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Improved Structural Order, Stability, and Anion-Exchange Capacity of Cation-Mediated Bridged Hybrid Mesoscopic Materials by Using Chelating Ligands

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The anion-exchange property of upgraded metal cation-mediated bridged hybrid mesoscopic material (MBH-S) is greatly improved by replacing initial unidentate ligands with chelating ligands in the framework. Compared to conventional MBH samples, the upgraded MBH-S shows a well-ordered hexagonal mesostructure and a remarkably high anion-exchange capacity. Significantly, the upgraded MBH-S shows a good hydrothermal stability and can keep its anion-exchange capacity unchanged during repeated ion-exchange procedures, which is very important for this type of material to be used in practical application as an anion exchanger. As examples, an anion molecule of tris(8-hydroxyquinoline-5-sulfonate)aluminum ($Al(SQ)_3$) with strong luminescence can be exchanged into MBH-S, forming composite solid of MBH-S-$Al(SQ)_3$ with very strong green luminescence under the excitation of UV light ($\lambda_{exc} = 360$ nm). A functional molecule of copper phthalocyanine tetrasulfonic acid (CuPcTS) has been employed as a guest to assemble hybrid solid material, MBH-S-CuPcTS.

Introduction

Anion exchange is an important process in many fields. The most commonly used anion exchangers are anion-exchange resins that are organically based. Inorganic materials with anion-exchange capacity, however, have rarely been studied. Hydrotalcite clays[1−3] are one class of inorganic materials with anion-exchange property. With respect to mesoporous materials,[4−10] there are only a few reported examples[11−13] on their anion-exchange properties. Stein et al. prepared ordered aluminophosphate and galloaluminophosphate mesoporous materials with anion-exchange properties using polyoxometalate cluster as precursors.[11,12] Bhaumik and Inagaki synthesized mesoporous titanium phosphate with unusually high anion-exchange capacity.[13] Recently, novel silica-based inorganic−organic hybrid mesoscopic materials were reported by Zhang et al.,[14] which are metal cation-mediated bridged hybrid mesoscopic materials and therefore designated MBH. MBH contains metal ions (Cd^{2+}, Zn^{2+}, and Ni^{2+}) as an integral part of their backbone, which have strong Coulombic interaction with anionic surfactant and are coordinated by functional ligands of 3-aminopropyltriethoxysilane (aptes, $H_2NCH_2CH_2CH_2Si(OEt)_3$). These aptes groups connect with one another by condensation to form the whole framework. Thus, metal ions, organic functional groups, and silica are uniformly distributed in the framework of MBH.

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More recently, we have observed a remarkable anion-exchange capacity of MBH,[15] which is even higher than that of some well-known anion exchangers (such as anion-exchange resins and hydrotalcites). We proposed that the anion-exchange property of MBH results from the presence of metal ions in the framework, and due to the soft alkyl chains in the framework, MBH is prone to change its structure to accommodate anions with various sizes. Additionally, reversible phase transitions along with the anion-exchange process in MBH have also been observed. This is the first example of silica-based inorganic−organic hybrid mesoporous material with high anion-exchange capacity. However, to fulfill the need of an anion exchanger that can be used in practical application, the stability of MBH has to be effectively improved. In previous reports,[14−16] the metal ions and siloxanes in the framework of MBH connect to each other via weak coordinate interactions. Especially, the siloxane used in this case, 3-aminopropyltriethoxysilane (aptes, $H_2NCH_2CH_2CH_2Si(OEt)_3$), is a unidentate ligand, which almost has the weakest coordinated ability among all kinds of ligands.[16] This means that the metal ions in the framework of MBH are easy to leach during repeated ion-exchange procedures and the anion-exchange capability will gradually decrease.

In this work, a new siloxane, *N*-(β-aminoethyl)-γ-aminopropyltrimethoxysilane (aeaptms, $H_2NCH_2CH_2HNCH_2CH_2CH_2Si(OMe)_3$), is used to prepare stable MBH instead of aptes and the obtained product is designated MBH-S. Because the two amine groups in aeaptms can chelate the metal ion in the framework, the metal ions in MBH-S are so resistant to leaching that the anion-exchange capacity of MBH-S is almost unchanged, even after repeated anion-exchange processes (more than 10 times). Moreover, MBH-S has a well-defined two-dimensional hexagonal mesostructure rather than in the case of MBH, where only a poorly ordered two-dimensional hexagonal phase could be obtained. Particularly, MBH-S shows a remarkably higher anion-exchange capacity and hydrothermal stability than MBH. Some functional anion molecules can be easily exchanged into MBH-S. For examples, a luminescent molecule of tris(8-hydroxyquinoline-5-sulfonate)aluminum ($Al(SQ)_3$) has been employed as a guest anion to prepare composite solid material, MBH-S-$Al(SQ)_3$, which exhibits very strong green luminescence under the excitation of UV light ($\lambda_{exc} = 360$ nm).[20] A functional molecule of copper phthalocyanine tetrasulfonic acid (CuPcTS)[21,22] could be easily exchanged into MBH-S, forming a composite solid material of MBH-S-CuPcTS.

Experimental Section

Various metal ions (Cd^{2+}, Zn^{2+}, and Ni^{2+}) can be used to prepare metal cation-mediated bridged hybrid mesoscopic materials. In this study, we chose Zn-containing samples to investigate the structural order, stability, and anion-exchange capacity of this novel type of materials. For the purpose of simplification, Zn-MBH and Zn-MBH-S were denoted as MBH and MBH-S respectively in the following.

Preparation of MBH and MBH-S. MBH was synthesized according to the literature.[14] In a typical synthesis, 1.86 g of sodium dodecyl sulfate (SDS) and 1.53 g of $Zn(NO_3)_2{\cdot}6H_2O$ were dissolved in 50 g of deionized water. After a clear solution had formed, 4.47 g of aptes ($H_2NCH_2CH_2CH_2Si(OEt)_3$) was added dropwise. The suspension was continuously stirred for another 24 h. The resulting precipitates were filtered and dried in air to obtain as-synthesized MBH. MBH-S was prepared in the same way as the procedures for MBH given above, except that equal aeaptms in molar instead of aptes was used.

Anion Exchanges. A circular anion-exchange procedure consists of two steps. (1) The anion surfactants (SDS^-) in MBH and MBH-S were first exchanged by sodium acetate (CH_3COONa). In a typical exchange process, 2.0 g of MBH (or MBH-S) was stirred for 5 h in 50 mL of 0.05 M ethanol solution of the sodium acetate. The obtained samples were then filtered, dried in air, and designated as MBH-Ac and MBH-S-Ac, respectively. (2) Reverse anion exchanges of MBH-Ac and MBH-S-Ac with SDS^- were made to restore the samples to MBH and MBH-S, respectively. Typically, 1.0 g of MBH-Ac (or MBH-S-Ac) was stirred for 20 h in 25 mL of 0.05 M aqueous solution of SDS and then filtered, washed by deionized water several times to remove redundant SDS, and dried in air.

This cycle (step 1 and step 2) was repeated various times to evaluate the stability and anion-exchange property of the samples. When the cycle was repeated 10 times, the sample for MBH and MBH-S was designated as MBH_{10} and MBH-S_{10}, respectively.

Preparation of MBH-S-Al(SQ)$_3$. $Al(SQ)_3$ was prepared by thermal reaction of $Al_2(SO_4)_3{\cdot}8H_2O$ with 8-hydroxyquinoline-5-sulfonic acid in the presence of K_2CO_3 and was purified by recrystallization. $Al(SQ)_3$ was incorporated into MBH-S by anion exchange as follows: 5 mg of $Al(SQ)_3$ was dissolved into 10 mL of water, followed by the addition of 100 mg of MBH-S and stirring for 5 h at room temperature. The resulting solid was then filtered to give a light yellow product, designated as MBH-S-$Al(SQ)_3$. To remove the unexchanged $Al(SQ)_3$ on the surface and determine if the soluble luminescent molecule $Al(SQ)_3$ was grasped by MBH-S, the solid MBH-S-$Al(SQ)_3$ was washed with deionized water a couple of times.

Preparation of MBH-S-CuPcTS. CuPcTS purchased from Aldrich was incorporated into MBH-S by anion exchange as follows: 5 mg of CuPcTS was dissolved into 10 mL of water, followed by the addition of 100 mg of MBH-S and stirring for 5 h at room temperature. The resulting solid was then filtered to give a light blue product, designated as MBH-S-CuPcTS.

Characterization. X-ray diffraction (XRD) patterns were obtained with a Siemens D5005 diffractometer using Cu Kα radiation. Chemical analyses for C, H, N, and S were conducted on a Perkin-Elmer 2400 element analyzer. Zn and Si analyses were determined by inductively coupled plasma (ICP), carried on a Perkin-Elmer Optima 3300DV spectrometer. The FT-IR spectra were recorded on a Nicolet Impact 410 FT-IR spectrometer. The emission spectra were recorded with a Shimadzu RF-5301PC spectrometer. UV absorption spectra were determined by a PE UV−Vis Lambda 20 spectrometer.

Results and Discussion

X-ray Diffraction (XRD). Figure 1 shows XRD patterns of as-synthesized and anion-exchanged MBH and MBH-S samples. As-synthesized MBH (Figure 1A) shows only one distinguishable peak (*d*-spacing of 2.7 nm) besides the main peak with a *d*-spacing of 4.2 nm,

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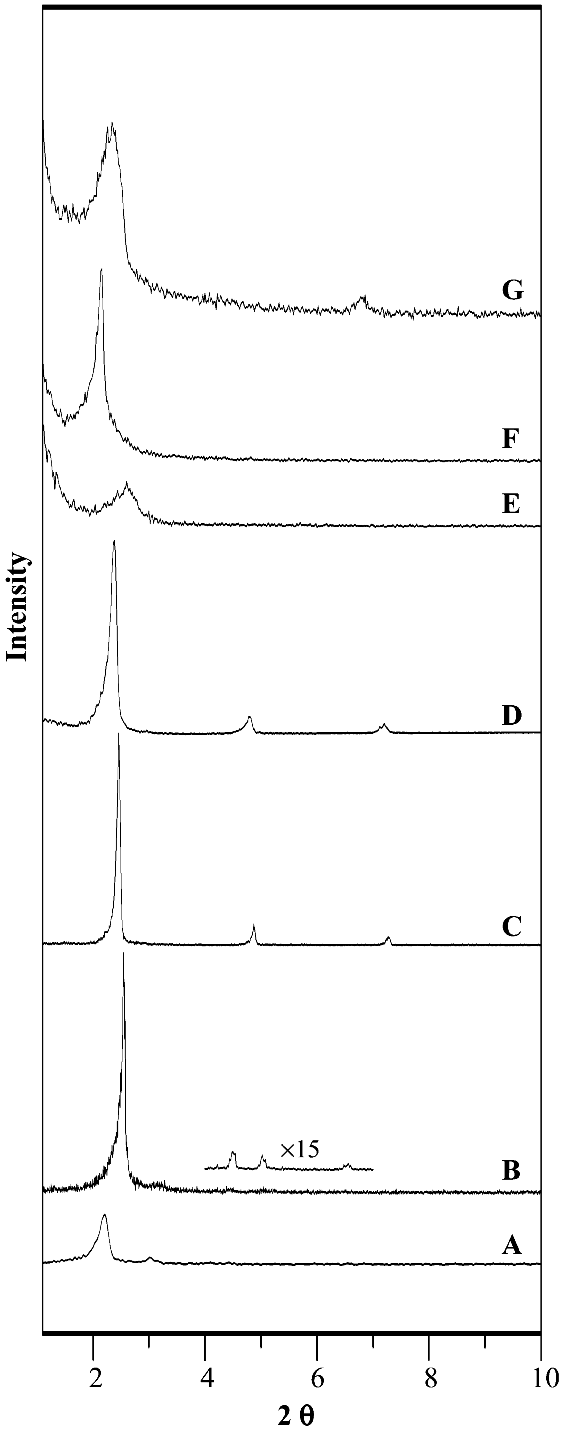


Figure 1. XRD patterns of MBH (A), MBH-S (B), MBH-Ac (C), MBH-S-Ac (D), MBH treated in boiling water for 150 h (E), MBH-S treated in boiling water for 150 h (F), and MBH-S-Al(SQ)$_3$ (G).

indicating a poorly ordered two-dimensional hexagonal mesostructure (cell parameter a = 4.8 nm), in good agreement with reported literature.[14] However, MBH-S (Figure 1B) exhibits four well-defined XRD peaks that can be indexed as the (100), (110), (200), and (210) diffractions associated with the *p*6*mm* hexagonal symmetry, indicating that MBH-S is an ordered two-dimensional hexagonal mesophase (cell parameter a = 3.9 nm). Obviously, the mesostructural order of MBH-S is greatly improved, compared with that of MBH. Furthermore, we observe that the first peak for MBH-S appears at 2.60°, which is relatively high as compared with that (2.11°) for MBH. Considering the use of the same surfactant micelle (SDS^-) in the synthesis of MBH and MBH-S, it is proposed that the difference in *d*-spacing value may be attributed to the various thicknesses of the mesostructured walls for MBH and MBH-S.

After anion-exchanged with acetate, both MBH-Ac (Figure 1C) and MBH-S-Ac (Figure 1D) exhibit three peaks in the region of 1−10°, giving the reflections with *d* values of 3.6, 1.8, and 1.2 nm, respectively, typical for the 00*l* crystal planes of a layered material. These results confirm that the nearly hexagonal MBH and well-ordered hexagonal MBH-S are transformed into the lamellar symmetry of MBH-Ac and MBH-S-Ac.

Interestingly, after the treatment of boiling water for 150 h, MBH-S still shows two well-resolved peaks at 2.03 and 3.50° (Figure 1F), possibly assigned to the (100) and (110) reflections associated with hexagonal symmetry, which indicates that MBH-S basically has a hexagonal mesostructure. In contrast, MBH only shows a very small peak at 2.35° (Figure 1E), indicating that the mesostructure of MBH is basically destroyed. These results show that MBH-S has much higher hydrothermal stability than MBH, which is an important factor for the ion exchangers in practical use because anion-exchange reactions are sometimes carried out in aqueous solution at higher temperature for promoting the anion-exchange process completely and quickly.

After anion exchange with Al(SQ)$_3$, MBH-S-Al(SQ)$_3$ (Figure 1G) exhibits three relatively broad peaks at 2.3, 4.5, and 6.8° in the region of 1−10°, also suggesting a layered material. This result also confirms that the well-ordered hexagonal MBH-S are transformed into the lamellar symmetry of MBH-S-Al(SQ)$_3$.

Chemical Analysis. The results of chemical analysis for various samples are presented in Table 1. As-synthesized MBH shows the molar ratios of Zn/Si (1/3.9) and Zn/N (1/3.7) are very near 1/4 (Table 1), suggesting that Zn^{2+} is coordinated by four aptes ligands, consistent with what Zhang and Dai proposed in their paper.[14] Furthermore, as-synthesized MBH shows the molar ratio of Zn/S (1/2.1) near 1/2 (Table 1), which is explained that two anionic surfactant molecules (SDS^-) are expected to be in as-synthesized MBH to balance the positive charge for each Zn^{2+}. Thus, the composition of as-synthesized MBH should be expressed as $Zn^{2+}(H_2NCH_2CH_2CH_2SiO_{1.5})_4(SDS^-)_2$, and the proposed interaction between Zn^{2+} and aptes ligands are shown in Scheme 1a. Inevitably, there may be some water molecules in this compound.

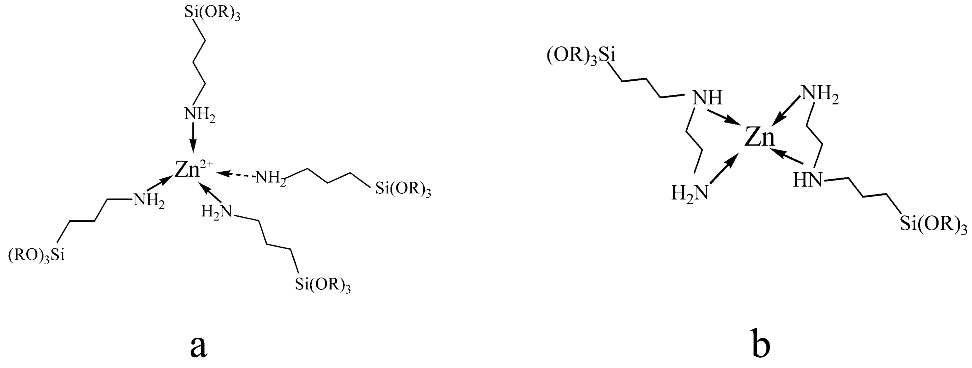
However, in an as-synthesized MBH-S sample, the molar ratios of Zn/Si (1/2.2) and Zn/N (1/4.2) are approximately 1/2 and 1/4, respectively (Table 1). These results mean that Zn^{2+} in MBH-S is chelated by four amine ligands from two aeaptms molecules. Possibly, the chelation of Zn^{2+} with two aeaptms is formed by double five-rings, as proposed in Scheme 1b. Moreover, just as in the case of MBH, the molar ratio of Zn/S in as-synthesized MBH-S is very near to 1/2. According to these data, the chemical composition of as-synthesized MBH-S can be expressed as $Zn^{2+}(H_2NCH_2CH_2HNCH_2CH_2CH_2SiO_{1.5})_2(SDS^-)_2$.

Table 1. Elements Analysis Results and Structures of Various Samples[a]

sample	content (%) C	N	S	Zn	Si	C:N:S:Zn:Si (molar ratio)	phase
MBH	41.62	4.96	6.53	6.32	10.61	35.7:3.7:2.1:1.0:3.9	nearly hexagonal
MBH-S	44.51	5.63	6.68	6.29	5.93	38.3:4.2:2.2:1.0:2.2	hexagonal
MBH-Ac	36.12	5.21	3.29	7.27	11.30	29.5:3.7:0.9:1.0:3.7	lamellar
MBH-S-Ac	40.07	6.46	3.89	7.14	6.77	30.4:4.2:1.1:1.0:2.2	lamellar
MBH_{10}	36.75	5.68	3.45	5.96	11.59	33.4:4.4:1.2:1.0:4.5	poorly hexagonal
$MBH\text{-}S_{10}$	40.76	6.52	4.17	6.92	6.85	31.9:4.4:1.2:1.0:2.3	nearly hexagonal

[a] Chemical analyses for C, H, N, and S were conducted on a Perkin-Elmer 2400 element analyzer. Zn and Si analyses were determined by inductively coupled plasma (ICP), carried on a Perkin-Elmer Optima 3300DV spectrometer.

Scheme 1. Proposed Interaction between Zn^{2+} with Ligands in MBH (a) and MBH-S (b)



After anion exchange with acetate, the carbon content of both MBH-Ac and MBH-S-Ac decreases, but the molar ratio of Zn/N (1/3.7 and 1/4.2 for MBH-Ac and MBH-S-Ac) basically remains the same (Table 1), compared with those of as-synthesized MBH and MBH-S. The decrease of carbon content in the samples is attributed to the anion exchange of SDS^- with Ac^-, and the same molar ratio of Zn/N in the samples suggests that the interaction between all of Zn^{2+} with ligands is almost retained.

After anion exchange ($SDS^- \rightarrow Ac^-$) and reverse anion exchange ($Ac^- \rightarrow SDS^-$) for 10 times, MBH_{10} shows the values for Zn/Si and Zn/N at 1/4.5 and 1/4.4 (Table 1), which is slightly different from those of as-synthesized MBH. The change for Zn/N ratio from 1/3.7 in as-synthesized MBH to 1/4.4 in MBH_{10} suggests the partial destruction of the interaction between Zn^{2+} ions with aptes ligands. In contrast, $MBH\text{-}S_{10}$ exhibits a much lower change for Zn/N ratio (Table 1). Zn/N ratio in MBH-S and $MBH\text{-}S_{10}$ is 1/4.2 and 1/4.4, respectively. This indicates that the interaction between Zn^{2+} with aeaptms ligands in the MBH-S sample is stronger than that between Zn^{2+} with aptes ligands in the MBH sample.

IR Spectroscopy. Figure 2 shows IR spectra of aptes, MBH, aeaptms, MBH-S, and SDS. Notably, aptes exhibits bands at 3359 and 597 cm^{-1} (Figure 2a), which are assigned to stretching and bending vibrations of the N−H bond.[17−19] However, MBH sample shows new bands at 3257 and 607 cm^{-1} (Figure 2b) associated with N−H vibrations. Obviously, the stretching band for the N−H bond in MBH is shifted to lower frequencies, while the bending band is shifted to higher frequencies, compared with those of aptes. Considering the fact that each Zn^{2+} is coordinated with 4 aptes ligands, it is believed that the shifts for N−H frequencies result from the interaction between Zn^{2+} ions with aptes ligands, in good agreement with reported literature.[17−19] Similarly, aeaptms exhibits bands at 3380 and 590 cm^{-1} (Figure 2c), but MBH-S shows the new bands at 3266 and 607 cm^{-1} (Figure 2d) associated with N−H stretching and bending vibrations. Interestingly, the wavenumber shifts for N−H vibrations in MBH-S (114 and 17 cm^{-1} for stretching and bending vibrations) are larger than those (102 and 10 cm^{-1} for stretching and bending vibrations) in MBH. The larger wavenumber shifts for N−H vibrations indicate the stronger coordinated bond for Zn^{2+}−N in MBH-S.[17−19]

It is worth noting that MBH-S is much more ordered than MBH since they are prepared under the same conditions with the same surfactant (SDS) as the template. The only difference between them lies in the different organosilanes used for their synthesis and the ways in which Zn^{2+} ions are coordinated. In MBH, the bridge spacer between metal ions, aptes, is a unidentate ligand, which almost has the weakest coordinate ability among all kinds of ligands.[16] As for MBH-S, the bridge spacer (aeaptms) has two amine groups that can grasp a metal ion via a strong chelation,[16] possibly forming a stable 5-membered ring. Therefore, it is suggested that the well-ordered hexagonal mesophase contributes to the strong interaction between Zn^{2+} and ligands. This conclusion is also confirmed by FT-IR spectroscopy (Figure 2). MBH shows the wavenumber shifts at 102 and 10 cm^{-1}, while MBH-S gives rise to the shifts at 114 and 17 cm^{-1} for N−H stretching and bending vibrations. These results confirm that the interaction between Zn^{2+} with ligands in MBH-S is stronger than that in MBH.[17−19]

Generally, several factors can influence the mesophase including surfactant concentration, surfactant packing parameter $g = V/(a_0 l)$, synthetic temperature, etc. Most of these parameters are related to the surfactant template, but there are few examples to control the mesophase by adjusting the interactional style between the species in the framework. In this study, the order

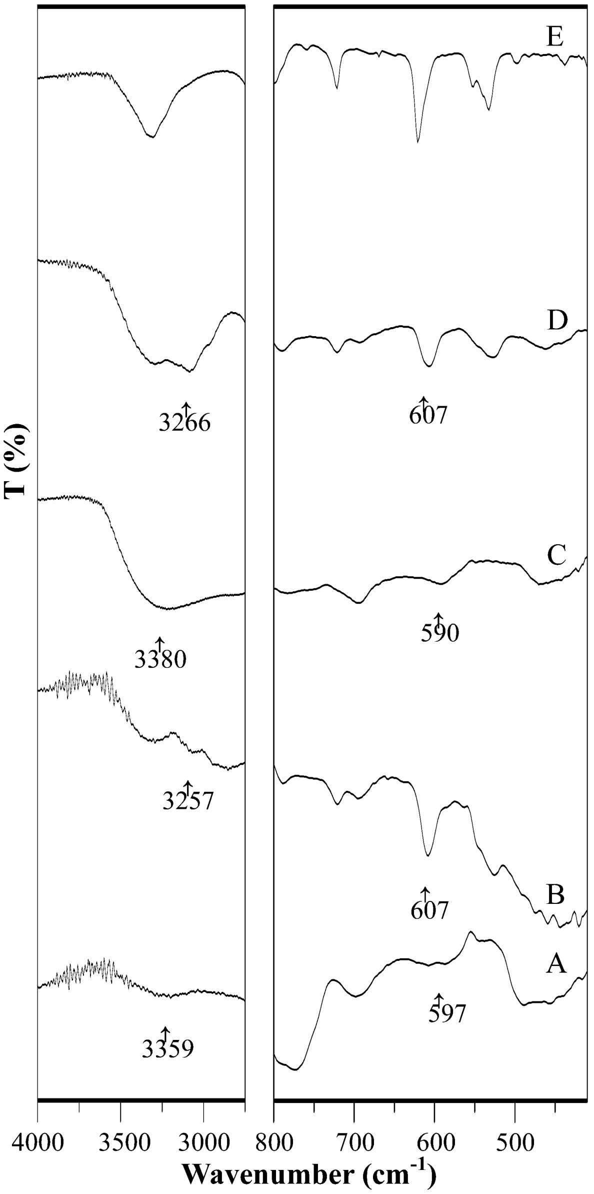


Figure 2. FT-IR spectra of aptes (A), MBH (B), aeaptms (C), MBH-S (D), and SDS (E).

of the mesophase is much improved (from poorly ordered MBH to well-ordered MBH-S) when unidentate ligands are replaced by chelate ligands in the framework, which is an unreported and valuable phenomenon for the mechanistic study of mesoscopic materials. It is proposed that close interaction among the species in the framework is favorable for obtaining better ordered mesophase.

The anion-exchange property of MBH has been reported in our previous paper.[15] It was proposed that the anion-exchange sites in MBH result from the metal cations in the framework originally balanced by the anion surfactant template (SDS^-) and, due to the flexible nature of the framework in MBH, both small anions and bulky anions can easily be exchanged. Since the chemical composition in the framework is $Zn^{2+}(H_2NCH_2CH_2CH_2SiO_{1.5})_4$ and all anion sites in MBH are exchangeable, it is concluded that MBH has a remarkable anion-exchange capacity of 3.9 mmol g $^{-1}$. The as-synthesized MBH is treated by sodium acetate/ethanol solution to make an anion exchange and the resulting material is MBH-Ac. MBH-Ac shows a quite different XRD pattern (Figure 1c) from that of as-synthesized MBH, typical for the 00*l* crystal planes of a layered material.

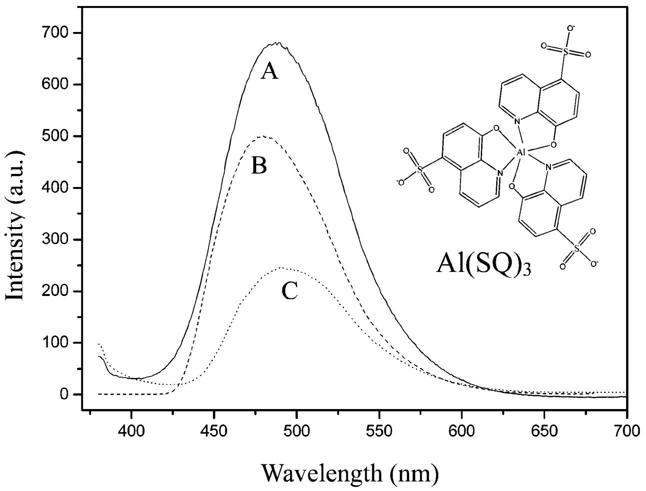


Figure 3. Emission spectra of MBH-S-Al(SQ)$_3$ (A), Al(SQ)$_3$ aqueous solution (B), and Al(SQ)$_3$ solid (C). Inset: molecular structure of Al(SQ)$_3$.

MBH-S has a chemical composition of $Zn^{2+}(H_2NCH_2CH_2HNCH_2CH_2CH_2SiO_{1.5})_2$. When all anion sites in MBH-S are exchanged, it is estimated that MBH-S exhibits a remarkably higher anion-exchange capacity (5.4 mmol g^{-1}) than MBH (3.9 mmol g^{-1}). Furthermore, the anion-exchange capacity of MBH-S is almost unchanged, even after repeated anion-exchange processes (Table 1). The molar ratio of Zn/Si in as-synthesized MBH-S is a little changed from 1/2.2 to 1/2.3 after repeated exchanges, 10 times. In contrast, the molar ratio of Zn/Si in as-synthesized MBH changes to 1/4.5 from the initial ratio 1/3.7 after the sampe process. The stable anion-exchange capacity in MBH-S is attributed to the Zn ions being “grasped” more tightly in MBH-S than in MBH, owing to the different coordination of Zn ions, and the metal ions in MBH-S are so resistant to leaching during the anion-exchange process.

Emission and Absorption Spectroscopy. Figure 3 shows emission spectra of Al(SQ)$_3$ solution and MBH-S-Al(SQ)$_3$ solid. Al(SQ)$_3$ exhibits strong green luminescence under the excitation of UV light (λ_{exc}= 360 nm, Figure 3A),[20] but it is a soluble complex, from which it is difficult to fabricate high-efficiency organic photoelectric devices. To solve the problem, one of the efficient methods is to prepare solid luminescent materials. Considering that MBH-S has good anion-exchange capacity, Al(SQ)$_3$ can be incorporated into the MBH-S by anion exchange, forming solid materials of luminescence. As shown in Figure 3B, MBH-S-Al(SQ)$_3$ shows similar emission spectral features with Al(SQ)$_3$ aqueous solution, suggesting that the emission of MBH-S-Al(SQ)$_3$ is attributed to Al(SQ)$_3$. Interestingly, the emission peak of MBH-S-Al(SQ)$_3$ displays a slightly red shift compared with that of Al(SQ)$_3$ aqueous solution. This is due to the fact that luminescent molecule aggregation takes place in MBH-S-Al(SQ)$_3$ materials. More importantly, luminescent molecules of Al(SQ)$_3$ are easily exchanged into MBH-S, resulting in the formation of water-insoluble solid luminescent material of MBH-S-Al(SQ)$_3$. It is worth noting that MBH-S-Al(SQ)$_3$ exhibits obvi-

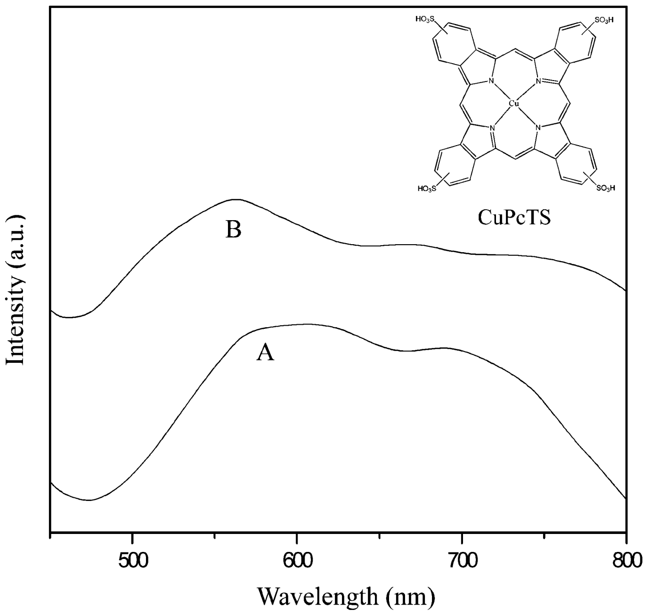


Figure 4. UV−visible diffuse reflectance spectra of MBH-S-CuPcTS (A) and CuPcTS (B). Inset: molecular structure of CuPcTS.

ously stronger emission than pure Al(SQ)$_3$ solid (Figure 3C). The assembly of MBH-S and Al(SQ)$_3$ could enhance the luminescent property.

Figure 4 shows the UV−visible diffuse reflectance spectra of MBH-S-CuPcTS and CuPcTS. MBH-S-CuPcTS and CuPcTS display similar absorption properties in the visible light range. Tris(8-hydroxyquinolinato)aluminum (Alq$_3$), phthalocyanine, and their derivatives are organic semiconductors with high performance and have been used to fabricate organic luminescent devices,[20] organic solar cells,[21] and organic thin-film transistors.[22] Further results for fabrication of MBH-S-Al(SQ)$_3$, MBH-S-CuPcTS, and photophysics properties are in progress.

Conclusion

Upgraded metal cation-mediated bridged hybrid mesoscopic material (MBH-S) is successfully synthesized by replacing initial unidentate ligands with chelating ligands in the framework. Compared to conventional MBH samples, the upgraded MBH-S shows a well-ordered hexagonal mesostructure and a remarkably high anion-exchange capacity. Importantly, the upgraded MBH-S shows good hydrothermal stability and can keep its anion-exchange capacity almost unchanged during repeated ion-exchange procedures, which is very important for this type of material to be used in practical application as an anion exchanger. In addition, organic semiconductor molecules of Al(SQ)$_3$ and CuPcTS can be exchanged into MBH-S, forming composite solids of MBH-S-Al(SQ)$_3$ and MBH-S-CuPcTS, which have very strong green luminescence and visible light absorption properties, respectively.

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