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Dummy molecularly imprinted mesoporous silicates for selective adsorption of 2-naphthol

Abstract: Dummy molecularly imprinted mesoporous silicates (MIMS-2) were made by co-condensation of tetraethyl orthosilicate (TEOS) with precursors of bi-functional mimic of 2-naphthol, 2,7-dihydroxynaphthalene, around triblock copolymer surfactant Pluronic (P123) micelles. The bi-functional template was linked to two functional monomers through thermally cleavable covalent bonds to generate imprint precursor. This provides the possibility of incorporating the target into the cross-linked mesoporous silicate matrix in the non-ionic surfactant templated sol-gel process. P123 was eluted by ethanol extraction and template molecules were removed by refluxing the materials in a mixture of dimethyl sulfoxide (DMSO) and water. MIMS-1 was prepared similarly except that 2-naphthol was used as template instead of 2,7-dihydroxynaphthalene. Solid phase extraction studies showed that MIMS-2 exhibited good retention and selectivity for 2-naphthol among its structural analogues. The mono-functional molecule 2-naphthol was unable to be incorporated into the silica matrix of mesoporous material by the identical method, and the resulting material MIMS-1 exhibits poor selectivity to the template analogues.

Keywords: sol-gel preparation, porous materials, molecular imprinting, organosilicates, 2-naphthol

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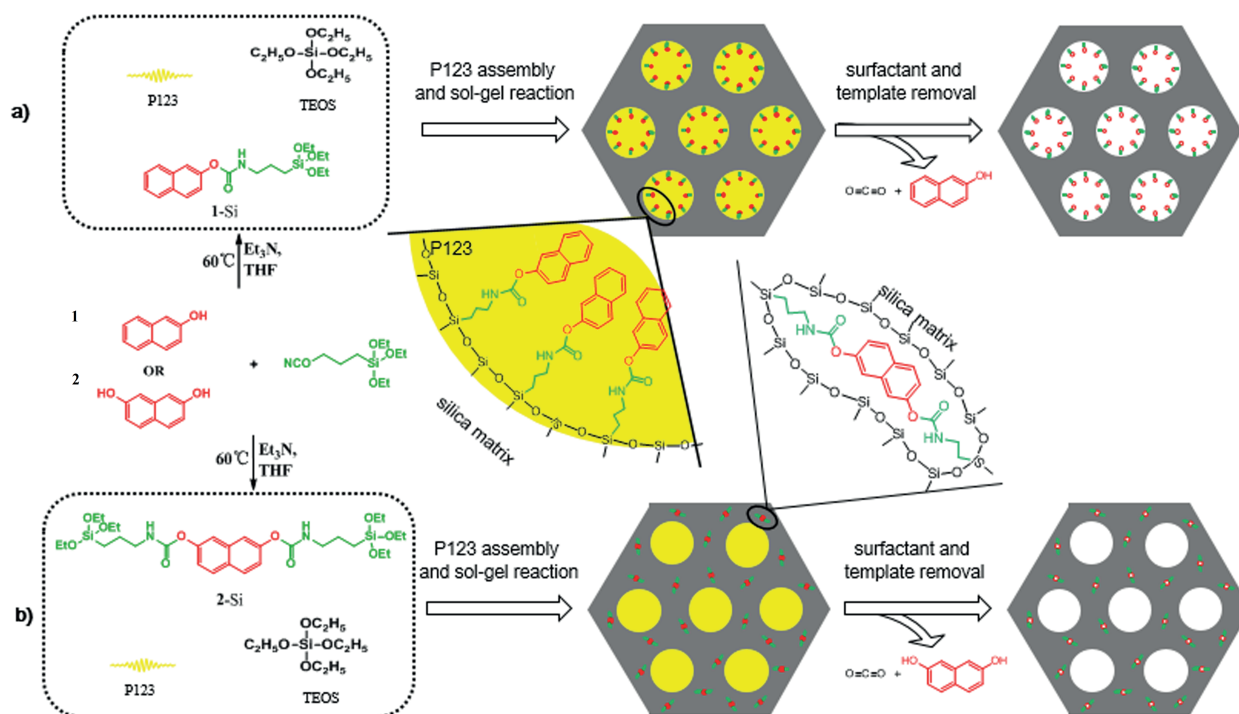Qiang Lin: Chemistry & Chemical Engineering College, Hainan Normal University, Haikou 571158, China

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1 Introduction

Molecular imprinting is a technique, which involves the formation of binding sites in a synthetic polymer matrix that have complementary functional and structural characteristics of substrate molecules. It has been widely recognized as the most promising methodology for preparation of tailor-made artificial "receptors" that can selectively bind target molecules. Traditionally, molecular imprinted polymers (MIPs) are prepared in the form of bulk monoliths. Davis et al. first reported the imprinting of bulk amorphous silica [1]. The major drawback associated with the imprinted material was the difficult diffusion of adsorbents to imprinted sites. Thus, many new imprinting methodologies have emerged to address the limitation of conventional MIPs, such as surface imprinting [2] and thin membrane [3,4]. These methods still suffer from low selectivity and binding capacity. Molecularly imprinted mesoporous silicates (MIMSs) are synthesized by condensing alkoxysilane and template precursor around surfactant micelles. Their high surface area, pore homogeneity, and nanoscale pores render imprinted sites readily accessible to substrates. The MIMSs could find applications as catalysts [5], separation media [6,7], adsorption matrices [8], sensors [9] and nanoreactors [10]. Jung et al. first reported the plausible adsorption properties of molecularly imprinted mesoporous silica [11]. Ozin et al. confirmed the imprinted sites in the silica matrix and the selectivity of imprinted mesoporous material to template molecule over its analogues [12].

2-Naphthol (**1**, Scheme 1) is an organic pollutant present in the environment as a result of dye manufacture, pharmaceutical production, and some biogeochemical processes [13]. 2-Naphthol can be absorbed through skin and has a bad effect on liver, kidneys, blood circulation, etc. [14]. Efficient removal and recycling of 2-naphthol from aqueous solutions are critically important and have to be brought into concerns. Guo et al. used 2-naphthol as template to prepare imprinted silica gel by bulk polymerization for naphthalene recognition [15]. The selective adsorption of naphthalene was achieved over other polycyclic aromatic hydrocarbons (PAHs)

Scheme 1: Schematic process for preparation of MIMSs, a) MIMS-**1** and b) MIMS-**2**.

through imprinted sites. In our work to seek an efficient and selective adsorbent for 2-naphthol, we thought the adsorption efficiency could be generated through the formation of MIMS, since it can provide more open pores which make the imprinted sites more accessible to substrates. However, when 2-naphthol is used as the template to prepare MIMS by a surfactant directed sol-gel process, the mono-functionalized template was unable to be incorporated into the silica matrix. The material turned out to be a periodic mesoporous silicate with inner organic functionalized mesoporous pores and without effective imprinting (Scheme 1a). We rationalized this was due to the mono-functionalized organic template tends to interact with the hydrophobic core of the surfactant micelle. In this paper, we demonstrate that a dummy molecular imprinting approach can be used to resolve the problem. By using 2,7-dihydroxynaphthalene (**2**), a bi-functional mimic of 2-naphthol, as template, MIMS-**2** was successfully prepared and displayed highly selective adsorption for 2-naphthol. The influence of template on the porous structures of the materials was investigated by nitrogen adsorption/desorption experiments and transmission electron microscopy (TEM). The affinity and selectivity of the prepared MIMSs and non-imprinted mesoporous silicates (NIMSs) as well as the blank periodic mesoporous silicates (PMSs) were evaluated by solid phase extraction studies. To the best of our knowledge, there is

no report on the preparation and application of imprinted mesoporous materials for selectively adsorption of mono-functionalized targets.

2 Experimental Procedure

2.1 Materials

2-Naphthol (**1**), 2,7-dihydroxynaphthalene (**2**), phenol (**P**), 2-naphthalene sulfonic acid (**NSA**), pyrene-1-sulfonic acid hydrate (**PSA**) and tetraethyl orthosilicate (TEOS) were purchased from Gracia Chemical Technology Co., Ltd. Chengdu. 3-Isocyanatopropyltriethoxysilane (IPTES), (3-aminopropyl)triethoxysilane (APTES) and Pluronic P123 ($EO_{20}PO_{70}EO_{20}$, MW = 5800 Da) were purchased from Sigma Chemical Co., St. Louis. All other chemicals used were of analytical grade. All solvents and reagents were used without further purification except THF (dried).

2.2 Synthesis

The template precursors of 2-naphthol (**1**) and 2,7-dihydroxylnaphthalene (**2**) were prepared according to published procedure [12]. Phenol moieties were reacted with a stoichiometric amount of (3-isocyanatopropyl)

Table 1: Analytical parameters of four analytes.

analytes	parameters				
	LOD (µg mL^{-1})	LOQ (µg mL^{-1})	r^2	equation	Linearity range (µg mL^{-1})
P	0.10	0.27	0.9997	Y = 68400X + 826	0.282 - 28.2
1	0.04	0.12	0.9996	Y = 428000X + 653	0.144 - 33.2
NSA	0.05	0.17	0.9973	Y = 403000X − 1980	0.208 - 62.4
PSA	0.02	0.07	0.9992	Y = 1300000X − 5910	0.282 - 84.6

triethoxysilane (IPTES) using triethylamine as catalyst in dried THF at 65°C for 24 h. The products were obtained by evaporation of solvents, and identified as **1**-Si and **2**-Si respectively.

Molecularly imprinted mesoporous silicates (MIMSs) were prepared by a triblock-copolymer-templated sol-gel method. Typically, 4.2 g of surfactant P123 was fully dissolved in 135 mL of H$_2$O and 20 g of 12 M HCl. To the solution was added 1.56 mmol of **1**-Si (or **2**-Si), which was pre-dissolved in 46.8 mmol of TEOS. The mixture was stirred at 40°C for 24 h, then transferred into an autoclave aging at 100°C for 24 h. After cooling down to room temperature, the resultant particles were isolated by filtration and rinsed with water. P123 was extracted by Soxhlet extraction with ethanol for 24 h, followed by refluxing the particles in a mixture of DMSO and water at 160°C for 6 h to cleave the carbamate bond and remove the template molecules. After filtration, the materials were rinsed with DMSO and water successively, and vacum dried for 24 h. Samples were designated as MIMS-**1** and MIMS-**2** respectively. The blank periodic mesoporous silicates (PMS) were prepared by the same method by using TEOS only. The control non-imprinted mesoporous silicates (NIMS) were prepared by a pre-hydrolysis sol-gel process, in which TEOS was allowed to pre-hydrolyze for 1.5 h before APTES was added.

2.3 Characterization

The infrared spectra were recorded with Perkin-Elmer system 2000 FT-IR spectrometer. TEM images were obtained on a Tecnai-G2-F20 electron microscope operating at 200 kV. Nitrogen adsorption-desorption isotherms were measured at 77K using a HYA2010-B2 system. The Barret-Joyner-Halenda (BJH) pore size distribution was calculated from the desorption branch of the isotherm.

2.4 Solid phase extraction

Typically, each of the MIMS-**2**, MIMS-**1**, NIMS, or PMS (100 mg) was packed between two pieces of filter paper in a polyethylene syringe. 1.0 mL of an aqueous stock solution, which contains phenol (**P**), 2-naphthol (**1**), 2-naphthalene sulfonic acid (**NSA**), 1-pyrenesulfonic acid hydrate (**PSA**) at a concentration of 1.0×10^{-4} M, was added to this simplified solid phase column. The stock solution was allowed to flow through the syringe by gravity and collected in vial-**1**, 2 mL of water was added to rinse off loosely bounded substances, which was combined with solution in vial-**1**, named load residue. Next, 12 mL of methanol was used to wash out the adsorbed substance and collected in vial-**2**, named methanol elute. TLC technique was applied as a quick test to ensure each fraction was collected thoroughly. To extract **NSA** and **PSA**, the materials were dispersed into 25.0 mL solution of aqueous hydrochloride (pH = 1.0) and methanol (v/v, 1/1). The mixture was stirred for 4 h and filtered. The residue was rinsed with 2 mL of the hydrochloride/methanol solution. The filtrate and rinse solution were collected in the same flask, named acid extract. The load residue, methanol elute and acid extract were dried and re-dissolved in 1.0 mL of methanol respectively. The three fractions were analyzed by UPLC to determine the concentrations.

Before reusing of the materials, the filtrated solids were suspended into 25.0 mL of NaOH solution at pH 10.0 and stirred for 20 h to recover the amino functionality of the materials. The regenerated materials were reused in above SPE for three cycles with only slightly variation in results.

2.5 UPLC measurements

UPLC measurements were performed on an ACQUITY UPLC BEH-C18 column. A PDA detector, a Waters quaternary

solvent pump, a sample manager-FIN, sample injections of 1 μL, and a column temperature of 4°C were used. The mobile phase was methanol and water (v/v, 60/40). Flow rate was maintained at 0.4 mL min^{-1} and the detector was set at 254 nm.

Four calibration curves were calculated from the analysis of working standard solutions, with correlation coefficients (r^2) than 0.99 (five points curves). The instrumental detection (LOD) and quantitation limits (LOQ) were calculated by using a signal-to-noise ratio of 3 and 10, respectively. The details of analytical parameters are listed in Table 1.

3 Results and Discussion

3.1 Synthesis of MIMSs

In order to prepare the functional monomer linked precursors for sol-gel condensation, 2-naphthol (**1**) and 2,7-dihydroxylnaphthalene (**2**) were reacted with (3-isocyanatopropyl)triethoxysilane (IPTES) to form carbamates **1**-Si and **2**-Si, respectively (Scheme 1), which were confirmed by ^{1}H NMR and FT-IR spectroscopies.

1-Si and **2**-Si were respectively incorporated into cross-linked periodic mesoporous silicates via a triblock-copolymer-templated sol-gel process. Successive removal of surfactant and template by ethanol extraction and heating in DMSO/H$_2$O resulted in amino-functionalized MIMSs (Scheme 1). It was interesting to find that the template molecule 1 worked as a protecting group for amino group in preparation of MIMS-**1** under acidic condition, which was similar as described by Mehdi et al. [16] To clarify the imprinting effects, non-imprinted periodic mesoporous silicates (NIMS) were prepared using the same amount of Si from APTES in place of the template containing precursors. Blank periodic mesoporous silicates (PMS) were prepared by the same method using only TEOS.

3.2 FT- IR characterization

To confirm the incorporation of the template molecules in the as-synthesized MIMS and the generation of the rebinding sites in the imprinted MIMS, Fourier transform infrared spectra (FT-IR) were recorded. For illustration, FT-IR spectra of the as-synthesized MIMS-**2**-as and imprinted MIMS-**2** made by bi-functional template and TEOS, as well as the non-imprinted NIMS are presented in Fig. 1.
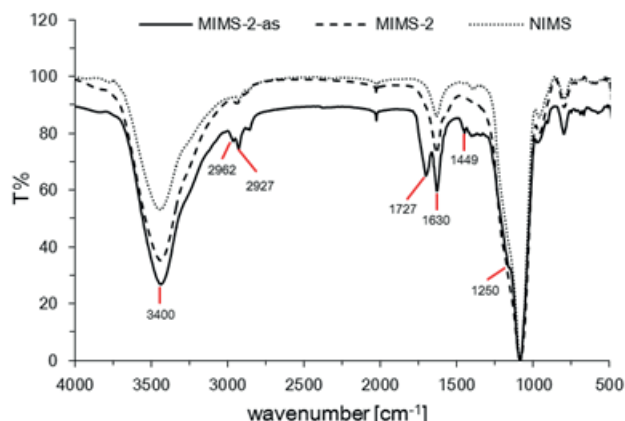

Figure 1: FT-IR spectra of MIMS-**2**-as, MIMS-**2**, and NIMS.

The bands at 2962 and 2927 and 1449 cm^{-1} of MIMS-**2**-as can be attributed to CH$_2$ absorption of P123 surfactants [17]. However, these bands are not observed for ethanol extracted MIMS-**2**. The characteristic bands of carbamate C=O stretching vibration at 1727 cm^{-1} and N-H bending peak at 1630 cm^{-1} are clearly visible for MIMS-**2**-as, indicating the incorporating of template molecules. The band at 1727 cm^{-1} is disappeared in MIMS-**2**, revealing the successful removal of the templates. The peak of 1250 cm^{-1} for the vibration of Si-C indicates that the functional monomers are incorporated in the as-synthesized MIMS-**2**-as and after removal of template MIMS-**2**. N-H bending peak at 1630 cm^{-1} in both MIMS-**2** and NIMS reveals the existence of amino groups. All bands of MIMS-2 resemble those of NIMS, confirming the similarity of their contents.

3.3 Nitrogen adsorption/desorption characterization

Nitrogen adsorption/desorption experiments were carried out on samples to investigate the porosity. All samples exhibited typical type-IV isotherms according to IUPAC classification [18] (Fig. 2), indicating mesoporous materials.

The Brunauer-Emmett-Teller (BET) surface area, pore size, and pore volume are listed in Table 2. MIMS-**1** displayed periodic mesoporous channels with pore size centered at 5.4 nm, which is slightly larger than 5.1 nm of the blank PMS (Fig. 2b). This suggests that during the sol-gel process, the mono-functional one site bounded template 1 protruded from the wall into the hydrophobic core of surfactant micelle, causing swelling of the pore size (Scheme 1a). After the surfactant extraction and template
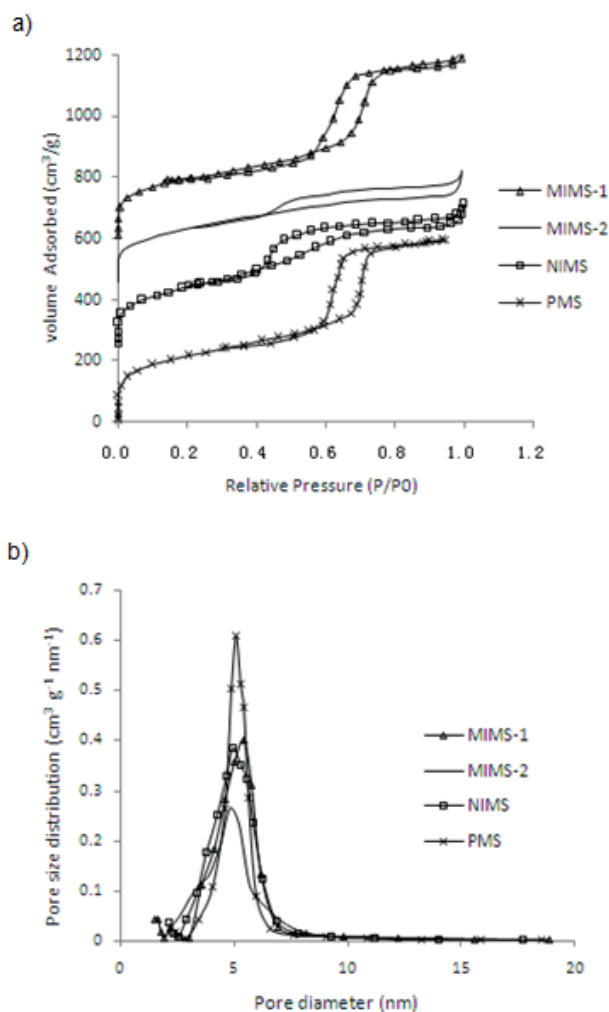
Figure 2: a) Nitrogen adsorption/desorption isotherms and b) BJH pore size distributions of MIMS-**1**, MIMS-**2**, NIMS and PMS.

Table 2: Physical properties of prepared materials.

Sample	BET surface area (m² g⁻¹)	pore size (nm)	pore volume (cm³ g⁻¹)
MIMS-**1**	773	5.4	0.93
MIMS-**2**	684	4.8	0.90
NIMS	693	5.0	0.72
PMS	708	5.1	0.97

removal, well-ordered amino functionalized interior mesostructures without effective imprinting cavities were obtained.

In order to incorporate the template molecule into the silicate matrix, we used **2**, which is a structural analogue of **1**, but possessing two hydroxyl groups that could be linked covalently with two trialkoxysilanes functional monomers, to obtain MIMS-**2**. As can be seen in Fig. 2a,

the broad hysteresis in the isotherm of MIMS-2 indicates a less ordered mesoporous material with a smaller pore size (4.8 nm) than that of PMS (5.1 nm). This is in accordance with the trend of imprinted mesoporous silica reported by Lofgreen et al [12]. NIMS was made by pre-hydrolysis sol-gel process to avoid the interruption of the amino groups from the silica matrix to the surfactant template [19]. The isotherm of NIMS resembles with that of MIMS-**2** due to the incorporation of amino-groups into the silica matrix, while the pore size distribution of NIMS is similar with that of PMS (Fig. 2b and Table 1).

3.4 Transmission Electron Microscopy

The texture structures of the prepared materials were further investigated by TEM (Fig. 3). Excellent hexagonal ordering of mesopores in a uniform straight pore channel was observed for blank PMS (Fig. 3d). Similar mesostructure of MIMS-**1** (Fig. 3a) was obtained with a slightly larger pore size than PMS, in agreement with the pore size distribution in nitrogen adsorption/desorption experiments. MIMS-**2** (Fig. 3b) shows lower ordering than MIMS-**1,** due to the incorporation of organic template into the silica matrix. The morphology of NIMS (Fig. 3c) is similar with that of MIMS-**2,** with amino propyl (AP) groups incorporated into the silica matrix.

3.5 Evaluation of adsorption

In order to explore the selectivity of the dummy molecularly imprinted MIMS-**2** and the target imprinted MIMS-**1** toward 2-naphthol, the selective assays were performed on MIMS-**2**, MIMS-**1**, NIMS and PMS columns by solid phase extraction (SPE), respectively. Three structurally analogues of 2-naphthol (**1**), including phenol (**P**), 2-naphthalene sulphuric acid (**NSA**) and 1-pyrene sulfonic acid (**PSA**), were chosen as analytes for the solid phase extraction. The load residue, methanol elute and acid extract were dried and re-dissolved in I mL of water respectively and analyzed by UPLC (Section 2.4 and 2.5). The concentration of each analyte was compared to the corresponding stock solution. The results are summarized in Fig. 4.

More than 90% of P and 1 remained in the load residues (Fig. 4c and 4d), indicating silanol and amino groups do not adsorb phenol species effectively. On the other hand, MIMS-**1** and MIMS-**2** retained, respectively, 30% and 80% of **1** after water rinse (Fig. 4a and 4b, in the methanol elute), while PMS and NIMS have little retention
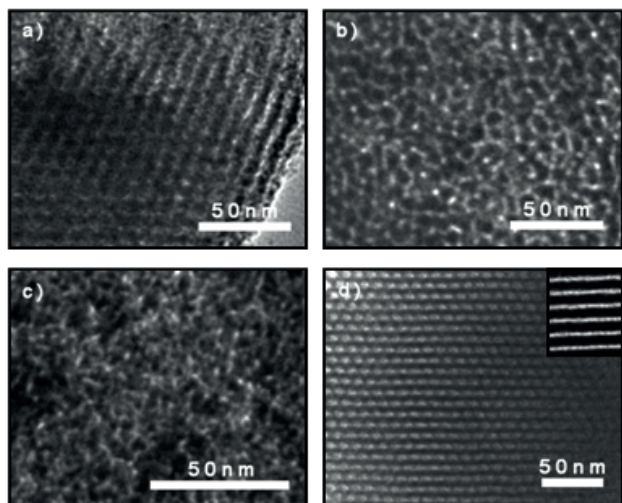
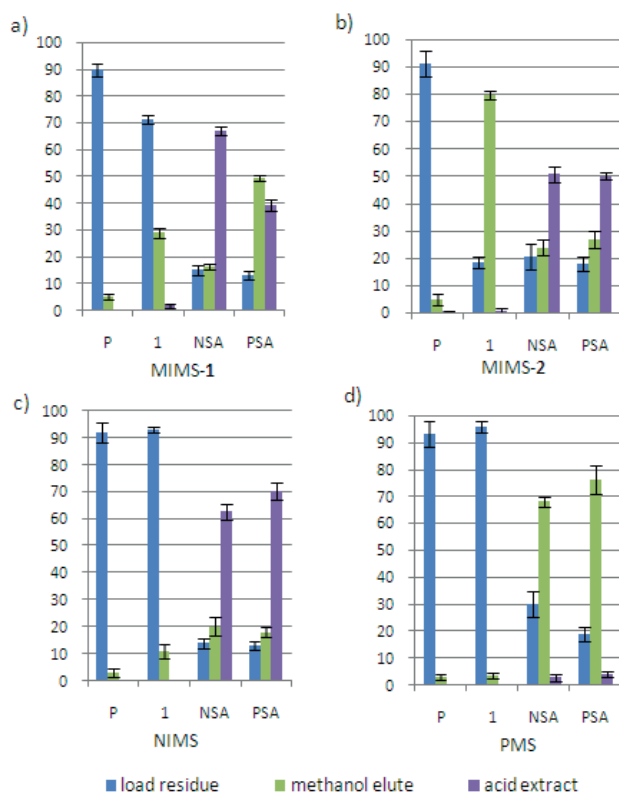**Figure 3:** TEM images of a) MIMS-**1**; b) MIMS-**2**; c) NIMS; d) PMS.

Figure 4: Solid phase extraction of a) MIMS-**1**, b) MIMS-**2**, c) NIMS and d) PMS for **P**, **1**, **NSA** and **PSA**.

for 1 after water rinse (Fig. 4c and 4d, methanol elute), suggesting 1 in methanol elutes of MIMS-**1** and MIMS-**2** were due to not purely amino functional group binding. The retained **NSA** and **PSA** on PMS after water rinse, can be eluted by methanol (Fig. 4d), but cannot be eluted from NIMS (Fig. 4c), suggesting the remaining **NSA** and **PSA**

on NIMS could be due to adsorption by aminopropyl (AP) groups on silicates.

Since a pre-hydrolysis process was used for synthesis of NIMS, in which AP groups were distributed both in the pore channels (minor) and inside the walls of the resulting materials [20], MIMS-**1**, prepared by 2-naphthol (**1**) as template, incorporated similar amount of AP groups (calculated by the molar ratio of TEOS/**1**-Si) with did in NIMS (calculated by TEOS/APTES). By comparison of the adsorption behavior of MIMS-**1** and NIMS, the location of AP groups in the materials could be distinguished. MIMS-**1** retained approximately 20% more of **1** (methanol elute), 10% more of **NSA** (acid extract) and 30% less of **PSA** (acid extract) than did NIMS, suggesting AP groups of MIMS-**1** were more accessible for **1** and NSA, but less accessible for **PSA** than those of NIMS. We rationalized that this was due to the AP groups were mostly located on the inner surface of the mesopores with minority buried in the silica matrix, rather than mostly buried in the silica matrix and partially on the outer surface of NIMS. Thus, it is easy to understand that AP groups of MIMS-1 were more accessible for **1** than those of NIMS. Due to the strong hydrophobicity and the large conjugated π-system of **PSA** molecule, it tends to form dimer [21] in polar solvents. These dimeric blocks of PSA could be easily adsorbed by amino groups located on the outer surface of mesopores (NIMS), but could hardly diffuse into the mesopores of MIMS-1, where most amino groups could be found. As a result, lower adsorption by MIMS-1 (37%) than NIMS (70%) were obtained.

MIMS-**2**, prepared by 2,7-dihydroxylnaphthalene (**2**) as template, showed best retention (80%) for **1** in methanol elute (Fig. 4b). It was interesting to notice that while MIMS-**2** retained about 20% more **1** (methanol elute) than **NSA** (acid extract), MIMS-**1** showed almost no selectivity for **1** and **NSA**, suggesting that the AP groups in MIMS-2 were arranged in the manner, which could selectively bind to molecule whose shape and functional group(s) match with the imprinted site. In other words, the imprinted sites did exist in MIMS-**2**. The similar percentage of **NSA** and **PSA** adsorbed by MIMS-**2** indicated that they were bounded by AP groups from imprinted sites at/or closing to the surfaces, not in the imprinted sites. In Fig. 4b, 80% of **1** could be recovered from methanol elution. Although MIMS-1 adsorbed similar amount of **1** and **NSA**, they could be separated by methanol elute and acid wash. This suggests that MIMS-**1** may be used for size selective isolation of structural analogues through the functionalized mesopores rather than through molecular imprinting.

4 Conclusions

In summary, we have demonstrated that dummy molecularly imprinted mesoporous silicates (MIMS-**2**) made with bi-functional template, 2,7-dihydroxylnaphthalene (**2**), can be used to adsorb mono-functional target, 2-naphthol (**1**) with high affinity and good selectivity toward its analogues. Nitrogen adsorption/desorption experiments and TEM images showed that MIMS-**1** imprinted with **1** possesses well ordered and expanded pores. MIMS-**1** turned out to be functionalized with amino group on the inner surface of mesopores. Solid phase extraction revealed this material did not have the ability to recognize the template molecule. However, MIMS-**1** type mesoporous materials may be useful for size selective adsorption of structural analogues through the functionalized mesopores. The dummy molecular imprinting strategy may be used to make imprinted mesoporous organosilicates for other mono-functional organic molecules, in application of separation and toxicity remediation.

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