indicating the association of CuPc molecules into the pores of MIL-101.



SCHEME 1 Procedure for *in situ* synthesis of CuPc@MIL-101

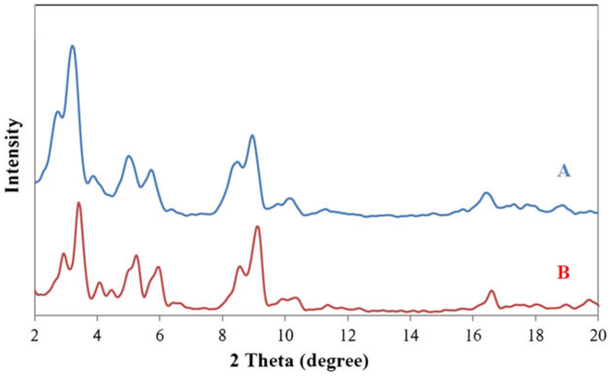


FIGURE 1 XRD patterns of (A) MIL-101 and (B) CuPc@MIL-101

SEM analysis was carried out to study the structure and morphology of MIL-101 and CuPc@MIL-101. As shown in Figure 4, the SEM images confirm that the structure of MIL-101 is stable in the catalyst preparation process. Also, EDS analysis indicates the presence of copper in CuPc@MIL-101 (Figure 5).

According to BET data, specific surface area and total pore volume of MIL-101 are estimated to be 1835 $m^2\ g^{-1}$ and 0.87 $cm^3\ g^{-1}$. These values for CuPc@MIL-101 are 1516 $m^2\ g^{-1}$ and 0.78 $cm^3\ g^{-1}$. The reduction of specific surface area and total pore volume indicates that CuPc molecules are certainly encapsulated within the pores of MIL-101.

The applicability of the *in situ* synthesis for the preparation of other MPcs into the pores of MIL-101 was investigated, and CoP@MIL-101 and NiPc@MIL-101 were successfully synthesized in the presence ionic liquid by heating at 180 °C. Powder XRD, FT-IR and UV–visible spectroscopic, SEM and EDS studies confirm their formation (supporting information, Figures S2–S11).

To elaborate the advantages of the *in situ* synthesis strategy compared to existing methods, the preparation of CuPc@MIL-101 using the impregnation approach was attempted. Immersing MIL-101 into a mixture of CuPc and tetrahydrofuran ultrasonically dispersed at room temperature for 20 h provided CuPc@MIL-101, but due to the low solubility of CuPc,[33] this method failed and only a negligible amount of phthalocyanine was loaded on MIL-101 without good dispersity. Therefore, this observation highlights the

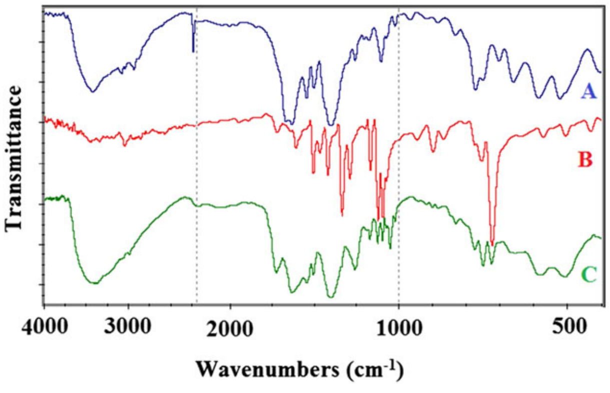


FIGURE 2 FT-IR spectra of (A) phthalonitrile-loaded Cu^{2+}@MIL-101, (B) CuPc and (C) CuPc@MIL-101

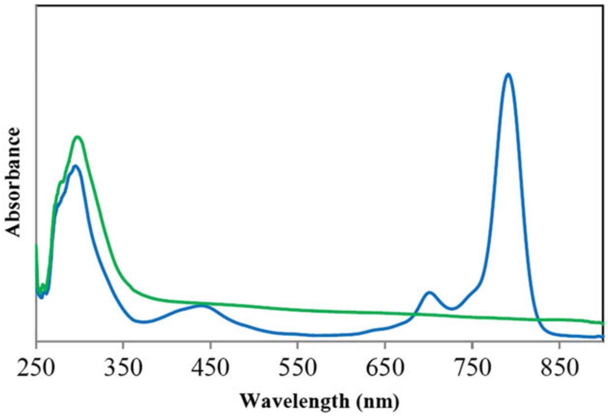


FIGURE 3 UV–visible spectra of the MIL-101 (green) and CuPc@MIL-101 (blue)

novelty of the *in situ* synthesis of CuPc into MIL-101. It is interesting to note that one of the most important advantages of this method is the controlled loading of phthalocyanine into the pores of MIL-101.

To evaluate the catalytic properties of CuPc@MIL-101, at the outset, a model reaction of benzaldehyde and benzylamine hydrochloride to form *N*-benzylbenzamide was selected. This reaction in the presence of CoPc@MIL-101, NiPc@MIL-101 and CuPc@MIL-101 affords certain yields of product (Table 1, entries 1–3). Among these catalysts, CuPc@MIL-101 is found to be the best catalyst to give *N*-benzylbenzamide in 55% yield (Table 1, entry 3). When the reaction is carried out in the presence of pristine MIL-101, the product is obtained in 35% yield within 6 h at 60 °C (Table 1, entry 4). As the amount of CuPc@MIL-101 is increased, the reaction goes to completion at room temperature (Table1, entries 5–8). Reaction in the presence of Cu^{2+}@MIL-101 as a heterogeneous catalyst produces the desired product in good yield after 5 h (Table1, entry 10). It is important to note that the catalytic activity of Cu^{2+}@MIL-101 decreases in the next runs in the reaction conditions experiment due to leaching of copper ions into the solution. Therefore, CuPc@MIL-101 is a better catalyst than Cu^{2+}@MIL-101 with either a higher catalytic activity in shorter reaction times or more stability towards the leaching Cu(II) ions. Control experiments in the presence of the CuPc and a mixture of the CuPc and MIL-101 give the product in 10 and 40% yields under the same reaction conditions (Table1, entries 11 and 12), whose catalytic activity is also lower than that of CuPc@MIL-101. The effect of various solvents was examined (Table1, entries 13–17), and it is found that acetonitrile is the preferred solvent. In order to determine the best oxidant, various oxidants, including air, oxygen, urea hydrogen peroxide (UHP) and TBHP, were tested (Table1, entries 18–20). TBHP is the best oxidant for this reaction. The effect of base in the reaction was also investigated (Table1, entries 21–23). $CaCO_3$ is the base that gives the best results. Control experiments (Table 1, entries 24–26) reveal that catalyst, base and oxidant are all necessary for this reaction. The optimized conditions for the oxidative amidation are 0.030 g of catalyst and 1.1 mmol of $CaCO_3$ in acetonitrile using TBHP as an oxidant at room temperature for 4 h.

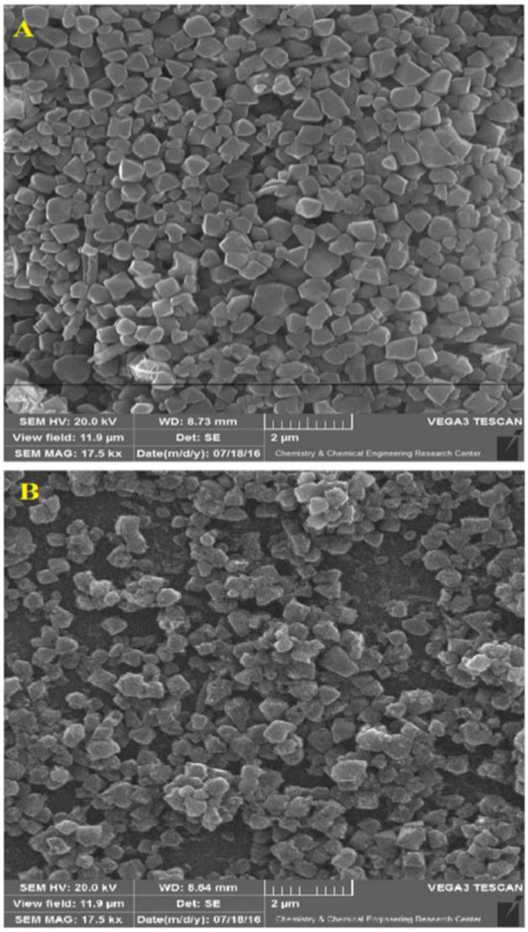


FIGURE 4 SEM images of (A) MIL-101 and (B) CuPc@MIL-101

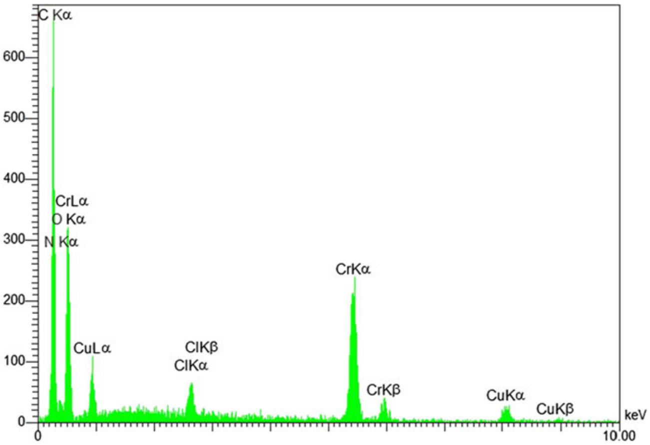
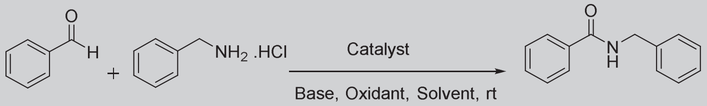


FIGURE 5 EDS analysis of CuPc@MIL-101

With the optimized reaction conditions established, a wide range of benzaldehydes was used for this reaction. Fairly good to excellent yields of amides were obtained in most cases (Table 2).

TABLE 1 Screening of reaction conditions[a]



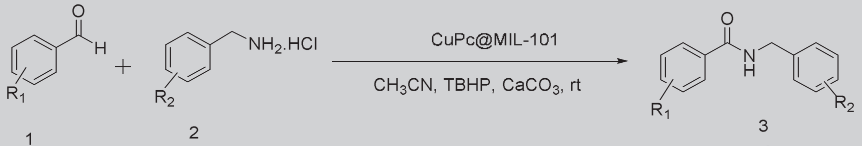
Entry	Catalyst (amount, g)	Solvent	Base	Oxidant	Time (h)	Yield (%)[b]
1	NiPc@MIL-101 (0.01)	CH_3CN	$CaCO_3$	TBHP	4	40
2	CoPc@ML-101 (0.01)	CH_3CN	$CaCO_3$	TBHP	4	45
3	CuPc@MIL-101 (0.01)	CH_3CN	$CaCO_3$	TBHP	4	55
4	MIL-101 (0.03)	CH_3CN	$CaCO_3$	TBHP	6	35[c]
5	CuPc@MIL-101 (0.015)	CH_3CN	$CaCO_3$	TBHP	4	63
6	CuPc@MIL-101 (0.020)	CH_3CN	$CaCO_3$	TBHP	4	72
7	CuPc@MIL-101 (0.025)	CH_3CN	$CaCO_3$	TBHP	4	84
8	CuPc@MIL-101 (0.030)	CH_3CN	$CaCO_3$	TBHP	4	92
9	CuPc@MIL-101 (0.035)	CH_3CN	$CaCO_3$	TBHP	4	92
10	Cu^{2+}@MIL-101	CH_3CN	$CaCO_3$	TBHP	5	80
11	CuPc-MIL-101 (0.03)	CH_3CN	$CaCO_3$	TBHP	5	40
12	CuPc (0.008)	CH_3CN	$CaCO_3$	TBHP	5	10
13	CuPc@MIL-101 (0.030)	DMF	$CaCO_3$	TBHP	7	52
14	CuPc@MIL-101 (0.030)	DMSO	$CaCO_3$	TBHP	7	45
15	CuPc@MIL-101 (0.030)	EtOH	$CaCO_3$	TBHP	7	46
16	CuPc@MIL-101 (0.030)	H_2O	$CaCO_3$	TBHP	7	35
17	CuPc@MIL-101 (0.030)	Toluene	$CaCO_3$	TBHP	7	48
18	CuPc@MIL-101 (0.030)	CH_3CN	$CaCO_3$	O_2	12	27
19	CuPc@MIL-101 (0.030)	CH_3CN	$CaCO_3$	Air	15	18
20	CuPc@MIL-101 (0.030)	CH_3CN	$CaCO_3$	UHP	15	24
21	CuPc@MIL-101 (0.030)	CH_3CN	Na_2CO_3	TBHP	8	32
22	CuPc@MIL-101 (0.030)	CH_3CN	K_2CO_3	TBHP	8	23
23	CuPc@MIL-101 (0.030)	CH_3CN	NaOH	TBHP	8	16
24	CuPc@MIL-101 (0.030)	CH_3CN	—	TBHP	15	11
25	CuPc@MIL-101 (0.030)	CH_3CN	$CaCO_3$	—	15	0
26	—	CH_3CN	$CaCO_3$	TBHP	15	8

[a] Reaction conditions: benzaldehyde (1.00 mmol, 0.068 g), amine hydrochloride salt (1.20 mmol),oxidant, solvent, base, catalyst.

[b] Isolated yield.

[c] Reaction temperature was 60 °C.

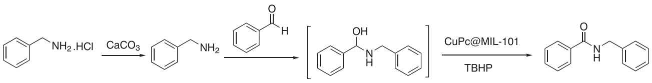
TABLE 2 CuPc@MIL-101-catalyzed oxidative amidation from aldehydes and amine hydrochloride salts[a]



Entry	R_1	R_2	Product	Time (h)	Yield (%)[b]	Melting point (°C)
1	H	H	**3a**	4	92	102–104[34]
2	OMe	H	**3b**	5	80	128–131[35]
3	Me	H	**3c**	5	85	137–139[36]
4	Cl	H	**3d**	4	83	161–163[34]
5	Br	H	**3e**	4	88	166–168[34]
6	NO_2	H	**3f**	6	84	134–137[35]
7	H	Me	**3 g**	4	90	138–140[37]
8	Me	Me	**3 h**	5	85	140–142[38]

[a] Reaction conditions: CuPc@MIL-101 (30.0 mg), aldehyde (1.00 mmol), amine hydrochloride salt (1.20 mmol), $CaCO_3$ (110 mg, 1.10 mmol) and TBHP (70% in water, 0.16 ml, 1.10 mmol), acetonitrile (2 ml), room temperature.

[b] Isolated yield.



SCHEME 2 Plausible reaction mechanism

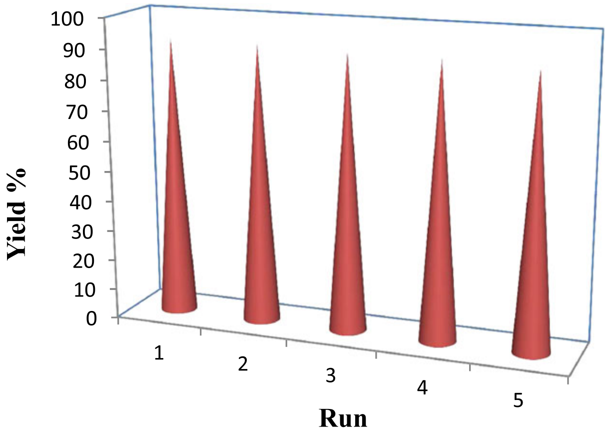


FIGURE 6 Recycling of CuPc@MIL-101 for oxidative amidation of benzaldehyde with benzylamine salt

Based on previous reports,[39] a plausible mechanism is proposed, as shown in Scheme 2. Because of the potential for oxidation of free amines in the presence of TBHP, using amine salts is necessary. Slow formation of amines using amine salts and $CaCO_3$ as the base minimizes amine oxidation under the reaction conditions. The reaction of amine and benzaldehyde produces a hemiaminal intermediate which is oxidized to amide in the presence of CuPc@MIL-101.

The stability of CuPc@MIL-101 towards the leaching Cu(II) ion was also examined. After removal of CuPc@MIL-101 by filtration, no detectable CuPc or Cu(II) ions in the reaction solution was observed. The recyclability of CuPc@MIL-101 was surveyed for oxidative amidation under the optimized conditions. After completion of the reaction, CuPc@MIL-101 was filtered, was washed and dried at 150 °C and was used in the next run. It was found that CuPc@MIL-101 could be reused for five cycles without a significant decrease in its catalytic activity (Figure 6).

4 | CONCLUSIONS

In summary, we developed a novel strategy for encapsulation of MPc into the cavities of MIL-101. This method demonstrates unique advantages such as using ionic liquid, simple synthetic method, utilizing commercially available raw materials, elimination of the use of organic solvents and short reaction time compared to approaches for preparation of MPcs on supports. CuPc@MIL-101 was efficiently employed as a new heterogeneous catalyst for oxidative amidation. The reaction was carried out at room temperature with good to excellent yields. Ongoing work in our laboratory includes using this novel strategy for simple preparation of organometallic complexes and metallorganic compounds on supports for heterogeneous catalysis investigations.

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