# Novel Supramolecular Assemblies Based on Coordination of Samarium Cation to Cucurbit[5]uril

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S *Supporting Information*

ABSTRACT: In the present study, we introduce the coordination of samarium−Q[5] systems in the absence and presence of the third species, and the corresponding supramolecular assemblies are dependent upon the addition of the third species. In the absence of the third species, a samarium cation (nitrate salt) coordinates to a Q[5] molecule and forms a molecular bowl; in the presence of an organic molecule (hydroquinone), a one-dimensional polymer of ···Sm−Q[5]−Sm−Q[5]−Sm··· is formed through direct coordination of Sm cation to the portal carbonyl oxygens. In the presence of nickel cations (chloride salt), an infinite 1D supramolecular chain is constructed of samarium/cucurbit[5]uril molecular bowl through ion−dipole interaction and hydrogen binding; in addition, the stacking of the supramolecular chains forms a novel hexagonal open framework. Remarkably, in the presence of copper cations (chloride salt), Q[5]-based hexagonal netting sheets are constructed of 6-Q[5]-ring structures.
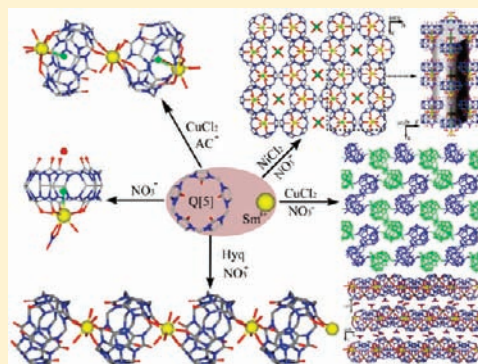
■ INTRODUCTION

Cucurbit[n]uril[1]-based coordination chemistry has been becoming an important research area in cucurbit[n]uril chemistry since the first complex of calcium to cucurbituril (Q[6] as shown in Figure 1) was reported by Mock and co-workers, by whom the structure of Q[6] was first characterized.[1a] Q[6]-based coordination chemistry began to develop as a result of the initial work demonstrated by Mock[1a,2] and Kim and co-workers.[3] Interest in the Q[n]-based coordination chemistry has increased dramatically in the new millennium following the preparation of a series of homologues of Q[6],[1] and fully and partially alkyl-substituted Q[n]s[4] and analogues.[5] Fedin, Kim, and Thuery et al. demonstrated a series of Q[6]-based complexes with alkali and alkaline earth metal ions,[1a,c,6] transition metal ions,[6a,7] lanthanide metal ions, uranyl metal ions, and their complexes[6a,8] or clusters[6a,9] and have been reviewed elsewhere.[10] Among these complexes are a few of Q[n]-based polymers or metal−Q[n] networks and frameworks with not only intriguing structures but also their potential applications in separation, catalysis, and optoelectronics.[11] The first Q[6]-based one-dimensional polymer demonstrated by Kim and co-workers was a tubular polymer formed by direct coordination through rubidium ions and cucurbiturils (Q[6]s) alternately; in addition, the coordination polymer chains were arranged to form a honeycomb structure with large linear hexagonal channels parallel to the polymer chains.[3c,12] Recently, Thuéry reported a series of uranyl ion complexes with Q[n]s, and some of them showed characteristics of uranyl−cucurbit[n]uril networks or frameworks.[8a,g−k] In recent years, our group has focused on the design and synthesis
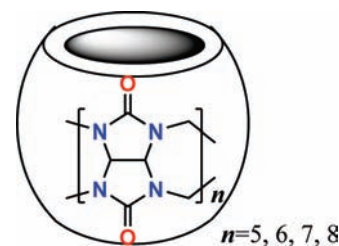

Figure 1. Structures of the cucurbit[n]urils.

of coordination polymers of metal ions to cucurbit[n]urils. We found that partially and fully alkyl-substituted cucurbit[5]urils (SQ[5]s) have a tendency to form SQ[5]-based networks or frameworks based on the direct coordination of the metal ions to the portal carbonyl oxygen of SQ[5]s.[13] It was suggested that the key to the success for producing SQ[5]-based networks and frameworks was the use of alkyl-substituted cucurbit[5]urils as the molecular 'beads", with perhaps the affinity of the carbonyl oxygens (including each bridging carbonyl oxygen) of the substituted glycoluril moieties for a metal ion (in particular, the potassium ion) being enhanced due to the electron donating effect of the alkyl substituents based on quantum chemistry calculations of density functional theory (DFT, B3LYP/3-21G* basis set).[13b] More recently, we found that the introduction of the third species into Q[n]−metal systems could result in the

Table 1. Crystallographic Data for Complexes 1−5

	1	2	3	4	5
empirical formula	$C_{30}H_{60}N_{21}O_{28}SmCl_2$	$C_{60}H_{140}N_{40}O_{65}Sm_3Cl_9$	$C_{60}H_{122}N_{42}O_{56}Sm_2NiCl_8$	$C_{60}H_{118}N_{45}O_{64}Sm_3Cl_4$	$C_{66}H_{104}N_{46}O_{59}Sm_2$
fw	1384.32	3232.22	2971.01	3086.84	2786.65
cryst syst	monoclinic	triclinic	orthorhombic	monoclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$Pnnm$	$P2_1/c$	$P2_1/n$
a, Å	15.4151(8)	13.955(4)	15.278(4)	20.855(3)	15.273(2)
b, Å	14.7704(8)	14.408(4)	23.987(6)	19.540(3)	21.836(3)
c, Å	23.7057(12)	34.004(10)	14.607(3)	26.642(4)	16.089(2)
α, deg	90.00	95.933(3)	90.00	90.00	90.00
β, deg	104.561(2)	96.422(3)	90.00	112.022(4)	101.622(4)
γ, deg	90.00	118.848(3)	90.00	90.00	90.00
V, Å^3	5224.1(5)	5853(3)	5353(2)	10 065(2)	5255.5(13)
Z	4	2	2	4	2
λ, Å	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
D_{calcd}, g cm^{-3}	1.760	1.834	1.843	2.037	1.761
T, K	233	233	233	233	233
μ(Mo Kα), mm^{-1}	1.337	1.810	1.577	1.973	1.235
unique reflns	10 080	19 989	5308	19 308	10 110
obsd reflns	8741	14 492	4762	16 517	8600
params	622	1279	384	1390	744
R_{int}	0.0420	0.0517	0.0290	0.0539	0.0440
R^a [$I > 2\sigma(I)$]	0.0390	0.0425	0.0356	0.1002	0.0474
$R_w{}^b$ [$I > 2\sigma(I)$]	0.1118	0.0982	0.1024	0.2770	0.1385

^{a} Conventional R on Fhkl: $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} Weighted R on $|Fhkl|^2$: $\Sigma[w(F_o{}^2 - F_c{}^2)^2]/\Sigma[w(F_o{}^2)^2]^{1/2}$.

formation of novel Q[n]-based networks and frameworks: the species can be organic molecules, or inorganic metal salts and even counteranions.[8d,f,14] For example, potassium metal ions can coordinate to Q[5] molecules and form one-dimensional coordination polymers;[6c] when an organic molecule, such as *p*-hydroxybenzoic acid, is introduced into the Q[5]−K$^+$ system, Q[5]-based hexagonal netting sheets are constructed of 6-membered Q[5]-ring structures.[15]

In the present study, we introduce a samarium-Q[5] system in the absence and presence of the third species, and the corresponding supramolecular assemblies are dependent upon the addition of the third species. In the absence of the third species, a samarium cation coordinates to a Q[5] molecule and forms a molecular bowl; in the presence of an organic molecule [hydroquinone (**Hyq**)], a one-dimensional polymer of ···Sm−Q[5]−Sm−Q[5]−Sm··· is formed through direct coordination of Sm cation to the portal carbonyl oxygens. In the presence of nickel cations, an infinite 1D supramolecular chain is constructed of samarium/cucurbit[5]uril molecular bowl through ion−dipole interaction and hydrogen bonding, and the stacking of the supramolecular chains forms a novel hexagonal open framework.[3c,12] Remarkably, in the presence of copper cations, similar Q[5]-based hexagonal netting sheets in the presence of *p*-hydroxybenzoic acid[15] are constructed of 6-membered Q[5]-ring structures.

■ EXPERIMENTAL SECTION

General Materials. Chemicals, such as hydroquinone (**Hyq**), $NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $SmAc_3$, and $Sm(NO_3)_3 \cdot 6H_2O$, were of reagent grade and used without further purification. The ligand compound Q[5] was prepared by the reported procedures previously.[1b,c] Elemental analysis was carried out a EURO EA-3000 element analyzer.

Preperation of {Sm(H$_2$O)(NO$_3$)[Cl@Q[5]]}·Cl·14H$_2$O (1). A mixture of Q[5]·10H$_2$O (50 mg, 0.05 mmol) and Sm(NO$_3$)$_3$·6H$_2$O (132 mg, 0.30 mmol) in ∼5 mL of 1.0 mol L^{-1} HCl was refluxed for 5 min and then filtered, yielding colorless crystals of complex **1** within 5 days (39% yield on the basis of Q[5]·10H$_2$O). Anal. Calcd for $C_{30}H_{60}N_{21}O_{28}SmCl_2$ (%): C 26.03, H 4.37, N 21.25. Found: C 26.47, H 4.12, N 21.54.

Preperation of {Sm$_3$(H$_2$O)$_{10}$[Cl@Q[5]]$_2$}·7Cl·35H$_2$O (2). A mixture of Q[5]·10H$_2$O (50 mg, 0.05 mmol) and a 4-fold excess of CuCl$_2$·2H$_2$O (34 mg, 0.20 mmol) was dissolved in ∼5 mL of 1.0 mol L^{-1} HCl at 50 °C while being stirred until the Q[5] and CuCl$_2$ dissolved completely. A 6-fold excess of SmAc$_3$ (98 mg, 0.30 mmol) was added with stirring. The solution was allowed to stand for slow evaporation in air at room temperature. Colorless crystals were obtained from the solution over the course of 5 days. The yield in terms of cucurbit[5]uril was 39%. Anal. Calcd for $C_{60}H_{140}N_{40}O_{65}Sm_3Cl_9$ (%): C 22.30, H 4.37, N 17.33. Found: C 22.73, H 4.03, N 17.64.

Preperation of {Sm(H$_2$O)$_3$[Cl@Q[5]]$_2$}·[Ni(H$_2$O)$_6$]·2NO$_3$·6Cl·2H$_3$O·16H$_2$O (3). A mixture of Q[5]·10H$_2$O (50 mg, 0.05 mmol) and a 4-fold excess of NiCl$_2$·6H$_2$O (47 mg, 0.20 mmol) were dissolved in ∼5 mL of 1.0 mol L^{-1} HCl at 50 °C while being stirred until the Q[5] and NiCl$_2$ dissolved completely. A 6-fold excess of Sm(NO$_3$)$_3$·6H$_2$O (132 mg, 0.30 mmol) was added with stirring. The solution was allowed to stand for slow evaporation in air at room temperature. Colorless crystals were obtained from the solution over the course of 5 days. The yield in terms of cucurbit[5]uril was 39%. Anal. Calcd for $C_{60}H_{122}N_{42}O_{56}Sm_2NiCl_8$ (%): C 24.26, H 4.14, N 19.80. Found: C 24.61, H 3.98, N 20.29.

Preperation of {Sm$_3$(H$_2$O)$_8$[Cl@Q[5]]$_2$}·5NO$_3$·2Cl·21H$_2$O (4). A mixture of Q[5]·10H$_2$O (50 mg, 0.05 mmol) and a 4-fold excess of CuCl$_2$·2H$_2$O (34 mg, 0.20 mmol) were dissolved in ∼5 mL of 1.0 mol L^{-1} HCl at 50 °C while being stirred until the Q[5] and CuCl$_2$ dissolved completely. A 6-fold excess of Sm(NO$_3$)$_3$·6H$_2$O (132 mg, 0.30 mmol) was added with stirring. The solution was allowed to stand
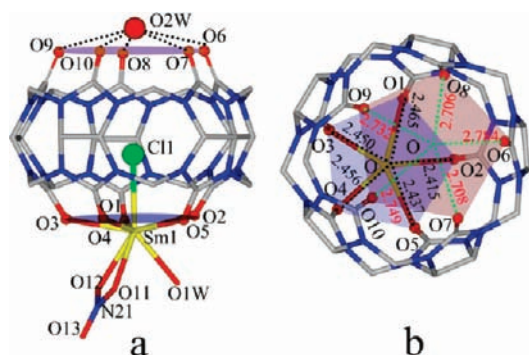
Figure 2. X-ray crystal structure of the samarium metal ions/cucurbit-[5]uril molecular bowl: (a) side view; (b) top view.
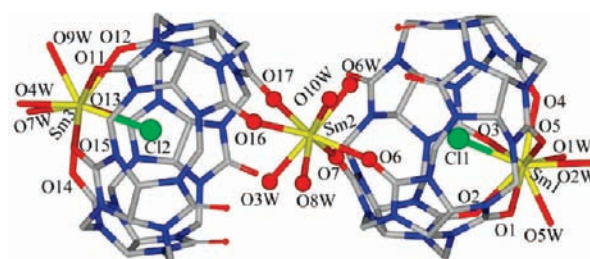

Figure 3. X-ray crystal structure of samarium cation/cucurbit[5]uril pair linked by a $[Sm(H_2O)_4]^{3+}$ cation through direct coordination.

to allow slow evaporation in air at room temperature. Colorless crystals were obtained from the solution over the course of 5 days. The yield in terms of cucurbit[5]uril was 50%. Anal. Calcd for $C_{60}H_{118}N_{45}O_{64}Sm_3Cl_4$ (%): C 23.35, H 3.85, N 20.42. Found: C 23.65, H 3.89, N 20.31.

Preperation of $\{Sm(H_2O)_4Q[5]\}_2 \cdot Hyq \cdot 6NO_3 \cdot 11H_2O$ **(5).** A mixture of Q[5]·10H₂O (50 mg, 0.05 mmol) and a 4-fold excess of **Hyq** (21.8 mg, 0.20 mmol) were dissolved in ∼5 mL of 1.0 mol L⁻¹ HCl at 50 °C while being stirred until the Q[5] and **Hyq** dissolved completely. A 6-fold excess of Sm(NO₃)₃·6H₂O (132 mg, 0.30 mmol) was added with stirring. The solution was allowed to stand for slow evaporation in air at room temperature. Red-brown crystals were obtained from the solution over the course of 5 days. The yield in terms of cucurbit[5]uril was 37%. Anal. Calcd for $C_{66}H_{104}N_{46}O_{59}Sm_2$ (%): C 28.45, H 3.76, N 23.12. Found: C 28.88, H 3.31, N 23.46.

Crystallography. The data of the five samarium−Q[5] supramolecular assemblies were collected on a Bruker Smart Apex2 CCD diffractometer using graphite monochromated Mo Kα radiation (λ = 0.710 73 Å) in ω and φ scan mode. Lorentz polarization and absorption corrections were applied. Structural solution and full-matrix least-squares refinement based on F^2 were performed with the SHELXS-97 and SHELXL-97 program package,[16] respectively. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically. Most water molecules in the unit cell have been taken into account to SQUEEZE option of the PLATON program. The squeezed water molecules are 13, 35, 12, 21, and 8 for the compounds **1**−**5**, respectively. Details of the crystal parameters, data collection, and refinements for complexes **1**−**5** are summarized in Table 1.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as deposition nos. CCDC 823417 (**1**), CCDC 823418 (**2**), CCDC 823419 (**3**), CCDC 823420 (**4**), CCDC 823421 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax +44 1223/336 033; e-mail deposit@ccdc.cam.ac.uk).

■ RESULTS AND DISCUSSION

In the present work, we demonstrate five supramolecular assemblies based on the coordination of samarium cations to cucurbit[5]urils in the presence of the third species. The features of the supramolecular assemblies of Sm−Q[5] are dependent upon the addition of the third species or supramolecular assembly inducers. We start with the Sm(NO₃)₃−Q[5] system in the absence of the inducer, and a Sm−Q[5] complex with a stoichiometry of $\{Sm(H_2O)(NO_3)[Cl@Q[5]]\} \cdot Cl \cdot 14H_2O$ (**1**) can be obtained in an HCl solution containing Sm(NO₃)₃

and Q[5]. The X-ray structural analysis reveals discrete samarium/cucurbit[5]uril molecular bowls in **1**, that is a portal of a Q[5] molecule that is is fully capped by a samarium cation, while the other portal of the Q[5] molecule is capped without metal ion, but a water molecule O2W through ion−dipole interaction and hydrogen bonding (referring to Figure 2a). In each molecular bowl, a Sm1 cation coordinates to nine atoms: five carbonyl oxygens (O1, O2, O3, O4, and O5); one water molecule (O1W); two oxygens (O11 and O12) of a coordinated nitrate anion at the portal; one included chloride anion Cl1. The average distance between the capped ion Sm1 and carbonyl oxygens of Q[5] is 2.482 Å; the distance between the capped ion Sm1 and the coordinated water molecule (O1W) is 2.454 Å. The distances between the capped ion Sm1 and the O11, O12 are 2.523, 2.574 Å, respectively; the distances between the capped ion Sm1 and the included Cl1 is 2.730 Å. The distances between O2W and the portal carbonyl oxygens are in the range 2.821−2.908 Å. It should be noted that when the Sm³⁺ cation fully coordinates on a portal of a Q[5] molecule, the other portal of the Q[5] molecule is enhanced. The average distances of the center of the portal plane to these portal carbonyl oxygens are 2.736 Å (without metal ion) and 2.444 Å (Sm³⁺ capped), respectively: there is ∼0.3 Å difference (referring to Figure 2b). This portal enhancement could result in the following: (1) The second metal ion becomes difficult to fully coordinate to the rest portal of the Q[5] molecule, which results in the formation of the molecular bowl. (2) The second metal ion could be partially coordinated to the rest portal of the Q[5] molecule. (3) If the second metal ion is large enough, it can also fully coordinate to the rest portal of the Q[5] molecule, and result in the formation of the heterometallic molecular capsule.

Although the portal enhancement could frustrate a full coverage of the second samarium cation to the other portal of Q[5], it is interesting that, in the presence of an inorganic salt, such as CuCl₂, and SmAc₃ instead of Sm(NO₃)₃, a compound containing discrete Q[5]-pairs with a stoichiometry of $\{Sm_3(H_2O)_{10}[Cl@Q[5]]_2\} \cdot 7Cl \cdot 35H_2O$ (**2**) was obtained from an acidic SmAc₃−Q[5] solution. The X-ray structural analysis reveals that the Q[5]-pair is constructed of two Sm−Q-[5] molecular bowls which are linked by the third samarium cation (Figure 3). Two Q[5] molecules are linked by a $[Sm2(H_2O)_4]^{3+}$ ion through direct coordination of samarium to portal carbonyl oxygens of these two Q[5]s in the Q[5] pair, while the other opening portal of the two Q[5] molecules in the pair is fully capped by the other two samarium cations (Sm1 and Sm3). The Sm2 cation coordinates to eight atoms: four carbonyl oxygens belong to two Q[5] molecules in the unit (O6, O7, and O16, O17); four water molecules (O3W, O6W, O8W, and O10W). Similar to the molecular bowl in **1**, the Sm1 or Sm3

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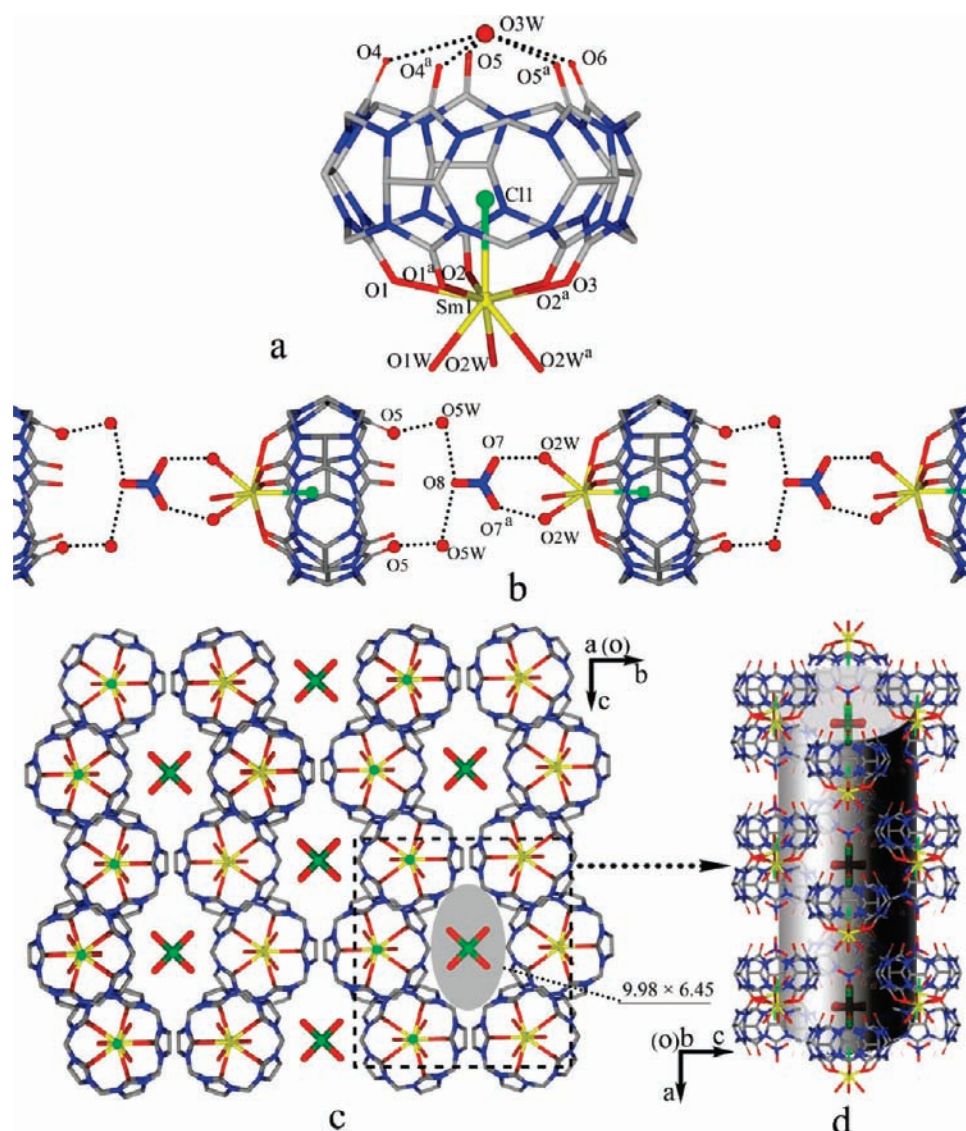dx.doi.org/10.1021/ic200902g |*Inorg. Chem.* 2011, 50, 7754–7760

Figure 4. X-ray crystal structure of (a) the heterometallic metal ions/cucurbit[5]uril capsule (symmetry code: a = $x, y, -z$); (b) the 1D supramolecular chain based on the capsules (symmetry code: a = $x, y, -z$); (c) view of honeycomb structure with linear channels extended along the a axis; (d) side view of a hexagonal channel filled with $[Ni(H_2O)_4Cl_2]$.

cation coordinates to nine atoms: five carbonyl oxygens (O1, O2, O3, O4, and O5 or O11, O12, O13, O14, and O15); three coordinated water molecules (O1W, O2W, and O5W or O4W, O7W, and O9W); an included chloride anion (Cl1 or Cl2). The average distance between the Sm2 and carbonyl oxygens of two Q[5]s in the pair is 2.379 Å, while the average distance between the fully capped Sm1 or Sm3 and carbonyl oxygens of Q[5] in the pair is 2.514 Å, about ~0.15 Å longer. The average distance between Sm2 and the coordinated water molecules is 2.419 Å, and the average distance between the capped ion Sm1 or Sm3 and the coordinated water molecules is 2.497 Å, about ~0.08 Å longer. The distance between Sm1 or Sm3 and the included chloride anion Cl1 or Cl2 is 2.727 or 2.722 Å, respectively. The average distances of the center of portal plane to these portal oxygens are 2.698 Å (without metal ion), 2.476 Å ($Sm1^{3+}$ capped), and 2.515 Å ($Sm3^{3+}$ capped), respectively; there also is ~0.2 Å difference (referring to Figure 3). When a portal of a Q[5] is capped by a samarium cation, the other portal size of the

Q[5] can be enhanced, and the second metal ion with a smaller ionic radius, such as the samarium cation, cannot fully cap over, but could partially coordinate to this portal. In this case, the samarium cation (Sm2) does partially coordinate to the enhanced portal in the presence of $CuCl_2$.

In the presence of an inorganic salt, such as $NiCl_2$, a compound with a stoichiometry of $\{Sm(H_2O)_3[Cl@Q[5]]_2\}\cdot$ $[Ni(H_2O)_6]\cdot 2NO_3\cdot 6Cl\cdot 2H_3O\cdot 16H_2O$ (**3**) was obtained from an acidic $Sm(NO_3)_3$–Q[5] solution. The X-ray structural analysis reveals a one-dimensional supramolecular chain constructed of Sm–Q[5] molecular bowls through the hydrogen bonding interaction in **3** (Figure 4a). A similar Sm–Q[5] molecular bowl to that in **1** is formed by the coordination of a Sm1 cation to a portal of Q[5]. The distances between the capped cation Sm1 and the carbonyl oxygens of Q[5] are in the range 2.486–2.548 Å; Sm1 also coordinates to an included chloride Cl1 (disordered over two positions) and three water molecules (O1W and 2 O2W). The distances between the Sm1
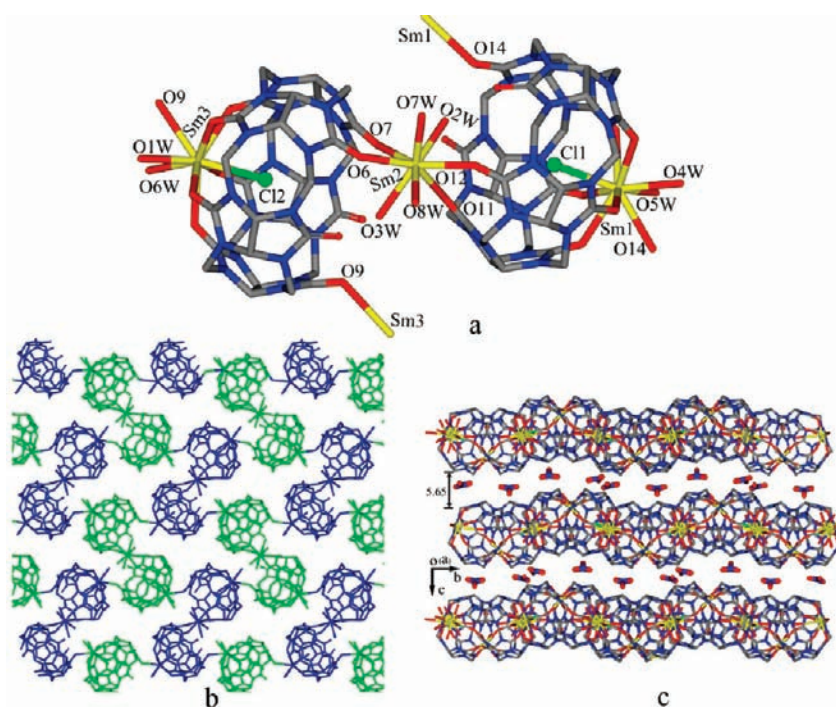
Figure 5. X-ray crystal structure of (a) samarium cation/cucurbit[5]uril pair linked by a $[Sm(H_2O)_4]^{3+}$ cation through direct coordination; (b) the network constructed of the Q[5] pairs; (c) stacking of the networks filled with nitrate anions.

cation and the included Cl1 anion is 2.738 Å, and the distances between the Sm1 cation and the coordinated water molecules are in the range 2.434−2.518 Å. A water molecule (O3W) is capped at the center of the other portal; the distances between the capped O3W and the portal carbonyl oxygens are in the range 2.777−2.886 Å. The hydrogen bonding interaction of a nitrate anion with two water molecules O5W and two coordinated water molecules O2W results in the formation of a one-dimensional chain (Figure 4b). Remarkably, the chains arranged in a honeycomb structure with linear hexagonal channels extended along the *a* axis in compound **3** (referring to Figure 4c).[3c,12] Each channel constructed of six paralleled supramolecular chains has around 10 Å × 6 Å section, and is filled with $[Ni(H_2O)_4Cl_2]$ complex (referring to Figure 4d). The channels or the void constructed of the wall of the cucurbit[5]uril appear to favor including or containing larger anions. In one of our recent works, we demonstrated the ring with eight interlinked Q[5] "beads" including four large anion $InCl_4^-$.[13a] More recently, when we tried to precipitate K−Q[5] complex by using a H_2ZnCl_4 solution, we found a compound with a stoichiometry of $\{K[(H_2O)@Q[5]][Zn(H_2O)_3Cl]\}ZnCl_4 \cdot 6H_2O$. The X-ray structural analysis reveals that supramolecular chains constructed of heterometallic Zn^{2+}−K^+/Q[5] complexes also arranged in a honeycomb structure with linear hexagonal channels, and each linear hexagonal channel was filled with $ZnCl_4^{2-}$ anions.[17]

It has been proven that some organic molecules could lead to the formation of some novel supramolecular assemblies.[15] However, it is rare that an inorganic species could result in the formation of novel supramolecular assemblies, such as Q[*n*]-based networks or frameworks. Remarkably, when a $CuCl_2$ salt was introduced into the $Sm(NO_3)_3$−Q[5] system, such a novel network with a stoichiometry of $\{Sm_3(H_2O)_8[Cl@Q[5]]_2\} \cdot 5NO_3 \cdot 2Cl \cdot 21H_2O$ (**4**) was obtained. The X-ray structural analysis for compound **4** also shows Q[5]-pairs (Figure 5a),

which appear to be the Q[5]-pairs in compound **2**. However, the pairs are not discrete, but the essential building blocks to construct the Q[5]-based network (Figure 5b). In the Q[5]-pair, two Q[5] molecules are linked by a $[Sm2(H_2O)_4]^{3+}$ cation through direct coordination of Sm2 cation to the portal carbonyl oxygens of the Q[5]s (O6, O7, and O11, O12). While the other portal of the two Q[5] molecules in the pair is fully capped by the Sm1 and Sm3 cations, respectively, both of the Q[5] molecules include a chloride anion (Cl1 and Cl2), respectively. It should be noted that the Sm1 and Sm3 coordinates not only to two water molecules but also to the neighboring portal oxygens (O14 or O9), respectively. The average distances of Sm−O (carbonyl), Sm−O (water), and Sm−Cl (included) are 2.476, 2.459, and 2.730 Å, respectively; they are similar to those in compounds **1**−**3**. The extra coordination of the Sm1 cation to the carbonyl oxygen O14 or Sm3 cation to the carbonyl oxygen O9 distinguishes the Q[5]-pair in **4** from that in **2**. It is that the extra coordination leads to the formation of the novel network constructed from the Q[5] pair (Figure 5b,c). In our recent work, *p*-hydroxybenzoic acid acts as an inducer in the KI−Q[5] system, a similar porous material containing hexagonal netting sheets, which is absorbent to volatile organics, ranging in size from methanol to 1,4-dioxane.[15] However, the organic inducer, *p*-hydroxybenzoic acid molecules, is filled between the netting sheets, and appears to influence the absorption properties for the volatile organics. Although the inorganic salt $CuCl_2$ acts as a supramolecular assembly inducer in this case, Cu^{2+} cations do not show up in the crystal structure of **4**. The Sm−Q[5] porous material could have similar or even better absorption properties compared to the KI−Q[5]−*p*-hydroxybenzoic acid hexagonal netting sheets.

Above, we demonstrated three Sm−Q[5] systems in which inorganic inducers were introduced. Herein, when an acidic $Sm(NO_3)_3$−Q[5] solution was added to an organic species,
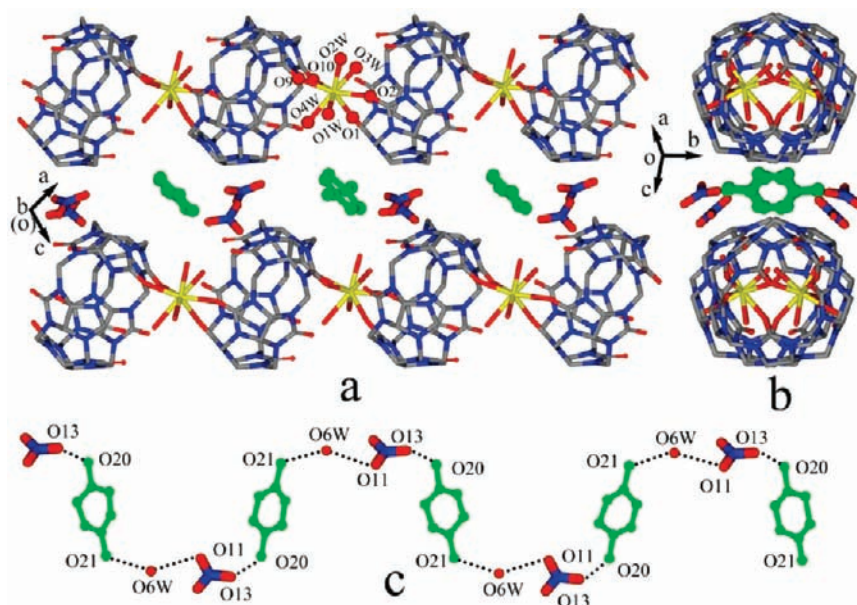
Figure 6. X-ray crystal structure of the linear chains formed by direct coordination of alternative Sm cations and Q[5] molecules (a) side view; (b) top view; (c) 1D supramolecular chain constructed of O6W, **Hyq** and NO_3^- through the hydrogen bonding.

such as **Hyq**, a Sm–Q[5] complex-based compound with a stoichiometry of $\{Sm(H_2O)_4Q[5]\}_2 \cdot \mathbf{Hyq} \cdot 6NO_3 \cdot 11H_2O$ (**5**) was obtained. The X-ray structural analysis reveals one-dimensional polymer constructed of alternative samarium cations and Q[5] molecules in **5** as shown in Figure 6a. In the one-dimensional polymer, each Sm cation (Sm1) coordinates to eight oxygen atoms: four carbonyl oxygen atoms belonging to the two neighboring Q[5] molecules (O1, O2 and O9, O10, respectively), and four water molecules (O1W, O2W, O3W, and O4W). Thus, an infinite linear chain is formed by direct coordination of Sm1 cations to the portals of Q[5] molecules. The distances between Sm1 cation and carbonyl oxygen atoms are in the range 2.385–2.404 Å, and the distances between the Sm1 cation and coordinated water oxygen atoms are in the range 2.359–2.427 Å. The organic inducer, **Hyq** molecules, are filled between two linear Sm–Q[5] polymers (Figure 6a,b), and also form a supramolecular chain through the hydrogen bonding of water molecules O6W, hydroxyl of **Hyq** molecules, and nitrate anions (Figure 6c). The distances of O–O are in the range 2.575–2.932 Å. Thus, when the Sm–Q[5] system is introduced into a third species, the basic coordination of the Sm metal ion to the portal of Q[5] shows no significant difference; however, the assembly of the Sm–Q[5] complexes presents quite different supramolecular arrangements.

CONCLUSION

In this report we describe the coordination of samarium cation to Q[5] in the presence of the third species, in particular, the supramolecular assemblies based on the arrangement of the Sm–Q[5] complexes. The third species, or supramolecular assembly inducer, could be organic molecules or inorganic metal salts. This synthetic strategy employed appears also very likely to be applicable to the use of other Ln^{3+}–Q[5] systems, as well as of larger Q[n > 5]s together with metal ions other than Ln^{3+}. The latter include alkali, alkaline earth, and even transition metals, displaying different ionic radii and/or cationic charges that will likely lead to new categories of coordination and the

supramolecular assembly materials. For example, the formation of porous netting sheets, chiral helical polymers, honeycomb based on coordination of Q[n]s, and different metal ion types in the presence of the third species or the supramolecular assembly inducers creates the prospect of obtaining networks or frameworks of the present general type. Further, the investigation of the solid state chemistry of such porous netting sheets or porous framework structures is at present virtually unstudied and provides an exciting challenge for the future. We are at present embarking on studies of this type.

ASSOCIATED CONTENT

ⓢ **Supporting Information.** CIF data. This material is available free of charge via the Internet at http://pubs.acs.org.

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