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Direct synthesis and application of bridged diamino-functionalized periodic mesoporous organosilicas with high nitrogen contents



Feng-Xia Zhu, Pu-Su Zhao*, Xiao-Jun Sun, Li-Tao An, Yong Deng, Jia-Min Wu

Jiangsu Key Laboratory for Chemistry of Low-Dimensional Materials, Huaiyin Normal University, Huaian, Jiangsu 223300, PR China

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ABSTRACT

Keywords: Diamino-bridged PMO Solid base-catalyst Water-medium and solvent-free organic reactions Green chemistry Bridged diamino-functionalized periodic mesoporous organosilicas [BD-PMO(Et), Et = ethyl] materials were synthesized directly by co-condensation of 2-bis (triethoxysilyl)ethane (BTEE) and 1,4-bis[3-(tirmethoxysilyl)-propyl]ethylenediamino (BTMSEN) under acidic conditions with pluronic triblock copolymer P123 as a template. The nitrogen content in BD-PMO(Et) could be adjusted up to 40% without disturbing the ordered mesoporous structure. These materials were proved to be effective heterogeneous catalysts for the liquid-phase reactions such as Knoevenagel and Henry condensations as well as in the intermolecular cross-double-Michael addition reaction between α -methyl- β -nitrostyrene and α , β -unsaturated ketone. They exhibited comparable catalytic activities with homogeneous catalyst piperazine and can be reused for several times without any negative environmental impact.

1. Introduction

Since the discovery of the MCM family of mesoporous molecular sieves by Mobil scientists, a variety of porous materials such as meosoporous metal oxides [1], meosoporous silicas [2], meosoporous carbon [3] and metal oganic framwork [4-6] have been synthesized using different templating approaches and reactions. Recent developments in this field have expanded this class of materials to periodic mesoporous organosilicas (PMO). To date, most surface functionalized PMO consisting of functional groups, such as amines, thiols, and cyanogen groups, have been used for the adsorption of heavy metal ions [7,8], catalysis [9,10] and immobilization of catalyst [11,12]. Of the various groups functionalized PMO [13-17], the amine group has been most used. The versatile applications provided by the amine have included base-catalyzed reactions (e.g., aldol, Knovenagel, Henry couplings) and reagents/ligands (e.g., functional group immobilization, adsorption of heavy metal ions and the synthesis of nanoparticles). Most of the amine functionalized PMO have been prepared by post grafting methods. These methods attached pendant organic groups, which could decrease access to the amine functional group due to the channel blockage [18]. Encircling this problem, the co-condensation method has been developed to prepare PMO with highly accessible functional groups. This method has additional advantages for preparing PMO with uniformly dispersed functional groups throughout the framework. Most importantly, the functional groups at the surface of the walls do not aggregate and therefore do not block the channel. In contrast to

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traditional inorganic silica, these PMO with their skeletal organic groups can present enhanced surface hydrophobicity and thus benefit to organic molecules diffusion and adsorption in aqueous medium [19]. Although a few groups attempt to introduce amine functionality in the PMO framework under basic conditions, these methods have limited success. For example, Hossain and Mercier reported the synthesis of an ethylenediamino-PMO by a base promoted co-condensation method. Unfortunately, they obtained poorly ordered mesostructural material with limited amine content (up to 5%) [20]. Herein, we describe the synthesis of a bridged diamino-functionalized PMO (BD-PMO(Et)) with an ordered mesoporous structure and variable nitrogen loadings were prepared under acid conditions. The nitrogen content can be adjusted up to 40% without disruption of the ordered mesoporous structure. This heterogeneous amine catalyst, BD-PMO(Et), displayed matchable catalytic efficiency with homogeneous catalyst in water-medium Knovevenagel, solvent-free Henry, and Michael addition reactions. In addition, this catalyst could be used repetitively (up to 6 times) without significantly deactivation, which ultimately reduces cost and waste.

2. Experimental section

2.1. Synthesis of the bridged diamino-functionalized PMO (BD-PMO(Et))

A typical synthesis procedure of bridged diamino-functionalized PMO is described as follows:

^{*} Corresponding author. E-mail address: zhaopusu@163.com (P.-S. Zhao).

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A mixture of P123 (1.0 g) and KCl (3.0 g) was dissolved in aqueous 0.50 mol/L HCl (31 mL) under vigorous stirring to get a clear solution, which was stirred at 40 °C for 4 h. Then, 5(1-x) mmol of 1, 2-bis(triethoxysilyl)ethane (BTEE) was added and stirred for 2 h at 40 °C. Finally, 5x mmol of 1,4-bis[3-(trimethoxysilyl)-propyl]ethylenediamine (BTMSEN) was added and the reaction mixture was stirred for 24 h at 40 °C, where x is the molar ratio of BTMSEN in the initial silane mixture, defined by (BTMSEN/(BTMSEN + BTEE)). The molar ratio of the different components of the mixture is 1 Si: 0.017 P123: 4.5 KCl: 1.6 HCl: 171 H₂O, where Si referred to the total silicon source. The resulting mixture was kept static at 100 °C for another 24 h. The white solid product was recovered by filtration and dried at 80 °C in vacuum. The block co-polymer P123 was removed by refluxing the sample in an acidic ethanol solution for 24 h. For 1.0 g of sample, 500 mL of ethanol and 40 mL of concentrated HCl (37 wt%) were used.

Deprotonation of the bridged-diamino groups was performed by stirring the extracted samples in saturated Na_2CO_3 aqueous solution (0.10 g of sample/10 mL of Na_2CO_3 solution) for 24 h at 25 °C. Thus treated samples were thoroughly washed with deionized water until the pH value of the filtrate is neutral. The deprotonated samples were denoted as BD-PMO(Et)-x.

For comparison, the BD-PMO(Et) was also prepared by traditional grafting method and denoted as BD-PMO(Et)-G, where G refers to grafting method. Briefly, A mixture of P123 (1.0 g) and KCl (3.0 g) was dissolved in aqueous 0.50 mol/L HCl (31 mL) under vigorous stirring to get a clear solution, which was stirred at 40 °C for 4 h. Then, BTEE (5.0 mmol) was added at 40 °C. After being stirred for 24 h at 40 °C, The resulting mixture was kept static at 100 °C for another 24 h. The white solid product was recovered by filtration and dried at 80 °C in vacuum. P123 was removed by refluxing the sample in an acidic ethanol solution for 24 h. The as-received PMO(Et) was added into 10 mL of dry toluene solution containing 0.50 mmol of BTMSEN, After stirring for 24 h at room temperature, the solid was centrifuged and dried at 40 °C under a vacuum condition, followed by Soxhlet-extraction with dichloromethane for another 24 h to remove physisorbed nitrogen species on the support. The nitrogen loading was determined as 0.039 mmol/g by elemental analysis.

For comparison, the ordered mesoporous silica catalyst containing $-CH_2-CH_2-N-CH_2-CH_2-N-CH_2-CH_2$ fragments incorporated into SBA-15 framework, denoted as BD-SBA-15, was synthesized by using cocondensation of tetraethylorthosilicate (TEOS) and BTMSEN. First, 2.0 mL of TEOS was introduced into 38 mL of aqueous solution containing 30 mL of 2.0 mol/L HCl and 1.0 g of P123. After prehydrolysis of TEOS at 40 °C for 80 min, a desirable amount of BESPDS was added dropwise into the solution, followed by rapid stirring for 20 h. After being aged at 100 °C for 24 h, the white precipitate was filtrated and then dried at vacuum overnight. Finally, the surfactants and other organic substances were extracted, and washed away according to the above methods. Deprotonation of the bridged-diamino groups was the same as the above method used.

2.2. Characterization

The nitrogen contents in the BD-PMO(Et)-x samples were analyzed on a CHN analyzer (Elementar Vario ELIII, Germany). All the samples were combusted completely at 1000 °C in pure oxygen. Fine structure of the samples was analyzed by Fourier transform infrared (FT-IR) spectra collected on a Nicolet Magna 550 spectrometer by using the KBr method. Chemical environment was probed by solid-state NMR spectra recorded on a Bruker AV-400 spectrometer. Thermogravimetric analysis and differential thermal analysis (TG/DTA) were conducted on a DT-60 to examine the thermal stability. The mesoporous structure was examined by low-angle Xray powder diffraction (XRD, Rigaku D/Max-RB, CuK α radiation) and transmission electron microscopy (TEM, JEOL JEM2010, 200 kV). N₂ adsorption-desorption isotherms were measured at -196 °C using a Quantachrome Nova 4000e analyzer. Specific surface area ($S_{\rm BET}$), pore size $(D_{\rm P})$ and pore volume $(V_{\rm P})$ were calculated based on the BET method and the BJH method, respectively. The surface electronic states were analyzed by X-ray photoelectron spectroscopy (XPS, Perkin-Elmer PHI 5000 C). All the binding energy (BE) values were calibrated by using the standard BE value of contaminant carbon ($C_{\rm 1S} = 284.6$ eV) as a reference.

2.3. Activity test

The Knovevenagel condensation reaction between aldehyde and ethyl cyanoacetate (Reaction 1), Henry reaction between aldehyde and nitromethane (Reaction 2), and the intermolecular cross-double-Michael addition reaction between α -methyl- β -nitrostyrene and α . β unsaturated ketone (**Reaction 3**) were used as probes to evaluate the basic catalytic performances of BD-PMO(Et). The Reaction 1 was carried out at 40 °C in a 10 mL round-bottomed flask containing a catalyst with 0.016 mmol nitrogen, 1.0 mmol ethyl cyanoacetate, 1.2 mmol aldehyde, 4.0 mL distilled water and n-decane as an internal standard. After stirring for 4 h, the products were extracted by ethyl acetate, followed by analysis on a GC-17A gas chromatograph (SHIMADZU) equipped with a JWDB-5, 95% dimethyl-1-(5%)-diphenylpolysiloxane column and a flame ionization detector (FID). The column temperature was programmed from 80 °C to 250 °C at a speed of 10 °C/min. N2 was used as carrier gas. The conversions and yields determined on the GC were calibrated by using commercially available samples. Besides the target product, no side products were detected in Reaction 1. The Reaction 2 was carried out at 90 °C by stirring a mixture containing a catalyst with 0.024 mmol nitrogen, 1.0 mmol aldehyde, 4.0 mL nitromethane and n-decane as an internal standard. After reaction for 5 h, product analysis was performed on the GC under the above identical conditions. The Reaction 3 was carried out at 40 °C in a 10 mL flask containing 0.50 mmol α-methyl-β-nitrostyrene, 1.0 mmol α,β -unsaturated ketone, 0.50 mmol DMAP and 2.0 mL dimethyl sulphoxide (DMSO), and a catalyst with 0.0080 mmol nitrogen. After vigorous stirring for 16 h, the catalyst was removed by centrifugation and washed with CH₂Cl₂ for several times. The organic layer was diluted with CH₂Cl₂. Then the organic phase was washed with water and brine. The combined organic layer was dried over anhydrous magnesium sulfate. The solvent was removed under reduced pressure and the remains were diluted with 10 mL tetrahydrofuran (THF). The liquid products were quantitatively analyzed on a high pressure liquid chromatograph (HPLC, Waters) equipped with an AD-H column *i*-propanol/hexane = 5/95, flow rate = 1.0 mL/min, λ = 254 nm, from which the conversion, selectivity and yield to target product were determined by using normalization. The conversion was calculated based on α -methyl- β -nitrostyrene since α , β -unsaturated ketone was greatly excessive. The reproducibility was checked by repeating each result at least three times and found to be within acceptable limits ($\pm 5\%$).

In order to determine the catalysts durability, the catalysts were centrifuged after each reaction and the clear supernatant liquid was decanted slowly. The catalyst was washed thoroughly with distilled water and ethanol, followed by drying at 80 °C for 8 h under vacuum condition. The recovered catalyst was reused with fresh reactants under nearly identical reaction conditions.

3. Results and discussion

3.1. Structural characteristics

The FT-IR spectra of the solvent-extracted BD-PMO-20(Et) (Fig. 1) revealed that the surfactant was mostly removed by extracting the solid in acidic ethanol since no significant signal characteristic of the P123 molecule was found. The FT-IR spectra also revealed that some organic moieties remained, as indicated by the presence of absorbances at 1422, 1267, 1167, 783 and 694 cm⁻¹. Sharp peaks at 1000–1100 cm⁻¹ confirmed the formation of siloxane bonds [21–24]. Furthermore, the



Fig. 1. The IR spectrum of the BD-PMO(Et)-20.

FT-IR spectra strongly supports the presence of absorption bands at 1643 and 3400 cm⁻¹, which were attributed to N-H bonds [25,26], while the relatively broad peaks at 783 and 1167 cm⁻¹ indicated the presence of an N–H wagging vibration and the antisymmetrical stretch of a C-N-C moiety, respectively. A peak belonging to a secondary amine was also clearly visible at 694 cm⁻¹ in each spectrum [22–26]. These FT-IR spectra confirmed that the organic moieties were linked covalently to the silica framework in the final hybrid materials BD-PMO-20(Et).

Solid-state NMR measurements were conducted on the BD-PMO(Et)-20 sample. Fig. S1 shows the ¹³C CP MAS NMR and ²⁹Si CP MAS NMR spectra of BD-PMO(Et)-20. In the ¹³C NMR spectrum, the strong signal at 5.0 ppm can be ascribed to the bridging ethyl group [27-29]. The signals at 10, 22, 43, 39, and 51 ppm were attributed to the ¹C, ²C, ³C, ⁴C and ⁵C carbons in \equiv Si¹CH₂²CH₂³CH₂-NH⁴CH₂⁵CH₂NH³CH₂²CH₂¹CH₂Si=, respectively [27,30]. The signals at 58.7 ppm could be ascribed to the ethoxy groups (only one of the two ethyl carbons) generated during the ethanol extraction process [28]. ²⁹Si CP MAS NMR spectrum showed two dominant broad peaks at -59 and -67 ppm, corresponding to T^2 ($\equiv CSi(OH)(OSi)_2$) and T^3 (=CSi(OSi)₃) silicon sites, respectively [27–29]. Small shoulder around -50 ppm could be ascribed to T¹ (\equiv CSi(OH)₂(OSi)) silicon site. Due to the similar chemical shift, it was difficult to distinguish the Si atoms connected to the ethyl from that connected to the diamine. The absence of signals corresponding to Q sites in the range of -90 to -110 ppm confirmed the retaining of the Si-C bonds during the synthesis process. The NMR results, together with the IR results, confirmed the integration of the both organic functionalities in the BD-PMO(Et)-20 sample.

Thermogravimetric analyses of the surfactant-free BD-PMO(Et)-20 material showed three major weight losses at 25–800 °C in air atmosphere (Fig. S2). A weight loss of less than 8% below 150 °C was observed, probably due to desorption of physisorbed water [31]. Also, the lack of the characteristic peak for template P123 removal at ~ 170 °C in the DTG curves demonstrates that most of the template was removed by the ethanol/HCl extraction [25]. Moreover, a gradual weight loss in the range of 250–450 °C was proportional to the content of the diamino groups incorporated in the framework. The result implied that the diamino-bridged groups can be stable up to 250–450 °C in air.

A series of samples with the different nitrogen content under acidic conditions were prepared. Fig. 2 shows the variation of the XRD patterns for samples BD-PMO(Et)-10, BD-PMO(Et)-20, BD-PMO(Et)-30, and BD-PMO(Et)-40, prepared with different BTMSEN molar ratio in the aqueous solution. All samples exhibited a prominent peak in the diffraction pattern at $2\theta \approx 0.90^{\circ}$. With increasing nitrogen content, the position of the sharp lowest angle peak remained almost constant. Nevertheless, the reflections at higher angle became less well resolved and their intensity decreased and disappeared completely for a



Fig. 2. The Low-angle XRD spectrum of BD-PMO(Et)-x samples.

BTMSEN molar percentage equal to 40%. This suggested that the channel arrays lose regularity. The ordered structure of BD-PMO(Et)-20 could be further confirmed by TEM images (Fig. 3).

Fig. S3 revealed that all the surfactant-free mesoporous samples BD-PMO(Et)-x exhibit typical type-IV isotherms with a sharp capillary condensation step in the relative pressure range of 0.45 ~ 0.55, indicative of uniform mesopores. With the increase of the BTMSEN contents, the nitrogen condensation shifted to low relative pressure (P/P_0), indicating the decrease of mesopore size. This could be attributed to the geometrical constrictions of the triblock copolymer template to accommodate a high content of diamino bridging groups in the pore walls [32]. The surface area and pore volume also decreased with the increased diamino contents, due to the mesostructural degeneration. Textural data for all the samples prepared using different BTMSEN concentrations were provided in Table S1.

X-ray photoelectron spectroscopy (XPS) results (Fig. 4) showed the presence of peaks at binding energies of ca. -101, -284, -399, and -532 eV corresponding to Si_{2p}, C_{1s}, N_{1s}, and O_{1s} ionization processes, respectively [33,34]. Particularly, the high-resolution N 1s spectrum in Fig. 4 indicated the presence of nitrogen atoms in the solvent-extracted materials, which also supported the BTMSEN functionalization in mesoporous organosilica materials.

3.2. Catalytic activity

3.2.1. The Knovevenagel reaction

Table 1 showed the results of the Knovevenagel condensation of benzaldehyde with ethyl cyanoacetate over different catalysts. All the reactions were found to proceed to the olefin products and no intermediate alcohols or other side products were detected. The BD-PMO(Et)-G exhibited much lower activity and selectivity than the BD-PMO(Et)-20 with the similar nitrogen loadings. This could be mainly attributed to the narrower pore channel and the lower ordering degree of mesoporous structure, leading to the enhanced diffusion limit [35]. For the BD-PMO(Et) series catalysts, the activity first increased and then decreased with the increase of N loading. The BD-PMO(Et)-10 catalyst with low N loading (0.019 mmol/g) exhibited poor activity due to the relatively long distance between the neighboring N active sites. Taking into account that either Reaction 1 needed two kinds of molecules adsorbed on the neighboring N active sites (see Scheme 1), the big space between the neighboring N active sites would diminish their synergetic effect. Meanwhile, the BD-PMO(Et)-30 with very high N loading (0.056 mmol/g) also showed poor activity possibly due to the steric hindrance which retarded the diffusion and even the adsorption of organic molecules on the N active sites. The BD-PMO(Et)-20 with the N loading of 0.041 mmol/g was determined as an optimum catalyst, which exhibited equivalent catalytic efficiencies with the



Fig. 3. The TEM images of the BD-PMO(Et)-20 sample along (100) and (110) planes, respectively.



Fig. 4. The XPS spectra of BD-PMO(Et)-20 sample.

Table 1Knovevenagel condensation reaction between benzaldehyde and ethyl cyanoacetate overBD-PMO(Et). a

Table 2
Knovevenagel condensation reaction between carbonyl compounds and ethyl cyanoace-
tate over BD-PMO(Et)-20. ^a

Entry	Catalyst	N Loading (mmol/g)	Conv. (%)	Yield (%)
1	Piperazine	/	98	98
2	BD-PMO(Et)-G	0.045	91	91
3	BD-SBA-15	0.039	81	81
4	BD-PMO(Et)-10	0.019	88	88
5	BD-PMO(Et)-20	0.041	96	96
6	BD-PMO(Et)-30	0.056	82	82
7	BD-PMO(Et)-40	0.077	79	79

 $^{\rm a}$ Reaction conditions : catalyst containing 0.016 mmol N; 1.2 mmol benzaldehyde; 1.0 mmol ethyl cyanoacetate; decane; 4.0 mL H₂O; T= 40 °C; t= 4 h.



Scheme 1. Knovevenagel condensation reaction between carbonyl compounds and ethyl cyanoacetate.

corresponding piperazine homogeneous catalyst. Table 2 compares the performance of the catalysts containing similar N loadings around 20% with different hydrophobicity. The BD-PMO(Et)-20 catalyst gave relatively higher conversions than BD-SBA-15, which could mainly be attributed to the organic groups within the PMO skeleton which enhance surface hydrophobicity, and promote the diffusion and adsorption of organic molecules on the catalysts, especially in aqueous medium. (Schemes 2 and 3)

Entry	R_1	R_2	Run	Temperature (°C)	Time (h)	Conv. (%)	Yield (%)
1	OCH ₃	Н	1	40	6	97	97
2	Н	н	1	40	4	96	96
3	NO_2	н	1	40	2	99	99
4	Н	CH_3	1	100	10	27	27
5	Н	Н	2	40	4	95	95
6	Н	Н	3	40	4	96	96
7	Н	н	4	40	4	93	93
8	Н	н	5	40	4	92	92
9	Н	Н	6	40	4	88	88

 a Reaction conditions: catalyst containing 0.016 mmol N; 1.2 mmol carbonyl compounds; 1.0 mmol ethyl cyanoacetate; decane; 4.0 mL $\rm H_2O.$



Scheme 2. Henry reaction between aldehyde and nitromethane.

The catalytic reactions between various aldehyde and ethyl cyanoacetate were carried out in water over catalyst BD-PMO(Et)-20. The results were summarized in Table 2. All the reactions showed relatively high conversions of BD-PMO(Et)-20 and absolutely high selectivities to the target products. The substituting groups in the aromatic rings had great influence on the catalytic activity. Consistent with aldehyde addition reaction, the presence of the electron-withdrawing group (-NO₂) at the para-position of benzaldehyde increased the reaction rate, while the electron-donating groups (-OCH₃) on benzaldehyde slowed the reaction.



Scheme 3. The intermolecular cross-double-Michael addition reaction between α -methyl- β -nitrostyrene and α , β -unsaturated ketone.

 Table 3

 H reaction between aldehyde and nitromethane over BD-PMO(Et)-20.0

Entry	R	Run	Conv. (%)	Yield (%)
1	OCH ₃	1	89	89
2	Н	1	97	97
3	Cl	1	99	99
4	NO_2	2	99	99
5	Н	3	95	95
6	Н	4	92	92
7	Н	5	87	87

 $^{\rm a}$ Reaction conditions: catalyst containing 0.024 mmol N; 1.0 mmol aldehyde; 3.0 mL nitromethane; T= 90 °C; decane; t= 5 h.



Fig. 5. The small-angle XRD pattern of the BD-PMO(Et)-20 sample after being reused for 6 times in Knovevenagel condensation reaction. The inset is the TEM image.

3.2.2. The Henry reaction

Henry reactions between aldehyde and nitromethane were also carried out with the BD-PMO catalysts. The catalytic results were shown in Table 3. From GC and GC/Mass analyses, it was found that all of the catalyzed reactions gave an α,β -unstaurated olefinic products, and no β -nitro alcohol product was detected. This is consistent with the reactions occurring through an imine intermediate. It had been proposed that this mechanism required the presence of a significant number of spatially isolated amino groups which act as the basic sites [36].

3.2.3. The intermolecular cross-double-Michael addition reaction

In order to demonstrate the catalytic performances of the BD-PMO(Et)-20 catalyst, an intermolecular cross-double-Michael addition reaction was preformed using BD-PMO(Et)-20 as a catalyst. This results are outlined in Table S2, which show the BD-PMO(Et)-20 smoothly catalyzed the reaction. In addition, the recovered catalyst could be used repetitively for 5 times without significant decrease in catalytic efficiency.

The superiority of the BD-PMO(Et)-20 over the traditional organic base homogeneous catalyst was that it could be used repetitively, which could reduce the cost and diminish the environmental pollution. As shown in Table 2, 4 and 5, BD-PMO(Et)-20 could be reused for 6, 5, or 5 times, respectively in water mediated the Knovevenagel, Henry and the intermolecular cross-double-Michael addition reactions without significantly deactivation. From the low-angle XRD and TEM (Fig. 5) of the used BD-PMO(Et)-20, it can be seen that the catalyst BD-PMO(Et)-20 still remained certain ordered structure after being used in water mediated the Knovevenagel for 6 times.

4. Conclusions

The bridged diamino-functionalized highly ordered periodic mesoporous organosilica materials (BD-PMO) were synthesized successfully via co-polymerization of ethane and diamino bridging group silanes. These materials possessed highly ordered mesostructures, uniform pore sizes, high specific surface areas and the relatively stronger base property because of high diamino loading for base-catalyzed reactions. Such catalyst not only exhibited higher activity in water-medium Knovevenagel, solvent-free Henry and the intermolecular cross-double-Michael addition reactions, but also displayed matchable catalytic efficiency with homogeneous catalyst. Importantly, because of diamino group incorprated into the framwork of BD-PMO, the catalyst could be used repetitively for several times without significantly deactivation in these organic reactions, which could reduce the cost and diminish the environmental pollution. The BD-PMO could also be used as complexing agent for metal, which offered more opportunities for designing powerful immobilized catalysts and eliminating pollution from heavy metallic ions for industrial applications.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jssc.2017.07.040.

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