

Synthesis, Characterization and Catalytic Application of MCM 41 Supported Phenanthrolinium Dibromide Catalyst for Aza-Michael Addition Reaction in Aqueous Medium

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Abstract MCM-41 immobilized phenanthrolinium dibromide (phen-MCM-Br₂) was easily prepared and applied as an efficient heterogeneous catalyst for aza-Michael addition of aromatic amines to α , β -unsaturated nitriles and nitro compounds in water. The catalyst was characterized by CHN, TGA, FT-IR, SEM, EDAX, XRD, BET, and TEM. It could be simply recovered and reused several times without significant loss of catalytic activity.

Graphical Abstract



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¹ Department of Organic Chemistry, Faculty of Chemistry, University of Mazandara, Babolsar, Iran **Keywords** Supported catalyst \cdot Functionalized MCM-41 \cdot Aza-Michael addition $\cdot \alpha, \beta$ -Unsaturated nitrile and nitro compounds \cdot Aromatic amines

1 Introduction

The conjugate addition of nucleophiles to electron deficient alkenes is one of the most important reactions in organic chemistry [1]. One nucleophilic addition is the reaction of amines with α,β -unsaturated nitriles and nitro compounds to produce β-amino derivatives which are useful intermediates in the synthesis of biological active compounds [2]. The aza-Michael addition is carried out in the presence of strong acids or bases that could produce harmful residues and undesirable by-products [3-6]. Milder procedures have been developed in the past few years. Lewis acid catalysts such as InCl₃ [7], CeCl₃·7H₂O [8], Bi(NO₃) [9], LiClO₄ [10], $Cu(OTf)_2$ [11] and $FeCl_3 \cdot 6H_2O$ [12] have been employed in aza-Michael reactions. The use of stoichiometric amounts of Lewis acids in these protocols can cause serious environmental problems from the strongly acidic waste streams. These methods, however, are homogenous and suffer from drawbacks such as product contamination with catalysts and require difficult catalyst separation procedures. The development of highly efficient and recyclable heterogeneous catalysts, such as the immobilization of catalytically active species onto a solid support is essential to overcome these shortcomings [13]. Heterogeneous catalysis helps minimize the cost and wastes derived from the reaction work-up and contribute to the development of green chemical processes [14].

Heterogeneous catalysts such as clay [15], silica gel [16, 17], polystyrene [18] and montmorillonite-K10 [19], alkaline Al_2O_3 [20], Amberlyst 15 [21], nano-cage Al-

KIT5 [22], 1-methylimidazolium trifluoroacetate [23], biomaterial supported organocatalyst [24] and guanidinebased ionic liquids [25] have been reported for aza-Michael addition reactions. Their limitations include the use of hazardous organic solvents like CH₂Cl₂ [15], CH₃CN [16] and THF [24], long reaction time [20] and in some cases, aromatic amines that do not undergo a Michael addition [15, 19, 21, 22, 25].

The use of water as a green medium for organic synthesis is a current topic of research. Other than the economical and environmental benefits of using water, it can exhibit more unique reactivity and selectivity than conventional organic solvents. The development of simple reactivity and selectivity that cannot be attained in conventional organic solvents is a challenging goal for the use of aqueous media [26–28]. Aza-Michael reactions in water as reaction medium either in the presence of boronic acid [29, 30] as catalyst or without a catalyst [31] have been reported. These methods suffer from one or more disadvantages, such as a homogenous system [29], long reaction time [30], and possible restriction to aliphatic amines. Although, heterogeneous catalysts including β-cyclodextrin [32], graphene oxide [33] and ionic liquid/quaternary ammonium salt [34] have been applied for this transformation in aqueous media, but they suffer from long reaction times [32] and lack of reactivity of aromatic amines [34]. Therefore, development of a general, facile, and environmentally benign methodology for the conjugate addition of amines, especially aromatic amines, to α,β unsaturated compounds under aqueous conditions using a heterogeneous catalyst is desirable.

On the other hand, modified mesoporous materials with different active sites have been extensively investigated in the last decade [35]. MCM-41 as a mesoporous silica, exhibits a highly ordered hexagonal array of one dimensional mesopores with adjustable pore diameters, high surface area and high chemical and thermal stability [36].

In the present study MCM-41 supported phenanthrolinium dibromide (phen-MCM-Br₂) was prepared, characterized and applied as a new heterogeneous catalyst in the aza-Michael addition of aromatic amines to acrylonitrile and β -nitrostyrenes in an aqueous medium at room temperature.

2 Results and Discussion

2.1 Preparation and Characterization of the Catalyst

MCM-41 immobilized phenanthrolinium dibromide was prepared using the three-step procedure summarized in Scheme 1. 5-(*N*,*N*-bis-3-(triethoxysilyl)propyl)ureyl-1,10-



Scheme 1 Synthesis of phenanthrolinium dibromide immobilized on MCM-41 (phen-MCM-Br₂)

phenanthroline (phen-Si) was first synthesized through the reaction of 5-amino-1,10-phenanthroline with 3-(triethoxysilyl)propyl isocyanate in CHCl₃ at 80 °C for 24 h (step 1). Next, the mesoporous MCM-41 reacted with the phen-Si in toluene at reflux temperature for 24 h (step 2). The latter was subsequently treated with 1,2-dibromoethane in acetonitrile under reflux conditions for 24 h to generate the MCM-41 immobilized phenanthrolinium dibromide (phen-MCM-Br₂) as a brown powder (step 3).

Figure 1 shows the TGA analysis of MCM-41 (Fig. 1a) and phen-MCM-Br₂ (Fig. 1b). For MCM-41, the weight loss below 150 °C is not significant, while for phen-MCM-Br₂, the weight loss at 100–200 °C is ~5.0 % which could be due to the desorption of physisorbed water on the surface of the catalyst. The weight loss (30 %, 0.54 mmol g⁻¹) at 200–600 °C can be attributed to the



Fig. 1 TGA patterns of MCM-41 (a) and phen-MCM-Br₂ (b)

decomposition of phenanthrolinium bromide immobilized on the MCM-41.

Elemental analysis of phen-MCM-Br₂ showed the contents of C, H and N to be 17.84, 2.53 and 3.92, respectively. The content ratio of N/C (0.22) is close to the calculated value (0.26). Based on the percentage of nitrogen, the loading of phen-Br₂ on the MCM-41 was found to be 0.56 mmol g^{-1} which is in good agreement with the value obtained from TGA analysis (Fig. 1).

FT-IR was employed for detailed investigation of the phen-Si, phen-MCM-41, phen-MCM- Br_2 and MCM-41 (Fig. 2) to confirm the successful functionalization of MCM-41.

As seen in Fig. 2a, there is a sharp band located at 1704 cm^{-1} that can be ascribed to the vibration of the carbonyl group. The bands located at 1652 and 1537 cm⁻¹ originate from the amide groups. The v(C-Si) vibration is located at 1194 cm⁻¹. The FT-IR spectra of the phen-MCM-41 Fig. 2b and phen-MCM-Br₂ Fig. 2c showed a broad band at about 1088 cm⁻¹ related to the formation of the Si–O–Si framework Fig. 2e. The vibration frequencies located at 1702, 1650, 1546, 1653 and 1545 cm⁻¹, originating from phen-Si groups, can also be observed in the phen-MCM-41 and phen-MCM-Br₂, which indicates that no disintegration or loss of phen-Si occurred during the reaction procedure.



Fig. 2 FT-IR spectra of phen-Si (a), phen-MCM-41 (b), fresh phen-MCM-Br₂ (c), phen-MCM-Br₂ after six runs (d) and MCM-41(e)

Figure 3 shows the low angle XRD patterns of the MCM-41 and phen-MCM-Br₂. The XRD pattern of the phen-MCM-Br₂ shows a strong peak at 2 θ of $<3^{\circ}$ along with some small peaks that are similar to the XRD pattern of the mesoporous MCM-41 and confirm the presence of MCM-41 in the catalyst [37]. The reduction in the intensity of the peak at 2 θ $<3^{\circ}$ after immobilization of organic moiety on MCM-41 for catalyst is clear in Fig. 3. The slight shift of this peak for the catalyst could be due to the accommodation of the phen-Br₂ inside MCM-41 channels which is in agreement with the previous reports [38–40].

Figure 4 shows the energy dispersive spectroscopy analysis of X-rays (EDAX) data for the phen-MCM- Br_2 catalyst. The EDAX data also confirm the bromine on the surface of the MCM-41.

Figure 5 shows the N₂ adsorption–desorption isotherms and BJH pore size distribution of the MCM-41 and phen-MCM-Br₂. The nitrogen adsorption–desorption isotherms of the samples were obtained at 77 K and the specific surface area was determined by applying the BET equation to the isotherm [41]. The pore size distribution was calculated using the desorption branch of the isotherm and the Barrett–Joyner–Halenda (BJH) formula [42]. The nitrogen adsorption–desorption isotherms of the MCM-41 and phen-MCM-Br₂ shows the typical profile of type IV, which consists of step condensation behavior caused by the formation of mesopores in the MCM-41 and the presence of mesoporous MCM-41 in the phen-MCM-Br₂ [37].

Table 1 shows the specific surface area, pore volume, and pore size of the MCM-41 and phen-MCM-Br₂ samples. The BET surface area of the phen-MCM-Br₂ sample was 76.14 m² g⁻¹, which is less than the surface area of the MCM-41 (771.43 m² g⁻¹). This may be a result of blocking of some pores of mesoporous MCM-41 (especially micropores) by the entry of phenanthrolinium dibromide.

Figure 6 shows the SEM image of mesoporous phen-MCM- Br_2 taken using a 2 min gold coat for high magnification. The average size of the mesoporous phen-MCM-



Fig. 3 XRD patterns of the MCM-41 and phen-MCM-Br₂



Fig. 4 EDAX pattern of phen-MCM-Br₂





Fig. 6 SEM images of pure MCM-41 (a) phen-MCM-Br $_2$ (b) and used catalyst (c)



Fig. 7 TEM images of fresh phen-MCM-Br₂ (**a**, **b**) and used catalyst (**c**)

Fig. 5 Nitrogen adsorption–desorption isotherms (a) and pore size distribution curves (b) of the MCM-41 and phen-MCM-Br $_2$

Table 1 Physical properties ofthe MCM-41 and phen-MCM-	Sample	BET surface area $(m^2 g^{-1})$	BJH pore diameter (nm)	Total pore volume (cm ³ g ^{-1})
Br ₂	MCM-41	771.43	2.34	0.46
	Phen-MCM-Br ₂	76.14	3.58	0.16

 Br_2 is less than 50 nm (Fig. 6b) in which free particles have placed beside agglomerated particles. Irregular agglomeration of the particles was unavoidable [43].

TEM image of fresh catalyst is shown in Fig. 7a, b. As can be seen, the TEM micrographs clearly reveal the

presence of ordered array of mesopores with uniform pore size which is also confirmed by XRD in Fig. 3. The pore size of phen-MCM-Br₂ is \sim 3.5 nm which is in good agreement with N₂ adsorption-desorption data (Fig. 5).

2.2 Catalytic Activity of the Catalyst in Aza-Michael Addition

To optimize the conditions for the aza-Michael reaction. the reaction of aniline with acrylonitrile was chosen as a model reaction and various solvents and catalyst loading were investigated in detail and the results are summarized in Table 2. Among the solvents examined: H₂O, EtOH, CH₂Cl₂, THF and CH₃CN (entries 1-5), water was the most effective for this reaction (entry 1). The model reaction under solvent-free condition did not proceed well and only a trace amount of product was obtained (entry 6). This is because the reaction mixture became a mass which was very difficult to stir magnetically. To examine the effect of catalyst, the model reaction was carried out in CH₂Cl₂ and H₂O without catalyst at room temperature for 2.5 h (entries 7-8). It was found that only 30 % of the desired product was obtained in water while the reaction did not proceed in CH₂Cl₂. This is probably due to hydrogen bonding ability of water with substrates [31]. Using MCM-41 as catalyst led to 42 % yield (entry 9). In order to explore the role of phenanthrolinium dibromide salt (phen-Br₂) in this reaction, the model reaction was carried out in the presence of phen-Br₂ as a homogeneous catalyst in water. Although the yield of this reaction was comparable with phen-MCM-Br₂ (entry 10), but separation from the reaction mixture is difficult. As the main goal of

Table 2 Reaction condition screening for the aza-Michael addition of aniline with acrylonitrile

Entry	Catalyst amount (g)	Solvent	Yield ^a (%)
1	0.070	H ₂ O	80
2	0.070	EtOH	48
3	0.070	CH_2Cl_2	46
4	0.070	THF	35
5	0.070	CH ₃ CN	32
6	0.070	_	Trace
7	0	H_2O	30
8	0	CH_2Cl_2	Trace
9 ^b	0.070	H_2O	42
10 ^c	0.020	H_2O	78
11	0.017	H_2O	58
12	0.035	H_2O	62
13	0.053	H_2O	75
14	0.089	H_2O	80

Reaction condition: aniline (1 mmol), acrylonitrile (1.2 mmol) and solvent (2 mL), r.t., 2.5 h $\,$

^a Isolated yield

^b In the presence of MCM-41 as catalyst

 $^{\rm c}$ In the presence of phenanthrolinium dibromide salt (phen-Br_2) as catalyst

the present work is to develop more suitable recyclable catalyst, phenanthrolinium dibromide supported on MCM-41 is selected as heterogeneous catalyst for the aza-Michael reaction. Screening different amounts of the catalyst in the model reaction (entries 1 and 11–13) showed that 0.070 g (4.0 mol %) of the catalyst was enough to perform good yield of the product (entry 1). Increasing the amount of the catalyst up to 0.089 g did not improve the reaction yield any further (entry 14).

In order to examine the scope and limitations of the protocol a variety of amines reacted with acrylonitrile under the optimized reaction conditions and the results are tabulated in Table 3. Electron-donating and electronwithdrawing substituted anilines reacted smoothly with acrylonitrile to give good yields of the corresponding products (entries 2-7). However, electron-donating substituted anilines such as p-anisidine, p-toluidine and *p*-hydroxyaniline reacted faster and afforded higher yields of the expected products (entries 4-6). While electronwithdrawing substituted aniline, 4-nitroaniline, gave a low yield (entry 8). Due to importance of the substituted diamines for the preparation of hybrid materials [44, 45], the aza-Michael addition reaction was applied to o-phenylenediamine and the mono-addition product was collected in high yield (entry 9). α-Naphthylamine as a nucleophile also gave a good yield of 3-(naphthalen-2-ylamino)propanenitrile (entry 10). As expected, reaction of aliphatic amines (entries 11 and 12) with acrylonitrile under reaction conditions afforded corresponding products in excellent yields.

The promising results described above, prompted us to extend further the scope of this reaction to the synthesis of β -nitroamines by the direct addition of amines to β-nitrostyrenes. β-Nitroamines are important intermediates for the synthesis of many organic compounds [46, 47]. When anilines were reacted with β -nitrostyrene instead of acrylonitrile under the same reaction conditions, in the presence of 0.070 g (4 mol %) catalyst at room temperature, interestingly, N-(2-nitro-1-phenylethyl) benzamine was formed in 80 % yield in 2 h (entry 13). To examine the generality of the procedure, various amines reacted with substituted *β*-nitrostyrene under the same reaction conditions. The desired β -nitroamines were obtained in high yields (entries 14-24). It was found that the nature of the substitution on the aromatic nucleus of the nitro-olefins and anilines had a strong influence on the reaction yields. For example, when *p*-anisidine reacted with *p*-cyano- β -nitrostyrene, an excellent yield of the product was obtained after only one hour (entry 22). In addition, morpholine as a secondary amine reacted smoothly with β -nitrostyrene and resulted in desired product in 95 % yield after 30 min (entry 24).

Mechanistically, from the rate acceleration of the aza-Michael addition by phenanthrolinium dibromide (Table 2, entry 10) and MCM-41 immobilized phenanthrolinium

			D2 NH2	CN .	HNCN	
	R ₂ 2a-1	4.0 mol % Phen-MGM-E water, r.t.	R ₁ 4.0 mo	l% Phen-MCM-Br ₂ water, r.t.	R ₁ 1a-l	
Entry	Amines	Michael acceptor	Product	Time (h)	Yield ^b (%)	TON ^c /TOF ^d
1	NH ₂	CN	1a	2.5	80	20/0.13
2	OCH3	CN	1b	1.5	84	21/0.23
3	OCH ₃	CN	lc	1	85	21/0.35
4	H ₃ CO NH ₂	CN	1d	1	95	24/0.40
5	H ₃ C	CN	1e	1	92	23/0.38
6	HO	CN	lf	1	96	24/0.40
7	CI NH2	CN	1g	3	75	19/0.10
8	O ₂ N NH ₂	CN	lh	3	Trace	-
9	NH ₂ NH ₂	CN	li	1.5	82	21/0.23
10		CN	lj	2	80	20/0.17
11	NH ₂	CN	1k	0.5	95	23/0.80
12	N H	CN	11	0.5	96	24/0.80
13	NH ₂	NO ₂	2a	2	80	20/0.17
14	OCH3	NO ₂	2b	2	85	21/0.18
15		NO ₂	2c	1.5	90	23/0.25

Table 3 continued

	R ₁ NH NO ₂ R ₂ 2a-l	4.0 mol% Phen-MCM-Br ₂ water, r.t. R ₁	4.0 mol% Phen- water, r	$\xrightarrow{\text{MCM-Br}_2} \overset{\text{HN}}{\underset{t}{\overset{\text{HN}}{\underset{t}{\overset{\text{HN}}{\underset{t}{\overset{\text{HN}}{\underset{t}{\overset{\text{HN}}{\underset{t}{\overset{\text{HN}}{\underset{t}{\underset{t}{\overset{\text{HN}}{\underset{t}{\underset{t}{\underset{t}{\underset{t}{\underset{t}{\underset{t}{\underset{t}{\underset$	CN la-l	
Entry	Amines	Michael acceptor	Product	Time (h)	Yield ^b (%)	TON ^c /TOF ^d
16	H ₃ CO	NO ₂	2d	1.5	93	23/0.26
17	H ₃ C	NO ₂	2e	1.5	90	10/0.11
18	CI NH2	NO ₂	2f	3	72	18/0.10
19	O ₂ N NH ₂	NO ₂	2g	3	Trace	-
20	NH ₂	Br NO ₂	2h	1.5	94	23/0.26
21	NH ₂	NO ₂	2i	1.5	98	24/0.27
22	H ₃ CO	NC NO2	2j	1	98	24/0.41
23	H ₃ CO	H ₃ C	2k	2	82	20/0.17
24 ^e	O N H	NO ₂	21	0.5	95	24/0.79

^a Reaction condition: aromatic amines (1 mmol), α , β -unsaturated nitriles and nitro (1.2 mmol), phen-MCM-Br₂ catalyst (0.07 g, 4 mol %) and water (3 mL) at room temperature

^b Isolated yield

^c TON: turn over number (mol of product/mol of catalyst)

^d TOF: turn over frequency [mol of product/(mol of catalyst \times reaction time)]

e Reaction was carried out with 1 mmol β-nitrostyrene and 1.3 mmol morpholine

dibromide (Table 2, entry 1), it can be postulated that the source of the bromide ion, increases the nucleophilicity of the nitrogen atom of the amine [48, 49]. Additionally, it is well established that MCM-41 [50] and urea or thiourea groups [51–53] can activate the electrophiles such as nitroolefins through hydrogen bondings. Activation of amines by bromide ions and β -nitrostyrene by both silanol groups of the MCM-41 and urea groups via hydrogen bonding is depicted in Scheme 2.

The major advantage of a heterogeneous catalyst is the possibility of recovering and reusing it during the reaction. The recovery of phen-MCM- Br_2 was investigated in the reaction of aniline with acrylonitrile for six consecutive cycles. After completion of the reaction, the catalyst was



Fig. 8 Aza-Michael addition of aniline to acrylonitrile by recycled catalyst under optimized condition



Scheme 2 Proposed mechanism for phen-MCM-Br₂ catalyzed aza-Michael addition

separated by simple filtration and washed several times with water, ethanol and diethyl ether and then dried under vacuum for direct reuse in the next run. The results summarized in Fig. 8 demonstrate that there was almost no change in catalytic activity even after the sixth run. The structure of the recovered phen-MCM-Br₂ after six runs did not change significantly as confirmed by comparing the IR spectra (Fig. 2c, d) and SEM (Fig. 6b, c) of the fresh catalyst with those of the recovered ones. Furthermore, comparison of TEM images of the fresh and used catalyst shows that catalyst pores have not been destroyed (Fig. 7ac).

In order to show the advantages and limitations of the present method, we have compared the preparation of 3-(phenylamino) propanenitrile using phen-MCM-Br₂ with some of those reported in the literature using other heterogeneous catalysts in Table 4. As it is clear in this table, in terms of reaction times and yields, phen-MCM-Br₂ showed better activity.

3 Conclusions

In summary, MCM-41 supported phenanthrolinium dibromide was prepared and applied as efficient catalyst for the aza-Michael addition of aromatic amines to α,β-unsaturated nitriles and nitro compounds in water under mild conditions. The stability of the catalyst under reaction conditions allowed the catalyst to be recovered by simple filtration and reused for at least 6 cycles without loss of activity, thus making this procedure environmentally more acceptable.

4 Experimental Section

1,10-Phenanthroline monohydrate, fuming sulfuric acid, 10 % Pd/C catalyst and 3-(triethoxysilyl)propyl isocyanate were purchased from Merck. Other commercially available chemicals were laboratory grade reagents obtained from local suppliers. All chemicals were used as received.

Melting points were measured on an Electrothermal 9100 apparatus. ¹H and ¹³C NMR spectra were recorded in CDCl₃ on a Brukeravance III 400 MHz spectrometer. C, H

Entry	Catalyst	Solvent/temperature/time	Yield (%)
1	Phen-MCM-Br ₂	H ₂ O/r.t./2.5 h	$80^{\rm a}$
2	SiO ₂ /AlCl ₃ [17]	Solvent free/60 °C/6 h	75
3	Ps/AlCl ₃ [18]	Solvent free/70 °C/2.4 h	94
4	K10/ZrOCl ₂ ·8H ₂ O [19]	Solvent free/r.t./2 h	32
5	[Hmim]TFA [23]	Solvent free/80 °C/4 h	56
6	ES-SO ₃ ⁻ C ₅ H ₅ NH ⁺ [24]	THF/r.t./3 h	65
7	[TMG][Lac] [25]	Solvent free/r.t./24 h	0
8	β-CD [32]	H ₂ O/r.t./8 h	88
9	Graphene oxide [33]	H ₂ O/r.t./0.75 h	65
10	SiO ₂ [54]	Solvent free/60 °C/144 h	78
	Entry 1 2 3 4 5 6 7 8 9 10	Entry Catalyst 1 Phen-MCM-Br2 2 SiO2/AlCl3 [17] 3 Ps/AlCl3 [18] 4 K10/ZrOCl2·8H2O [19] 5 [Hmim]TFA [23] 6 ES-SO3 ⁻ C3H3NH ⁺ [24] 7 [TMG][Lac] [25] 8 β -CD [32] 9 Graphene oxide [33] 10 SiO2 [54]	Entry Catalyst Solvent/temperature/time 1 Phen-MCM-Br2 $H_2O/r.t./2.5 h$ 2 SiO2/AlCl3 [17] Solvent free/60 °C/6 h 3 Ps/AlCl3 [18] Solvent free/70 °C/2.4 h 4 K10/ZrOCl2·8H2O [19] Solvent free/rt./2 h 5 [Hmim]TFA [23] Solvent free/80 °C/4 h 6 ES-SO3 ⁻ C3H3NH ⁺ [24] THF/r.t./3 h 7 [TMG][Lac] [25] Solvent free/rt./24 h 8 β -CD [32] H ₂ O/r.t./0.75 h 9 Graphene oxide [33] H ₂ O/r.t./0.75 h 10 SiO ₂ [54] Solvent free/60 °C/144 h

^a This work

and N analyses were performed with a Vario EL III elemental. Thermo gravimetric analysis (TGA) was performed using a Rheometric Scientific model STA-1500 analyzer. Fourier transform infrared spectroscopy (FT-IR) spectra were recorded using a Bruker vector 22 spectrometer using KBr pellets. Small-angle X-ray diffraction (XRD) patterns were recorded in the 2θ range of 0.8–10 using a X'Pert Pro MPDX-ray diffractometer using CuKa radiation. Nitrogen (N₂) adsorption/desorption isotherms were measured using a NOVA 2200e analyzer. The samples were out-gassed for 14 h at 60 °C under vacuum before measurement. Energy Dispersive X ray (EDAX) pattern was performed using a Rontec analyzer. Scanning electron microscopy (SEM) was performed using a KYKY-EM3200 analyzer. Transmission electron microscopy (TEM) experiments were conducted on a Philips EM 208 electron microscope.

4.1 General Procedure

4.1.1 Synthesis of Mesoporous MCM-41

MCM-41 was prepared according to reported procedure [55]. Typically, 0.6 g of CTAB was dissolved in 23 g of demineralized water and stirred for 15 min at a rate of 140 rpm. Then 3 g of sodium silicate was added and stirred for 30 min. The pH of the mixture was adjusted to 9 by gradual addition of 2 mol L^{-1} of sulfuric acid. After stirring the resulting solution for 4 h, the resulting gel was filtered, washed thoroughly with demineralized water, dried at 40 °C for 24 h and calcined at 540 °C for 6 h.

4.1.2 Synthesis of 5-(N,N-Bis-3-(triethoxysilyl) propyl) ureyl-1,10-phenanthroline (Phen-Si)

The starting reagent 5-amino-1,10-phenanthroline (phen-NH₂) and the modified phen group (phen-Si) were prepared according to the procedure described previously [56]. ¹H NMR (400 Hz, CDCl₃): δ 0.50–0.60 (m, 4H), 1.15 (t, 18H, J = 6.8 Hz), 1.56–1.63 (m, 4H), 3.21–3.26 (m, 4H), 3.71 (q, 12H, J = 6.8 Hz), 7.17 (bs, 2H), 7.69–7.72 (m, 2H), 7.89 (s, 1H), 8.24–8.29 (m, 2H), 9.24–9.28 (m, 2H).

4.1.3 Modification of MCM-41 with phen-Si (phen-MCM-41)

0.500 g of MCM-41 was slurried in about 80 mL of anhydrous toluene. Phen-Si (0.5 mmol; 0.344 g) was dissolved in 8 mL of anhydrous CHCl₃ and added to the previous mixture. The reaction mixture was stirred for 24 h under argon at reflux temperature. The reaction mixture was filtered and the collected solid was washed several times with toluene and dried overnight under vacuum. IR (KBr, cm⁻¹): C=O (1702 cm^{-1}) , -CONH- (1650, 1546 cm⁻¹), Si-O-Si (1088 cm⁻¹).

4.1.4 Synthesis of Phenanthrolinium Dibromide Immobilized on MCM-41(phen-MCM-Br₂)

To 5 g of phen-MCM-41 was added 15 g 1,2-dibromoethane in 30 mL anhydrous acetonitrile; the mixture was stirred at 80 °C for 24 h. The resulting brown solid was collected by filtration and washed with acetonitrile. This material was then transferred to a soxhlet tube in argon. The excess 1,2-dibromoethane was removed by soxhlet extraction with acetonitrile for 24 h. The resulting solid was denoted as phen-MCM-Br₂. The loading of phenanthrolinium dibromide on MCM-41 was quantified by CHN and found to be 0.56 mmol g⁻¹ based on nitrogen content determination. IR (KBr, cm⁻¹): C=O (1702 cm⁻¹), -CONH- (1653, 1545 cm⁻¹), Si-O-Si (1088 cm⁻¹).

4.1.5 General Procedure for the Aza-Michael Addition of Aromatic Amines to α,β-Unsaturated Nitriles and Nitro Compounds

Phen-MCM-Br₂ catalyst (0.070 g, 4.0 mol %) was added to a flask containing of aromatic amines (1 mmol) and acrylonitrile or nitro-olefin (1.2 mmol) in water (3 mL) and the mixture was stirred at room temperature until completion of the reaction as monitored by TLC. Ethyl acetate was then added and the mixture was stirred for 15 min to ensure product removal from the catalyst. The catalyst was filtered off, washed with water and the product was separated by extraction with ethyl acetate. The organic layer was evaporated under vacuum in a rotary evaporator to obtain the crude product. Further purification was achieved by column chromatography using an ethyl acetate/n-hexane gradient. Structural assignments of the products were based on their ¹H and ¹³C NMR data and their melting points.

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