Fabrication of multichannel microtubules by the self-assembly of pyridine-based macrocyclic compounds and their use for heavy metal ion adsorption

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Fabrication of multichannel microtubules by the self-assembly of pyridine-based macrocyclic compounds and their use for heavy metal ion adsorption

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Introduction

Investigation on heavy metal ion adsorption from wastewater has continued to gain tremendous interest in recent decades because of the non-biodegradable and environmentally toxic effects to plants, animals and human beings. Such metal ions can cause mental retardation, brain damage and harmful diseases for human beings (1–4). Usually effective adsorbents for the removal of heavy metal ion from wastewater system are based on pyridine polymers and monomers (5). By alteration of the pyridine-based framework for molecular synthesis, a selective complexation for separation and recovery of metal ions from hydrochloric acid solutions has also been realised (6). Currently, a large number of reports have been contributed to develop heavy metal ion adsorbents including organic and inorganic materials, such as hybrid porous materials with various chemical compositions and organic groups (7), periodic mesoporous titanium phosphonate materials (8), thermoplastic films (9), magnetic porous graphitic carbon (10) and α-FeOOH materials with ordered morphologies (11). In these studies, the materials are generally designed with regular shape to improve the capability for metal ion adsorption prepared by employing complicated synthesis and work-up procedures (12), limiting practical applications. In addition, materials obtained by these techniques typically present pore sizes within several nanometres, which are too small and frequently disadvantageous for improving the capability of metal ion adsorption.

For the preparation of the materials with large pore sizes between 100 nm and 1 mm, the approach using polymer colloidal crystals as templates has been developed (13). The large pores in these materials have been demonstrated to improve the accessibility of reactants to the active sites of the material (14); however, many steps are unavoidable to fabricate them. Variations in the shape and size have a significant effect on the performance of the fabricated adsorbents. Considering the pros and cons of previous reports, we have studied new type of multichannel microtubules (MMTs) as effective adsorbents for the removal of heavy metal ion from wastewater. The MMTs of ~1 μm in the aperture diameter and ~10 μm in length are successfully fabricated via the self-assembly of a series of the pyridine-based macrocyclic compounds (Scheme 1). In order to make the system commercially tangible, the pyridine-based macrocyclic compounds have been synthesised by employing a ‘one-pot’ condensation reaction of di(chlorocarbonyl)pyridine (DCCP) with diamine derivatives in dimethylformamide (DMF). Well controlling over reaction conditions, the main products as a 10-component [5 + 5] reaction are obtained in high yields (Scheme 1). The four-component [2 + 2] or six-component [3 + 3] macrocyclic structures were obtained by the condensation reaction of dimethyl pyridine-2,6-dicarboxylate and diamine derivatives in methanol (15–18).

The self-assembly of low-molecular-weight compounds or polymers for the formation of the practical morphology structures is a simple and economical protocol. After the self-assembly into regular structures...
such as MMTs, the surface area would be greatly increased, so that there are more probability for binding between metal ions and active groups of the MMTs in water. Note that the pyridine-based macrocyclic compounds also present promising performance as anion ligands (19). Therefore, the synthesis of pyridine-based macrocyclic compounds and further fabrication of the MMTs are of great significance in chemistry and engineering areas.

Experimental section

Materials

2,6-Pyridinedicarboxylic acid (99%), pyridine (99.5%), triethylamine (TEA; 95%), ethylenediamine (EDA; 99%), 1,3-diaminopropane (99%), cystamine dihydrochloride, and 1,4-diaminobutane (99%) were obtained from Sigma-Aldrich (St. Louis, USA) and used without further purification. All solvents including DMF, toluene, tetrahydrofuran (THF), chloroform and dichloroethane (DCE), and ethanol were purified before use. Transition metal compounds, Cu$_2$(NO$_3$)$_3$·5H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O and Ni(NO$_3$)$_2$·6H$_2$O, were purchased from Sigma-Aldrich and used without further purification.

Characterisation

$^1$H NMR spectra for all the synthesised samples were recorded using a Varian Unity Plus (300 MHz) spectrometer and fast-atom bombardment (FAB) mass spectra were recorded using a Jeol JMS DX300 apparatus (Jeol, Tokyo, Japan). Elemental composition was determined with the help of a Foss Heraeus Vario EL instrument. UV–vis spectra of the samples were recorded at room temperature using a UV–1650PC apparatus (Shimadzu, Kyoto, Japan). X-ray powder diffraction patterns of the dried and powdered products were measured using a Bruker D8 Focus diffractometer with Cu Kα radiation.

Y-rays were generated from a Cu anode, and the Cu Kα beam (λ = 1.5406 Å) was allowed to pass through a graphite monochromator. The diffraction patterns were recorded in the 2θ range 15°–90° in steps of 0.02° and at a counting time of 2 s/step. The surfaces of the samples were observed by scanning electron microscopy (SEM; S–4800, Hitachi, Tokyo, Japan). For SEM observations, a drop of the sample (ca. 0.1 mg) dispersed in acetone (1 ml) was applied onto a clean silicon wafer and slowly dried in air. Fourier transform infrared (FT-IR) spectra were measured using a Shimadzu IR Prestige–21 apparatus. Differential scanning calorimetry (DSC) analysis was carried out using a TA Instruments Thermal Analyzer (DSC 910) under an ultrapure nitrogen atmosphere at a heating rate of 10°C min$^{-1}$. Thermal analyses were carried out with a DuPont Instruments 951 Thermogravimetric Analyzer; the samples were heated from 20 to 600°C at the rate of 10°C min$^{-1}$ under nitrogen (flow rate: 100 cm$^3$ min$^{-1}$).

Synthesis of macrocyclic decamides

Macrocyclic decamides (MCs) shown in Scheme 1 were synthesised by condensational reactions. All the reaction processes were carried out at room temperature in dry DMF in nitrogen atmosphere, and TEA or pyridine applied for the removal of hydrogen chloride produced during the reaction.

Typically, EDA (10 mmol, 0.60 g) and pyridine (20 mmol, 1.58 g) in DMF (20 ml) were added into two-neck flask (100 ml). The flask was cooled by ice water bath to keep the system temperature lower than 5°C. The 2,6-DCCP (10 mmol, 2.03 g) dissolved in DMF (10 ml) was then injected into the flask in 30 min under vigorous stirring. The reaction was allowed to finish in 2 h after removing ice water bath. The water-insoluble precipitate was washed six times with water to get a pure product, MC-1, as a white powder in 65% yield. MC-2 and MC-3 were synthesised with similar procedures above.
MC-1
A colourless powder; m.p.: >350°C; Td: 379°C; 1H NMR (300 MHz, dimethyl sulfoxide (DMSO)-d6, δ): 9.36–9.51 (d, J = 22.5 Hz, NH–CO), 8.07 (s, –CH–pyridine–C3, C6), 8.00–8.02 (t, J = 6 Hz, –CH–pyridine–C4), 3.46 (s, –CH2–). 13C NMR (75 MHz, DMSO-d6, δ): 166.0, 148.5, 139.3, 123.8, 42.1; IR (KBr); ν = 3326(w), 3519(w), 2948(w), 2874(w), 1674(vs), 1548(vs), 1445(s), 1311(m), 1252(w), 1185(w), 139.8, 124.8, 39.2, 28.3; IR (KBr); 3445(w), 2904(w).

MC-2
A yellow powder; m.p.: >350°C; Td: 374°C; 1H NMR (300 MHz, DMSO-d6, δ): 9.26 (s, NH–CO), 7.9 (s, –CH–pyridine–C3, C4, C5), 3.28 (s, –CH2–). 170 (s, –CH2–). 13C NMR (75 MHz, DMSO-d6, δ): 167.0, 148.7, 139.8, 124.8, 39.2, 28.3; IR (KBr); 3445(w), 2904(w), 1682(w), 1541(s), 1445(s), 1378(w), 1252(w), 1185(w), 1074(w), 1007(m), 844(m), 748(m), 682(m); FAB-MS m/z (%): 957.1 (100) [M + H]+; anal calcd for C45H45N15O10: C 56.50, H 4.68, N 21.78; found C 56.42, H 4.71, N 21.70.

MC-3
A green powder; m.p.: >350°C; Td: 394°C; 1H NMR (300 MHz, DMSO-d6, δ): 9.23–9.30 (d, J = 21 Hz, NH–CO), 8.02–8.03 (d, J = 3 Hz, –CH–pyridine–C3, C4, C5), 3.26–3.28 (m, –CH2–), 1.49–1.50(m, –CH2–). 13C NMR (75 MHz, DMSO-d6, δ): 167.5, 148.7, 139.3, 123.7, 41.2, 28.5; IR (KBr); 3467(vs), 3289(vs), 2941(m), 2859(m), 1660(vs), 1541(vs), 1445(m), 1311(m), 1237(m), 1170(m), 1133(w), 1081(w), 1000(m), 857(m), 748(w), 682(w); FAB-MS m/z (%): 1065.0 [M + K]+; anal calcd for C50H45N15O10: C 58.50, H 5.39, N 20.38; found C 58.45, H 5.78, N 20.80.

Fabrication of the MMTs
Typically, macrocyclic compound (200 mg) was dispersed in DMF/water (100 ml, ratio 7:3 and pH 7.1) under sonication for 40 min in a 150-ml flask. The turbid solution mixture was then heated at 80°C to achieve a clear solution. Slow cooling to room temperature generated a mass of solid, and the solid was collected by filtration for SEM observation.

Molecular dynamics simulations and polymorph prediction
Molecular mechanics calculations were carried out using Materials Studio® v4.3 (20). For all solid-state simulations, the Ewald algorithm (21, 22) was used for the electrostatic and van der Waals interaction terms. Gasteiger charges were used for an initial conformational search. Subsequent calculations used electrostatic potential derived charges.

As the crystal structure prediction method uses a rigid body approximation in the initial search for crystal packing alternatives, it is necessary to carry out an analysis to determine low-energy geometry to be used as input for the packing calculations. The molecules were drawn and geometrical energy minimisation scans were carried out using Forcite module of Materials Studio®. The force field used was DREIDING 2.21 (23) with Gasteiger charges (as implemented in the Materials Studio packages). Initially, geometry optimisation was carried out by using Smart algorithm in Forcite module of Materials Studio (convergence tolerance energy of 2 × 10−5 kcal/mol, force of 0.001 kcal/mol Å−1 and displacement of 1 × 10−5 Å with maximum number of iterations of 500 for an independent optimisation) in the microcanonical ensemble. The optimised low-energy conformations were reoptimised by a molecular dynamics simulation using the same module (simulation length of 5 ps with a 1 fs time step at a temperature of 298 K, taking conformations every 5000 steps). These optimised gas phase conformations were used as the starting points for crystal structure prediction using the Materials Studio Polymorph Predictor (PP) (20, 24).

The PP was set to its default fine setting (this sets the simulated annealing algorithm to a temperature range of 300–100,000 K with a heating factor of 0.025, requiring 12 consecutive steps to be accepted before cooling and a maximum of 7000 steps) with the force field DREIDING 2.21 with Gasteiger charges. The 10 most common space groups found in organic crystals registered in the Cambridge structural database (CSD) were selected (P21/c, P1, P212121, P21, C21/c, Pbcn, Pn221, Pccn, Cc and C2) (25). Clustering of the predicted polymorphs was done using the polymorph clustering routine in Materials Studio, combined with a spreadsheet macro. The Materials Studio® polymorph clustering routine was unable to cluster all the polymorphs generated in this investigation within a reasonable amount of disc space and time. Therefore, the routine was only used to cluster all the polymorphs for each conformation used in the prediction. An excel macro was written which compares the lattice energy and density for each crystal structure, and this macro was subsequently used to cluster the unique polymorphs obtained for the different conformations. The polymorph predictions were repeated two times for each starting conformation to ensure adequate sampling of the crystal configurations.

Metal ion adsorption tests
Heavy metal ion adsorption tests were carried out in a batch mode. Fifty milligrams of self-assembled adsorbents
Results and discussion

Synthesis and characterisation of macrocyclic compounds

Reported method for the synthesis of the pyridine-based macrocyclic compound is to carry out the reaction of diamine with methyl dicarboxylate in methanol yielded macrocyclic tetraamides resulting from a four-component [2 + 2] or a six-component [3 + 3] reaction (15–18). In order to enhance the reactivity, we employed DCCP. With careful control of the temperature and the addition rate of the DCCP, water-insoluble MCs resulting from a 10-component [5 + 5] reaction were obtained in high yields simply by repeated washing with water, affording mass production.

The FT-IR spectra of the MCs showed bands at 3450 and 3410 cm\(^{-1}\) (NH2 stretching) and 1655 cm\(^{-1}\) (NH2 deformation), amide O\(\equiv\)C stretching bands at 1645 and 1682 cm\(^{-1}\), and N–H stretching (3445–3000 cm\(^{-1}\)) and bending (1541–1560 cm\(^{-1}\)) bands, confirming the presence of the amide motif, i.e. O\(\equiv\)C–\(\sim\)NH units. The \(^1\)H NMR spectrum of the MC-1 shows a strong signal at 3.3–3.5 ppm (d), indicating the presence of a singlet methylene. The region between 7.5 and 9.8 ppm shows two sharp multiplets (one due to amidation, and the other due to the addition of pyridine–H). The cyclic structure of MC-1, MC-2 and MC-3 were further confirmed by FAB-MS analysis. For example, the mass spectral information of MC-1 shows that the calculated molecular weight ([M+H]+ 957.1) of MC-1 is in good agreement with the experimental results, demonstrating that MC-1 is not a monochain structure but a macroyclic structure (15–18). Similar results were observed from the FAB-MS analysis of MC-2 and MC-3.

Molecular dynamics simulations and polymorph prediction

Figure 1 shows the macrocyclic crystal structures of the MC-1, MC-2 and MC-3 and their most plausible packing diagrams showing hydrogen bonding patterns predicted by Materials Studio\textsuperscript{8} v4.3. Intermolecular hydrogen bonding interactions between the amido and pyridine groups are observed in all the crystal structures. In addition, NH–NH hydrogen bonds are also observed. The formation of hydrogen bonding chains is the most common pattern. Hydrogen bonding chains propagate infinitely in specific directions through the crystal. These hydrogen bonding interactions that are selective, directional and strongly attractive can induce the self-assembly of predictable supramolecular aggregates (24). The strong tendency of macrocyclic amides to form hydrogen-bonded dimers allows them to be used as sticky sites that compel molecules to associate, thereby driving the self-assembly of aggregates joined by extensive networks of hydrogen bonds. Accordingly, the creative incorporation of multiple sticky sites in rigid frameworks might induce the self-assembly of 3D morphologies.

The lowest energy potential polymorphs from the 10 most common space groups found in organic crystals were predicted by using Materials Studio PP. The top 30 ranked structures were examined for each conformer in all 10 space groups producing a total of 5000 theoretical structures. A lattice energy/density plot of the output revealed a good spread of the data indicating that a well-distributed search of packing space was achieved. The MC-1 and MC-2 molecules are best fitted with P2\(_1\) space group and MC-3 is best fitted with C\(_2\). The density of predicted crystal structure decreases in the order of MC-2 (0.82) > MC-1 (0.62) > MC-3 (0.55) (g cm\(^{-3}\)).

Fabrication of the MMTs

The self-assembly of the MC compounds is expected to be a pH-mediated process due to the presence of amine, amide and pyridine groups. Thus, the self-assembled morphologies of the solution bearing MC compounds might be deeply influenced by the pH value. However, the poor solubility of MC compounds in most organic solvents such as ethanol, THF, DMF, chloroform and DCE limited the investigation on their pH-mediated self-assembly behaviour. In order to search for proper solvents, the self-assembly behaviours were also investigated in organic–inorganic solvent mixtures and DMF/water was chosen as a liquid phase for the self-assembly investigation. The condition is as follow: DMF/water ratio, 7:3; pH 7.1; concentration, 2 mg ml\(^{-1}\). SEM images of air-dried suspensions of MMTs, fabricated by the self-assembly of MCs under conditions of 2 mg ml\(^{-1}\) in DMF/water (7/3, v/v) at pH 7.1 showed the formation of multichannel tube assemblies with a uniform aspect ratio as illustrated in Figure 2. Produced MMTs are \(\sim\)1 \(\mu\)m in channel aperture diameter, \(\sim\)10 \(\mu\)m in length and \(\sim\)3 \(\mu\)m in channel external diameter. The open-ended feature in Figure 2(b),(d),(f) of these morphologies reveals a multichannel tubular structure. Magnified SEM images in Figure 2(b) show a novel rolled-up style of MMT. In contrast to single-channel tubes, which can be formed by rolling up sheets around the both edges seamlesly (26), or most of the lipid nanotubes that involve a helically coiled ribbon structure as an intermediate (27–29), the MMT derived from MC...
were of a scrolling structure formed by rolling up sheets (Figure 2(b)).

Increasing the pH of MC-1 solution to 8.5, organic multilayer structures are formed instead of MMT structures (Figure 3(a)). The organic multilayer structures might be produced from the simple stack of the multiple sheets (Figure 3(b)). MC-1 is more rigid than MC-2 and MC-3 because of the short alkyl chain, so that the intermolecular interactions caused by twisting or rotation of the molecules tend to be relatively weaker. The strong rigidity of MC-1 might limit the sheets to be rolled up or twisted into MMT structures. Self-assembly of MC-2 in the same conditions yields a rice-shaped morphology with narrowed ends as shown in Figure 3(c),(d). The MC-3 with longer alkyl chains self-assemble to give MMT structure, most probably due to the relatively free rolling up of the sheets (Figure 3(e),(f)), even though the MMT structure, such as exterior configuration and size, is much different from those formed at pH 7.1. When the solution pH was controlled at 6.0, no hierarchical structures were observed by the self-assembly of the three MC compounds, since the MC compounds readily form ammonium salts under acidic conditions, weakening or losing intermolecular hydrogen bonds, which may limit the self-assembly behaviour.

Based on all the results above, a plausible mechanism can be proposed for the formation procedure of multichannel tubular structure. As illustrated in Figure 4, the synergistic effects of $\pi-\pi$ stacking and directed intermolecular hydrogen bond firstly induce the hierarchical self-assembly of thin layers. The $\pi-\pi$ overlaps of the pyridine moieties and the translation-related hydrogen bonds of the secondary amides generate strong attractive forces, and are both capable of making MC compounds self-assemble to form monolayered nanosheets (routes a, Figure 4). The layered nanosheets with very high surface areas are unstable and have a strong tendency to either stack to form the belts or to form rolled-up-type microtubules (route b). Both of these procedures can
lower the energies through reducing the surface areas. In a basic condition, the primarily self-assembled sheets have a greater possibility to roll up themselves because of the intermolecular hydrogen bonds. These behaviours are limited in acid condition due to the protonation of the secondary amine, which greatly reduces the hydrogen bonding force. As a result, no specific morphology is observed after the self-assembly.

**Hydrogen bonding investigation**

The FT-IR spectroscopy as a powerful tool for investigating hydrogen bonding interaction has been proverbially applied in the analysis of morphology of self-assembling organic compounds. According to the FT-IR spectroscopy in Figure 5, the characteristic IR bands of the MCs were observed approximately 3319 cm\(^{-1}\) (\(\nu\)NHCO), 2932 cm\(^{-1}\) (\(\nu\)asCH\(_2\)), 2851 cm\(^{-1}\) (\(\delta\)sCH\(_2\)), 1669 cm\(^{-1}\) (\(\nu\)C=O), 1543 cm\(^{-1}\) (\(\nu\)NH) and 1451 cm\(^{-1}\) (\(\delta\)CH\(_2\)). After assembling into MMTs, the peak signals of diversified group assignments show red shift. The peak at 3319 cm\(^{-1}\) for the powdery sample that is assigned to \(\nu\)(N–H) shifts to 3302 cm\(^{-1}\), after forming MMTs. The similar red shifts have also been observed from the absorption bands of the asymmetric (\(\nu\)as) and symmetric (\(\nu\)s) CH\(_2\) stretching vibrations; as a result, the peak at 2932 (\(\nu\)as) for MC-1 shifts to 2923 cm\(^{-1}\) for MMTs. The frequencies of the alkyl chain antisymmetric and symmetric stretching bands are very sensitive to the conformation of the hydrocarbon chain (30). The eigenvalue of the carboxyl group also shifts from 1669 cm\(^{-1}\) (MC-1) to 1653 cm\(^{-1}\) (MMT). These results testify the existence of strong hydrogen bonding interactions between O–C and H–N as well as N–H and N–H bonds which play critical role in the formation of self-assembled MMT aggregates.

Figure 2. SEM images of the self-assembled MMTs: (a,b) from MC-1, (c,d) from MC-2 and (e,f) from MC-3.
Figure 3. (a) SEM image of the self-assembled organic multilayer structures from MC-1, (b) transmission electron microscopy (TEM) image of the organic multilayer structures from MC-1; (c,d) SEM image of the self-assembled rice-shaped structure from MC-2; (e, f) SEM image of the self-assembled multichannel morphology from MC-3. All the self-assemblies were carried out in DMF/water (7/3, v/v) at pH 8.5.

Figure 4. Plausible mechanism for the formation of self-assembled rolled-up MMTs: (a) primary self-assembly of MC by combined π–π stacking of pyridine units with intermolecular hydrogen bonding between amido functional groups and pyridine units, (b) secondary assembly is the rolling up of the resulting supramolecular monolayer sheets to form microtubules and (c) the stacking of the microtubules to form the MMTs.
Heavy metal ion adsorption

Since the MMTs contain pyridine and functional amido groups in the framework, which can be an anionic ligand for attracting heavy metal ions, they might be used as efficient adsorbents for metal ion removal from the water, and thus their performance for heavy metal ion adsorption was studied. The capability of the MMTs to remove Cu$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$ ions from the solution was tested by simply stirring the MMTs in the aqueous solution of the metal ions. The MMT (Figure 2(a)) obtained by the self-assembly of MC-1 at pH 7.1 was chosen for the test. After filtration, wash and dryness of the ion-bearing MMT, the metal element in MMTs was analysed by energy-dispersive X-ray spectroscopy (EDX) indicating the metal ion adsorption (Figure 6). The ion-bearing MMT was also measured by UV-vis spectrometer (Figure 7). There are no absorptions in 700–900 nm for the pure MMTs; however, new absorption bands are observed in 700–900 nm for MMTs-Cu$^{2+}$, 700–800 nm for MMTs-Zn$^{2+}$ and 600–800 nm for MMTs-Ni$^{2+}$, proving the adsorption of heavy metal ions to MMT.

The detailed results of the metal ion adsorption tests are also summarised in Table 1. The MC-1 compound before the self-assembly was also applied to the metal ion adsorption tests for comparison. The adsorption capacity of the MMT is calculated to be 0.107, 0.045 and 0.042 mmol/g–MMT for Cu$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$, respectively. In case of the MC-1 solid, the adsorption capacity was 0.081, 0.022 and 0.032 mmol/g–MMT for Cu$^{2+}$, Ni$^{2+}$ and Zn$^{2+}$, respectively. A series of data reveal that the adsorption capacity of the MMT is much higher than that of the MC-1. The MMT presents the best adsorption to Cu$^{2+}$ and the percentage ions removed reach 62.5%, while it is 30.0% for Zn$^{2+}$ and 32.4% for Ni$^{2+}$.

The adsorption processes for metal ions are affected by several factors such as initial metal ion concentration, sorption capacity, contact time, sorbent doses and the chemical stability of sorbents. The contact time required to reach equilibrium is an important parameter for the separation of metal ions. In order to make sure that the equilibrium was completely reached, a series of experiments regarding contact time were carried out at the initial
metal ion concentration of 0.008 mmol/ml (Figure 8). The Y-axis represents the remained metal ions concentration in water (Figure 8(a)). A fast adsorption process is observed in 30 h and then reached asymptotic value. The adsorption capacity (Cu$^{2+}$, Zn$^{2+}$ and Ni$^{2+}$) of MMTs is nearly balanced in 140 h. The investigations also reveal that the adsorption efficiency of MMTs is slightly influenced by initial concentration of the metal ions within enough adsorption time (160 h; Figure 8(b)). An increased adsorption efficiency of MMTs is only observed while the initial concentration is below 0.009 mmol/ml. Above this concentration, there is negligible influence on metal ion adsorption efficiency of MMTs. Therefore, in order to increase the metal ion adsorption efficiency of MMTs, properly extending the adsorption time is of great significance.

**Conclusion**

A series of pyridine-based MCs were synthesised in high yields by employing one-pot protocol and their self-assembling behaviours were investigated in DMF/H$_2$O at various pH conditions. An interesting multichannel tubular morphology was constructed via the self-assembly of MCs at pH 7.1 and 8.5 due to the synergistic effects of π–π stacking and directed intermolecular hydrogen bonds. The multichannel tubular structure with enhanced surface area exhibited promising performance on the removal of the heavy metal ions from water. The order of the adsorption capability to metal ions are Cu$^{2+}$ > Zn$^{2+}$ > Ni$^{2+}$. Extending the adsorption time helps to increase the adsorption capability of MMTs to all metal ions used here.

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### Table 1. Results of metal ions adsorption of the self-assembled MMT and MC-1 compound.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Cu$^{2+}$ (x 10$^{-2}$ mmol/g)</th>
<th>Zn$^{2+}$ (x 10$^{-2}$ mmol/g)</th>
<th>Ni$^{2+}$ (x 10$^{-2}$ mmol/g)</th>
<th>Cu$^{2+}$ removed (%)</th>
<th>Zn$^{2+}$ removed (%)</th>
<th>Ni$^{2+}$ removed (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MMT</td>
<td>10.7</td>
<td>4.2</td>
<td>4.5</td>
<td>62.5</td>
<td>30.0</td>
<td>32.4</td>
</tr>
<tr>
<td>MC-1</td>
<td>8.1</td>
<td>2.2</td>
<td>3.2</td>
<td>46.8</td>
<td>16.7</td>
<td>23.5</td>
</tr>
</tbody>
</table>
However, it is incapable to enhance the adsorption efficiency of MMTs by just increasing initial concentration of the metal ions.

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