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Construction of Cucurbit[7]uril Based Tubular Nanochannels Incorporating Associated $[CdCl_4]^{2-}$ and Lanthanide Ions

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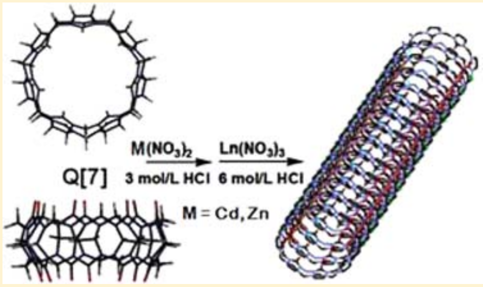
S Supporting Information

ABSTRACT: There is intensive interest in the design of tubular channels because of their novel structures and various applications in a variety of research fields. Herein, we present a series of coordination-driven Q[7]-derived organic nanochannels using an anion-induced strategy under different acid concentrations. An advantage of this approach is that the tubular channels not only retain the original character of the parent macrocyclic receptors but also provide deep hydrophobic cavities possessing guest binding sites. Importantly, this study also emphasizes the efficiency of the macrocyclic receptors in providing a tubular hydrophobic cavity by directly stacking on top of one another with the anion-fixed and by acid control. The resulting combination of hydrogen bonding, C−H···Cl, and ion-dipole interactions helps to stabilize these supramolecular architectures. Such systems are both tunable and versatile and allow for interconvertibility in the construction of nanochannels based on these macrocyclic receptors.



INTRODUCTION

Nanotubular materials have attracted considerable interest because of their novel structures and potential applications in chemistry, biology, and material science.[1] For example, such molecular sized containers can influence the properties, stability, and the reactivity of encapsulated or absorbed molecules with high regio- and stereoselectivity[2] and give important clues that extend our basic understanding of chemical processes.[3] Accordingly, the creation and construction of hollow tubular structures by the noncovalent self-assembly of appropriate organic units has been an important subject for supramolecular chemists over recent decades. Among the approaches adopted, the use of macrocycles to form nanotubular materials has a number of advantages over the use of smaller linear building blocks. For example, such macrocycles can inhibit interpenetration and can lead to a cavity with predetermined dimensions. Indeed, in this regard, the self-assembly of cyclic peptides,[4] bis-urea macrocycles,[5] cyclodextrins,[6] calixarenes,[7] and others[8] has been successfully documented. However, it is often difficult to control and tailor the macrocycles, especially when using classic macrocyclic receptors to form a tubular cavity via stacking. The difficulties arise from the need for a complementary ligand/cation pair, which are capable of offering reversible and mutually favorable interconnections. In practice, the situation can be influenced by many factors,[9] such as differing coordination geometry or radius of metal ions[10] or counter-anions,[11] as well as steric bulk,[12] solvent,[13] metal−ligand ratio,[14] and the pH of the system.[15] As a result, macrocyclic receptors have usually been used as channel skeletons, and only a few examples have been reported involving the construction of nanochannels formed by utilizing their own inner rigid cavities.[16] The inner cavity size of classic macrocyclic molecules, such as cucurbit[n]urils (Q[n], n = 5−10),[17] is in the range 4.4−12.6 Å, which is the same as most of the channel sizes established for small molecule systems. For example, Q[10], the largest homologue of the Q[n] series, can have an equatorial width of up to 12.6 Å and can easily accommodate Q[5] within its cavity.[18] Therefore, it would be interesting to develop a synthetic approach for the construction of tubular structures possessing inner cavities by self-assembly of macrocyclic receptors, while at the same time retaining or even improving the properties of each of the components.

From a structural viewpoint, the rigid hydrophobic cavities generally have a common depth (9.1 Å), and the two identical carbonyl-laced portals of the Q[n]s make them suitable molecular building units for the assembly of inorganic−organic coordination tubes. However, owing to the weak coordination ability of the carbonyl group, the cucurbituril-based tubular structures assembled thus far are mainly either assembled through hydrogen bonding interactions involving the terminal carboxy groups of adjacent cucurbiturils or via a pair of cations connected to the terminal carboxyl groups of adjacent Q[n]s.[19]

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Herein, we report a promising synthetic approach for building novel coordination-driven nanotubular channels using the inner cavity of Q[7] in a controlled fashion in aqueous solution.

■ EXPERIMENTAL SECTION

Synthesis. Chemicals, such as $Ln(NO_3)_3$, $Cd(NO_3)_2$, HCl solution, and HNO_3 solution, were of reagent grade and were used without further purification. The compound Q[7] was prepared by the reported procedure.[17a,b]

Preparation of {Cd-Q[7]} (00). To a mixture of Q[7] (20.0 mg, 0.015 mmol) and an 8-fold amount of $Cd(NO_3)_2 \cdot 4H_2O$ (36.8 mg, 0.12 mmol) was added 3 mL of 3.0 mol/L HCl with stirring until all components were dissolved at room temperature. The solution was sealed and kept at room temperature over two days; colorless crystals were obtained from the solution and the yield in terms of Q[7] was in the range 60−80%.

Preparation of {Ln-Q[7]-Cd}. In the present work, the $[CdCl_4]^{2-}$-triggered Ln-Q[7] complexes can be catalogued into three groups based on the crystal system, space group, and the unit cell parameters of the corresponding crystal structures. In each group, the compounds are isomophous. In group I, the isomophous compounds were formulated as $\{La_2(H_2O)_{12}Q[7])\} \cdot (CdCl_4)_3 \cdot 6Cl \cdot 50(H_2O)$ (**01**) and $\{Tb_2(H_2O)_{10}Q[7]\} \cdot CdCl_4 \cdot 4Cl \cdot 40(H_2O)$ (**08**). In group II, the isomophous compounds were formulated as $\{Ce_2(H_2O)_{12}Q[7]\} \cdot (CdCl_4) \cdot 4Cl \cdot 43(H_2O)$ (**02**), $\{Pr_2(H_2O)_{12}Q[7]\} \cdot (CdCl_4) \cdot 4Cl \cdot 40(H_2O)$ (**03**), $\{Nd_2(H_2O)_{12}Q[7]\} \cdot (CdCl_4) \cdot 4Cl \cdot 55(H_2O)$ (**04**), $[Sm_2(H_2O)_{10}Q7] \cdot CdCl_4 \cdot 4Cl \cdot 34(H_2O)$ (**05**), $[Eu_2(H_2O)_9ClQ7] \cdot CdCl_4 \cdot 3Cl \cdot 32(H_2O)$ (**06**), $[Gd_2(H_2O)_{10}Q7] \cdot CdCl_4 \cdot 4Cl \cdot 43(H_2O)$ (**07**), $[Dy_2(H_2O)_{10}Q7] \cdot CdCl_4 \cdot 4Cl \cdot 59(H_2O)$ (**09**), $[Ho_2(H_2O)_{10}Q7] \cdot CdCl_4 \cdot 4Cl \cdot 50(H_2O)$ (**10**), $[Er_2(H_2O)_{10}Q7] \cdot CdCl_4 \cdot 4Cl \cdot 44(H_2O)$ (**11**), and $[Tm_2(H_2O)_{10}Q7] \cdot CdCl_4 \cdot 4Cl \cdot 42(H_2O)$ (**12**). In group III, the isomophous compounds were formulated as $[La(H_2O)_5(Q7)] \cdot 2(CdCl_4) \cdot (H_3O)^+ \cdot 17(H_2O)$ (**01′**), $[Ce(H_2O)_5Q7] \cdot 2(CdCl_4) \cdot (H_3O)^+ \cdot 21(H_2O)$ (**02′**), $[Pr(H_2O)_5Q7] \cdot 2(CdCl_4) \cdot (H_3O)^+ \cdot 39(H_2O)$ (**03′**), $[Nd(H_2O)_5Q7] \cdot 2(CdCl_4) \cdot (H_3O)^+ \cdot 37(H_2O)$ (**04′**), $[Eu(H_2O)_4Q7] \cdot 2(CdCl_4) \cdot (H_3O)^+ \cdot 46(H_2O)$ (**06′**), and $[Dy(H_2O)_4Q7] \cdot 2(CdCl_4) \cdot (H_3O)^+ \cdot 18(H_2O)$ (**09′**). All compounds in groups I and II were obtained under identical conditions, as exemplified for M = La. To a mixture of Q[7] (20 mg, 0.015 mmol) and an 8-fold amount of $Cd(NO_3)_2 \cdot 4H_2O$ (36.8 mg, 0.12 mmol) was added 3 mL of a 6.0 mol/L HCl solution with stirring until all components were dissolved at room temperature, and then an 8-fold amount of $La(NO_3)_3 \cdot 4H_2O$ (51.6 mg, 0.12 mmol) was added to the solution. The solution was sealed and kept at room temperature overnight in the case of **01**-**06** and over one week in the case of **07**-**012**. Colorless crystals were obtained from the solution, and the yields in terms of Q[7] were in the range 60−80%. X-ray and elemental analysis results for compounds **01**-**12** are given in Tables S1 and S2.

Similarly, all compounds of group III were obtained under identical conditions, as exemplified for M = La. To a mixture of Q[7] (20 mg, 0.015 mmol) and an 8-fold amount of $Cd(NO_3)_2 \cdot 4H_2O$ (36.8 mg, 0.12 mmol) was added 3 mL of a 3.0 mol/L HCl solution with stirring until all components were dissolved at room temperature, and then an 8-fold amount of $La(NO_3)_3 \cdot 6H_2O$ (51.6 mg, 0.12 mmol) was added. The solution was sealed and kept at room temperature for 12 h in the case of **01′**-**04′** and **06′** and for one week in the case of **09′**. Colorless crystals were obtained from the solution, and the yields in terms of Q[7] were in the range 60−80%. X-ray and elemental analysis results for these compounds are given in Tables S1 and S2.

X-ray Crystallography. A suitable single crystal (~0.2 × 0.2 × 0.1 mm^3) was picked up with paratone oil and mounted on a Bruker SMART ApexII CCD diffractometer equipped with a graphite-monochromated Mo $K\alpha$ ($\lambda = 0.71073$ Å, $\mu = 0.828$ mm^{-1}) radiation source in the ω scan mode and a nitrogen cold stream (−50 °C). The data were corrected for Lorentz and polarization effects (SAINT),[21a] and semiempirical absorption corrections based on equivalent reflections were applied (SADABS).[21a] The structure was elucidated by direct methods and refined by the full-matrix least-squares method on F^2 with the SHELXS-97 and SHELXL-97 program packages respectively.[21b,c] All the non-hydrogen atoms were refined anisotropically, and the carbon-bound hydrogen atoms were introduced at calculated positions and were treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. Analytical expressions for neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Because the focus here is on the coordination of metal ions to the portal carbonyl oxygen atoms, most water molecules in the unit cell have been taken into account using the SQUEEZE option of the PLATON program, except the coordinated water molecules. Details of the crystal parameters, data collection conditions, and refinement parameters for the twenty compounds are summarized in Tables S1 and S2. In addition, the crystallographic data for the reported structures were recorded in the Cambridge Crystallographic Data Centre as CCDC numbers 875294 (**00**), 875295 (**01**), 875296 (**01′**), 875297 (**02**), 875298 (**02′**), 875299 (**03**), 875300 (**03′**), 875301 (**04**), 875302 (**04′**), 875303 (**05**), 875304 (**06**), 875305 (**06′**), 875354 (**07**), 875306 (**08**), 875307 (**09**), 875308 (**09′**), 875309 (**10**), 875355 (**11**), 875310 (**12**), and 875311 (**13**). These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc. cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Crystal of {Nd-Q[7]} in CH_3COOH Solution. To a mixture of Q[7] (20 mg, 0.015 mmol) and an 8-fold amount of $Cd(NO_3)_2 \cdot 4H_2O$ (36.8 mg, 0.12 mmol) was added 3 mL of a 6.0 mol/L CH_3COOH solution with stirring until all the components were dissolved at room temperature, and then an 8-fold amount of $Nd(NO_3)_3 \cdot 4H_2O$ (52.0 mg, 0.12 mmol) was added to the solution. The solution was sealed and kept at room temperature over one week. Colorless crystals were obtained from the solution, and the yield in terms of Q[7] was 67%. Anal. Calcd. ($C_{46}H_{92}N_{29}NdO_{43}$): C, 29.33; H, 4.92; N, 21.56; Found C, 29.17; H, 4.78; N, 21.71 (%). Crystal data: $M = 1883.73$; crystal system: orthorhombic; space group: *Pbca*; $a = 26.8431(13)$, $b = 16.8269(8)$, $c = 33.7960(16)$ Å; $\alpha = 90.00°$, $\beta = 90.00°$, $\gamma = 90.00°$; $V = 15265.2(13)$ Å^3; $Z = 8$; $D_c = 1.639$ g cm^{-3}; crystal dimensions 0.27 × 0.21 × 0.18 mm^3; $T = 293(2)$ K; $R_{int} = 0.0696$, R $[I > 2\sigma(I)]^a = 0.0509$ for 10689 unique reflections. Crystallographic data (excluding structure factors) for the structure reported have been deposited with the Cambridge Crystallographic Data Centre: CCDC-893410. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Crystal of {La-Q[7]-Zn}. To a mixture of Q[7] (20 mg, 0.015 mmol) and an 8-fold amount of $Zn(NO_3)_2 \cdot 4H_2O$ (32.0 mg, 0.12 mmol) was added 3 mL of a 6.0 mol/L HCl solution with stirring until all components were dissolved at room temperature, and then an 8-fold amount of $La(NO_3)_3 \cdot 4H_2O$ (51.6 mg, 0.12 mmol) was added to the solution. The solution was sealed and kept at room temperature over one week. Colorless crystals were obtained from the solution and the yield in terms of Q[7] was 71%. Anal. Calcd. ($C_{42}H_{128}Cl_{10}La_2N_{28}O_{57}Zn_2$): C, 18.68; H, 4.78; N, 14.52; Found C, 18.81; H, 4.71; N, 14.61 (%). Crystal data: $M = 2700.78$; crystal system: triclinic; space group: *P*-1; $a = 17.1365(14)$, $b = 17.9392(15)$, $c = 18.5138(15)$ Å; $\alpha = 104.378(3)$, $\beta = 102.328(3)°$, $\gamma = 110.919(3)°$; $V = 4854.1(7)$ Å^3; $Z = 2$; $D_c = 1.848$ g cm^{-3}; crystal dimensions 0.31 × 0.29 × 0.26 mm^3; $T = 223(2)$ K; $R_{int} = 0.0779$, R $[I > 2\sigma(I)]^a = 0.0512$ for 12437 unique reflections. Crystallographic data (excluding structure factors) for the structure reported have been deposited with the Cambridge Crystallographic Data Centre: CCDC-893409. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

■ RESULTS AND DISCUSSION

Previously, we found that hydronium dichloroferrate chloride can form an adduct with Q[6]; however, there was no direct coordination with the portal carbonyl oxygen atoms. Instead, it formed a novel supramolecular architecture comprising *trans*-$[FeCl_2(H_2O)_4]^+$@Q[6] and an unexpectedly highly symmetrical one-dimensional Q[6]-based chain formed by the linkage of cyclic hexameric water clusters.[20] The hydronium dichloroferrate cations in the architecture were arranged such that they produced a honeycomb framework with linear, hexagonal channels via hydrogen bonding to the counteranion and lattice water molecules. The symmetric Q[6]-based chains filled the hexagonal channels (Figure 1 and Figures S1−S3).

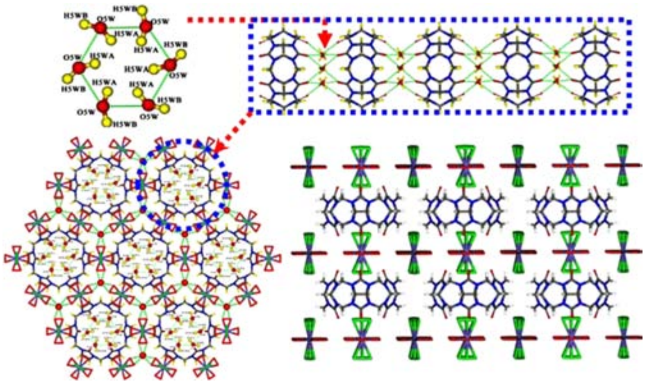


Figure 1. Tubular structure and honeycomb framework formed by water cluster and hydronium dichloroferrate cations.

This result prompted us to investigate if metal ions could coordinate to a larger homologue of Q[n] such as Q[7], thereby displacing the water cluster, in the expectation that hollow channels would result within the inner cavity of Q[7]. Given this, the approach adopted here was to use one kind of metal ion to build the framework or network and to employ a second type of metal ion to coordinate with the carbonyl atoms on the Q[7] receptors.

After screening various transition metal salts with Q[7] in hydrochloric acid solution, it was discovered that the cadmium cation in the form of the tetrachloride, *i.e.* $[CdCl_4]^{2-}$, could be arranged into honeycomb hallows, with the Q[7] forming a zigzag supramolecular chain in the hallows via a C−H···Cl interaction and metal coordination (Scheme 1a). Numerous attempts to grow single crystals of lanthanide metal ions complexed with Q[7] in various acidic media were unsuccessful. When the lanthanide cations were introduced into the original $[CdCl_4]^{2-}$-Q[7] hydrochloric acid solution, linear coordination nanochannels of lanthanide/Q[7] can easily be obtained. Interestingly, the nanochannel shapes could be finely tuned by the lanthanide metal ions when under high acid concentration. As shown in Scheme 1, in the presence of $[CdCl_4]^{2-}$ dianions, the lanthanide cations coordinated with Q[7] to form zigzag channels when in weakly acidic (HCl) media (<3.0 mol/L) (Scheme 1b) but when in stronger acidic media (>3.0 mol/L) formed tubular channels (Scheme 1c).

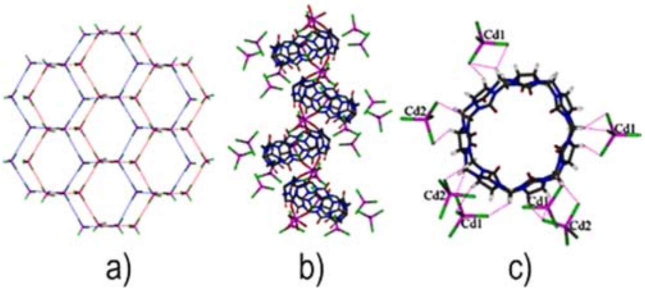
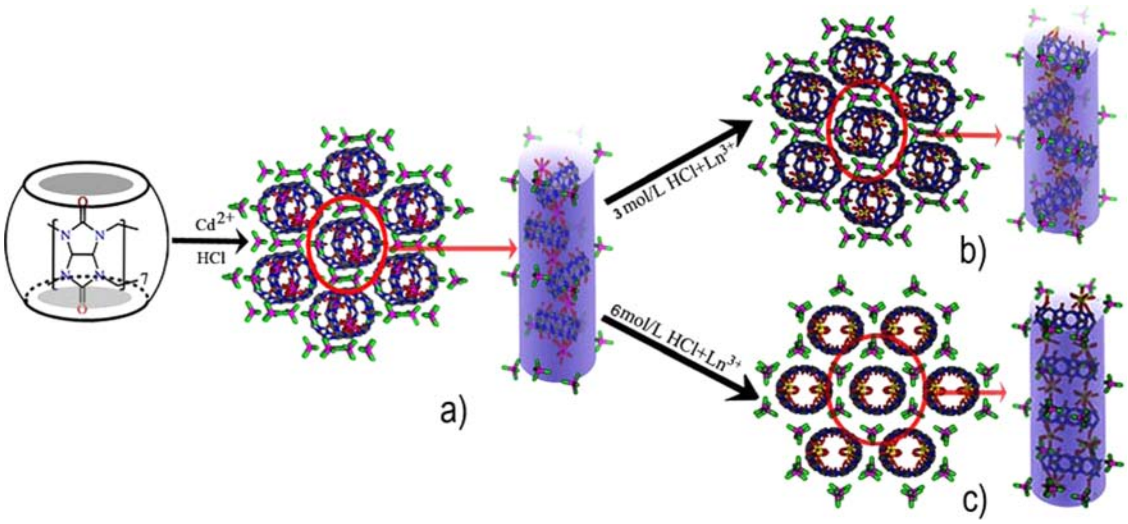


Figure 2. (a) The $[CdCl_4]^{2-}$-based honeycomb-like frameworks (the filled Q[7] molecules are omitted for clarity); (b) side view of a channel filled with Q[7] molecules; (c) the interactions between a Q[7] molecule with seven $[CdCl_4]^{2-}$ dianions via C−H···Cl and ion-dipole interactions.

The complexation of macrocyclic receptor Q[7] with 8.0 equivalents of $CdCl_2$ in a 3.0 mol/L HCl solution over two days generated diamond-like colorless single crystals. These crystals were subjected to single crystal X-ray diffraction (Figure 2), which revealed that a $[CdCl_4]^{2-}$-induced honeycomb-like framework had formed in the solid-state structure and that the Q[7] molecules filled the hexagonal hollows in a zigzag manner (Figures 2a and 2b). It appears that the water molecules in the

Scheme 1. (a) $[CdCl_4]^{2-}$-Based Honeycomb Architecture with Linear, Hexagonal Channels Filled with Q[7] Molecules in a Zigzag Manner and $[CdCl_4]^{2-}$-Induced Coordination and Self-Assembly of Lanthanide Ions to Cucurbit[7]urils in (b) Zigzag and (c) Tubular Channels



crystal structure do not contribute much to the honeycomb-like framework; little hydrogen bonding was observed in the crystal structure. The structure did reveal that seven $[CdCl_4]^{2-}$ dianions surrounded a Q[7] molecule via C−H···Cl interactions (Figure 2c), with Cl−H distances in the range 2.767−2.946 Å. Notably, as shown in Figure 3 and Figure 4, in 3.0 mol/L HCl solutions of $CdCl_2$, each La^{3+} cation rather than a Cd^{2+} is directly coordinated to the four carbonyl oxygen atoms on the two neighboring Q[7] molecules, as well as four water molecules (Figure 3a and Figure 4a). The distances for La−O (carbonyl oxygen) are in the range 2.431−2.514 Å, and the distances for La−O (water molecules) are in the range 2.512−2.807 Å. By contrast, in the case of 6.0 mol/L HCl solutions of Cd^{2+}, the repeat unit contained two La^{3+} cations which were sandwiched by two neighboring Q[7] molecules and coordinated with three carbonyl oxygen atoms on two adjacent Q[7] receptors and six water molecules to form tubular nanochannels with the assistance of hydrogen bonding, C−H···Cl contacts, and ion-dipole interactions. The distances for the La−O (carbonyl oxygen) are in the range 2.461−2.544 Å, and the distances for La−O (water molecules) are in the range 2.553−2.633 Å (Figure S4).

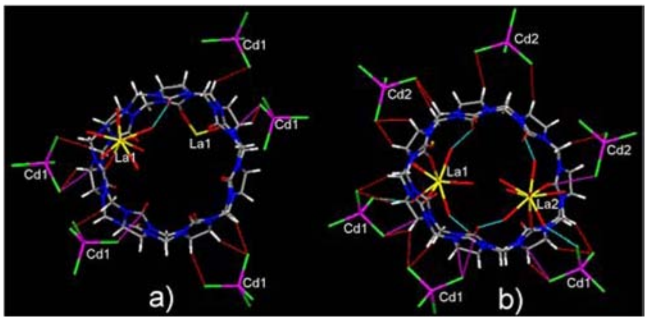


Figure 3. (a) Coordination details of La^{3+} to Q[7] molecules in 3.0 mol/L hydrochloric acidic media, 5 $[CdCl_4]^{2-}$ dianions with a total of 8 C−H···Cl contacts (red), 3 ion-dipole interactions (magenta), and 1 hydrogen bond (green) have been located for each Q[7]; (b) coordination details of La^{3+} to Q[7] molecules in 6.0 mol/L hydrochloric acidic media, 6 $[CdCl_4]^{2-}$ dianions with a total of 15 C−H···Cl contacts (red), 5 ion-dipole interactions (magenta), and 5 hydrogen bonds (green) have been located for each Q[7].

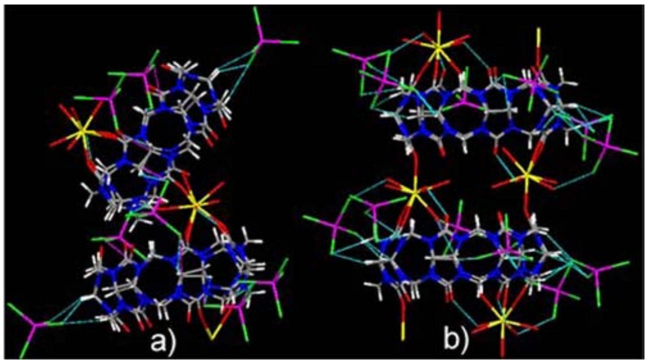


Figure 4. Coordination supramolecular architectures stabilized by hydrogen bonding, C−H···Cl and ion-dipole interactions: (a) details of La^{3+} to Q[7] molecules in a zigzag manner; (b) details of La^{3+} to Q[7] molecules in a tubular manner.

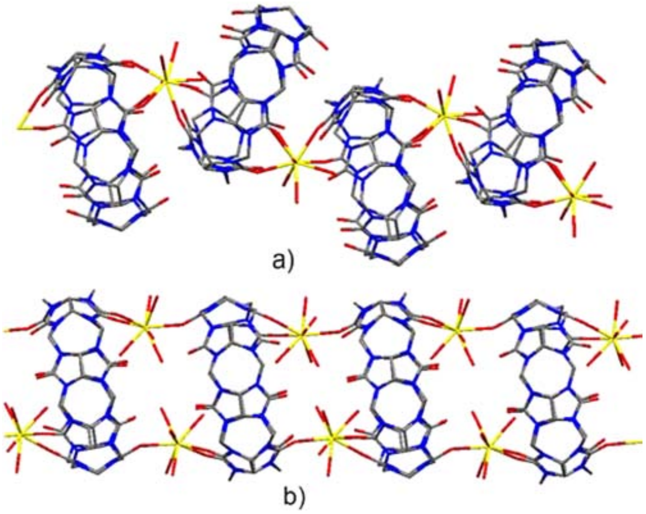


Figure 5. $[CdCl_4]^{2-}$ dianions induced Ln^{3+} cation coordination based Q[7] derived channels in different hydrochloric acidic concentration: a) zigzag fashions; b) tubular fashions. Hydrogen atoms, solvate water molecules, and $[CdCl_4]^{2-}$ dianions are omitted for clarity.

Control of the channel shapes (Figure 5) at different acid concentrations may be attributed to the high proton environment which can lessen the negative repulsive effects of the carbonyl oxygen atoms on two adjacent portals of the host receptor and thereby contributes to the coordination of La^{3+} with Q[7]. The thermal stability of these two types of channels was examined by thermal analysis including differential scanning calorimetry (DSC) and thermogravimetry (TG). As shown in Figure 6 and Figure S5, both channels display high thermal stability. The DSC with TG curves clearly suggested that the water molecules of crystallization were first eliminated with a weight loss of 14.13% (calcd 14.60%) and 16.10% (calcd 17.34%) for the zigzag and tubular nanochannels, when the temperature was increased from room temperature to about 81.7 and 85.4 °C, respectively. No further weight loss was observed until the temperature reached 380 °C. Compared to the decomposition temperature of the single Q[7] molecules at 367.1 °C, the final decomposition temperature of the zigzag and tubular channels reached 470.2 and 480.9 °C, respectively. These results indicated that the metal coordination-based channel polymers are highly stable. On comparison of the FT-IR spectra of the Q[7] molecules before and after coordination

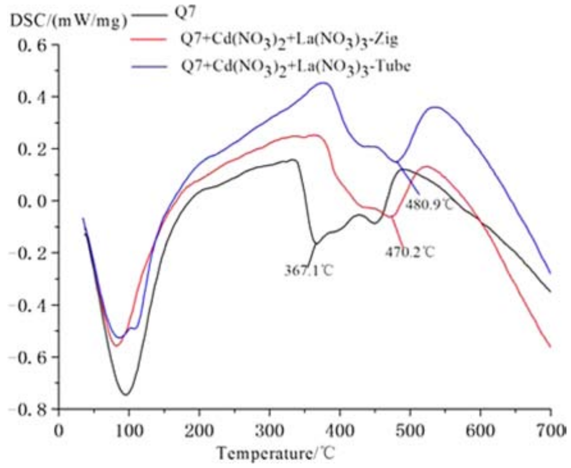
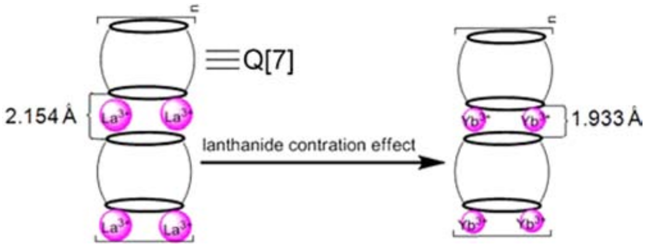


Figure 6. Thermal analysis of $[CdCl_4]^{2-}$ induced La^{3+} cation coordination-based Q[7]-derived channel structures.

with the metal ions (Figure S6), it can see that the vibration of the portal carbonyl of Q[7] shifts by up to 4−9 cm^{-1} in the presence of Cd^{2+} and La^{3+} ions compared to that of the free Q[7]. Additionally, the structures of these two type channels were further characterized and evaluated by X-ray powder diffraction analysis (Figure S7), the results of which were consistent with their crystal structures.

As mentioned previously, the coordination-based inorganic−organic architectures can be influenced by the ionic radius. Therefore, the role of other lanthanide cations in the construction of such macrocyclic receptor derived channels has been studied. The single crystal X-ray diffraction studies suggested that similar coordination behavior and tubular structures could be observed and constructed by other Ln^{3+} metal ions under the same conditions (Tables S1−2 and Figures S8−S9). Although the isomorphous compounds in the respective channels showed almost exactly the same structural features, the differences in these isomophous compounds could still be distinguished by the slightly differing ionic radii of the lanthanides. For example, there are two different distances for each coordinated Ln^{3+} cations to the portal planes of the neighboring Q[7] molecules in both of the zigzag or tubular channels (Figure S9). The average of these two distances versus the atomic number could be used to identify the different isomorphous compounds with the same channels. It can be seen that the average distances decreased on increasing the atomic number of the lanthanides in the respective compounds, which is in line with the lanthanide contraction effect (Scheme 2). However, attempts to grow single crystals of the lutecium metal ions complex with Q[7] molecules under the same conditions were unsuccessful. We supposed that this may be ascribed to the shortest ionic radius of Lu^{3+} cations (0.85 Å), which is slightly smaller than the critical radius required to stabilize and balance the coordination force to two neighboring carbonyl portals of Q[7]s.

Scheme 2. Schematic of the Lanthanide Contraction Effect Controlled Distance of the Two Adjacent Portals of Q[7]s in the Tubular Channels



In order to further evaluate the effect on the construction of nanochannels by Q[7] in the absence and presence of $[CdCl_4]^{2-}$ dianions, other acids such as HF, HI, HNO_3, and CH_3COOH were employed under various proton concentrations. For example, the addition of 8.0 equivalents of neodymium nitrate to the 6.0 mol/L CH_3COOH solutions of Cd^{2+} afforded an opened molecular capsule, as shown in Figure 7. There is only one crystallographically independent Nd^{3+} ion, which was captured and coordinated by two carbonyl atoms of Q[7] accompanied by five coordinated water molecules as well as one nitrate anion. Additionally, two CH_3COO^- anions were encapsulated in the cavity of the Q[7] molecules. Most importantly, it should be noted that the tubular channels based on (induced by) the cadmium ions have not been observed in the present system. This result suggested that counteranions such as chloride play an important role (perhaps greater than acid concentration effects) in the construction of Q[7] derived nanochannels. Experiments were also designed and adapted for the Zn^{2+} ion in the same system taking into account its similar physical and chemical properties to the Cd^{2+} cation. Upon addition of $La(NO_3)_3$ to various acid solutions of differing concentration, in the presence of Zn^{2+} ions, it was found that a similar tublar nanochannel can be formed by Q[7]s with La^{3+} cations in the presence of Zn^{2+} ions, *viz.* $[ZnCl_4]^{2-}$ dianions though hydrogen bonding, C−H···Cl, and ion-dipole interactions in the hydrochloric acid solution (Figures S10−12). These results indicated that the present divalent metal chloride dianions play a key role in the formation of coordination-based nanochannels by such macrocyclic receptors (Figure 8).

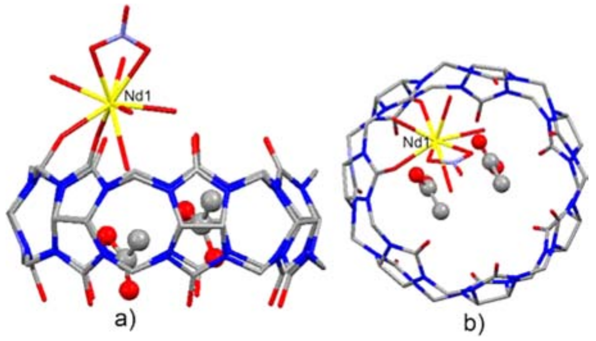


Figure 7. Coordination structure of Nd^{3+} with Q[7] molecules in CH_3COOH media in the presence of $Cd(NO_3)_2$. Hydrogen atoms and solvate water molecules are omitted for clarity.

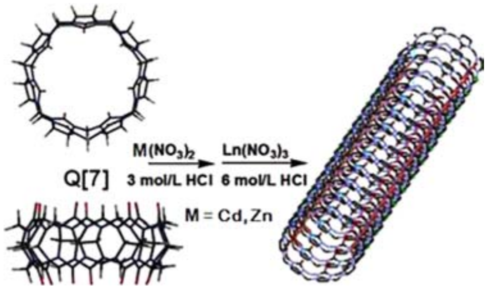


Figure 8. Tubular channel constructed by Q[7] in hydrochloric acid solution with the assistance of $[CdCl_4]^{2-}$ or $[ZnCl_4]^{2-}$ dianions.

■ CONCLUSION

In conclusion, a series of tubular nanochannels with inner cavities comprised of macrocyclic molecules have been synthesized and evaluated. In these systems, honeycomb hallows and zigzag nanochannels were formed by the $[CdCl_4]^{2-}$ dianions and Q[7] molecules via C−H···Cl interactions and metal coordination. Furthermore, subsequent treatment with Ln^{3+} cations allows for the transformation of the nanochannels from zigzag to tubular-like structures; the Ln^{3+} cations directly coordinate to the partial portal carbonyl oxygen atoms of Q[7] under high acid concentration. As a result, the system involving the interactions between anions and cucurbit[7]urils proved to be tunable, versatile, and exhibited interconvertibility in the construction of nanochannels based on such macrocyclic receptor. To the best of our knowledge, this is the first example of such acid control over the shape of nanochannels derived from the inner cavities of macrocycles. Because cucurbiturils possess multiple carbonyl binding sites for positive ions and hydrophobic cavities for neutral molecules, we believe that the present synthetic approaches will establish a novel method for creating precise molecular arrays leading to multifunctional containers with deeper cavities. Q[n]s as single macrocyclic host receptors have been extensively exploited in host−guest chemistry, but their use as elaborate supramolecular building blocks for the controlled synthesis of complex systems remains an interesting challenge. Further studies on this strategy are currently ongoing.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic file in CIF format and analytical data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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