

在四氯合锌离子诱导下反式六元瓜环与碱金属离子 构筑的配位超分子自组装体

邱胜超¹ 李 青¹ 张云黔¹ 肖 昕¹ 陶 朱¹ 祝黔江^{*1} 张振琴^{*2}

(¹ 贵州大学化学与化工学院, 贵州省大环化学及超分子化学重点实验室, 贵阳 550025)

(² 南京医科大学药学院化学系, 南京 210009)

摘要: 在盐酸介质中, 通过四氯合锌离子诱导, 碱金属离子能与反式六元瓜环端口羰基氧原子直接配位构筑形成超分子自组装体。单晶结构表明在 HCl 介质中, 四氯合锌离子形成“蜂巢结构”, 而且在 $[\text{ZnCl}_4]^{2-}$ 诱导作用下, 碱金属离子和反式六元瓜环端口羰基氧直接配位形成一维超分子自组装体而填充在“蜂巢结构”中。

关键词: 碱金属离子; 反式六元瓜环; 四氯合锌根离子; 超分子自组装体

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Supramolecular Assemblies Formed by Coordination of Alkali Metal Ions with Inverted Cucurbit[6]uril in the Presence of Tetrachlorozincate

QIU Sheng-Chao¹ LI Qing¹ ZHANG Yun-Qian¹ XIAO Xin¹

TAO Zhu¹ ZHU Qian-Jiang^{*1} ZHANG Zhen-Qin^{*2}

(¹Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, Guizhou University, Guiyang 550025, China)

(²School of Pharmacy, Nanjing Medical University, Nanjing 210009, China)

Abstract: Coordination in supramolecular assemblies formed in aqueous HCl solution was investigated by reacting alkali cations (M^+) and inverted cucurbit[6]uril ($i\text{Q}[6]$) in the presence of the structure-directing agent tetrachloride zincate anion ($[\text{ZnCl}_4]^{2-}$). Single-crystal X-ray diffraction analysis revealed that the $i\text{Q}[6]\text{-M}^+\text{-}[\text{ZnCl}_4]^{2-}$ -HCl interaction systems yielded a supramolecular assembly consisting of $i\text{Q}[6]/\text{M}^+$ -based linear coordination polymers residing within the pores of a honeycomb-like framework of $[\text{ZnCl}_4]^{2-}$ anions. Close inspection revealed that different $i\text{Q}[6]/\text{M}^+/\text{ZnCl}_4^{2-}$ -based supramolecular assemblies ($\text{M}=\text{Na}, \text{K}, \text{Rb}$) presented different porous conformations and displayed different absorption properties. CCDC: 1469246, **1**; 1469247, **2**; 1469248, **3**.

Keywords: alkaline metal ion; inverted cucurbit[6]uril; tetrachloride zincate anion; supramolecular assemblies

0 Introduction

An inverted cucurbit[6]uril ($i\text{Q}[6]$, Fig.1) was first reported by Isaacs and Kim in 2005^[1-2], and since then only a couple of theoretical investigations on their

potential properties have been reported^[3-4]. A low synthetic yield and difficulties in separating $i\text{Q}[n]$ s has hindered their investigation. Upon their discovery, it was suggested that $i\text{Q}[n]$ s could selectively recognize guests by the shape and dimensions of their cavity^[4].

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*通信联系人。E-mail: gzutao@263.net, zhangzhq@njmu.edu.cn, Fax: +86-851-3620906, Tel: +86-851-3623903

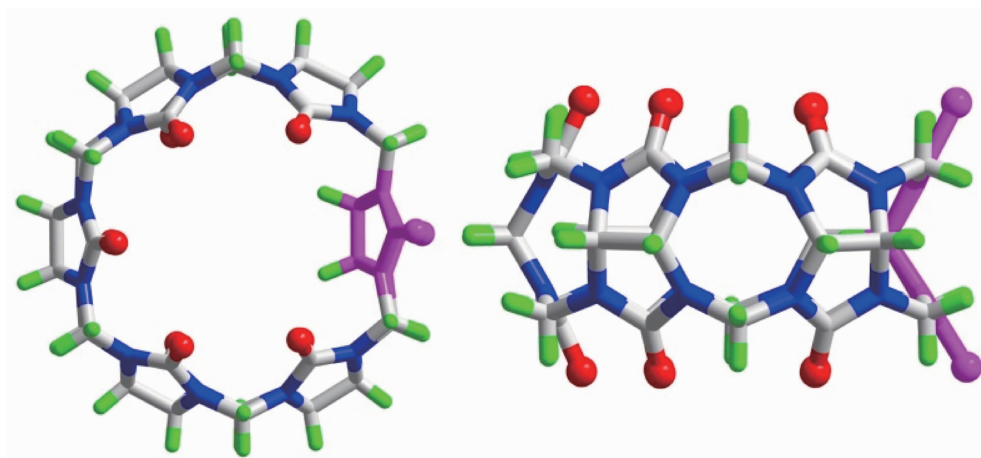


Fig.1 Structure of the inverted cucurbit[6]uril as viewed from the top (left) and from the side (right)

Indeed, X-ray crystallography and ^1H NMR spectroscopy revealed interesting host-guest interactions between *i*Q[6] and *p*-phenylenediaminium in both the solid state and aqueous solution. Two different complexes were observed in the solid state: an inclusion structure and a sandwich structure. In aqueous solution, the *i*Q[6] host can accommodate the *p*-phenylenediaminium guest, but the guest favours staying outside the pores of the *i*Q[6] host, and guest exchange is fast on the NMR time scale^[5].

We recently developed a convenient method for isolating *i*Q[6] from the normal cucurbit[6]uril (Q[6]) by column chromatography using a Dowex resin^[6]. Then we investigated the coordination properties of *i*Q[6] with various metal ions. Obtaining solid crystals of *i*Q[6]/ M^+ by simply mixing *i*Q[6] with alkali salts was proved difficult, without the addition of a structure directing agent such as tetrachloride zincate anion ($[\text{ZnCl}_4]^{2-}$). However, in the presence of $[\text{ZnCl}_4]^{2-}$, reaction of alkaline earth cations (AE^{2+}) and the inverted cucurbit[6]uril (*i*Q[6]) yielded linear coordination polymers in which *i*Q[6] and AE^{2+} cations are directly coordinated to the metal ions. In contrast, in the *i*Q[6]- Mg^{2+} - $[\text{ZnCl}_4]^{2-}$ -HCl system, there was no direct coordination between *i*Q[6] and Mg^{2+} or Zn^{2+} , presumably due to the shorter ionic radii preventing direct coordination^[6]. Recently, we found that the coordination of *i*Q[6] with Ln^{3+} gave rise to different interaction products and isomorphous groups with the heavier lanthanides. The interaction of *i*Q[6] with lighter lanthanides such

as La^{3+} , Ce^{3+} , Pr^{3+} and Nd^{3+} immediately yielded precipitation or single crystal solids, whereas interaction of *i*Q[6] with Sm^{3+} and Eu^{3+} did not generate solid material. Interaction of *i*Q[6] with heavier lanthanides gave rise to three isomorphous groups with different structure features, with Gd^{3+} , Tb^{3+} , Dy^{3+} and Ho^{3+} forming one group, Er^{3+} , Tm^{3+} and Yb^{3+} forming a separate group, and Lu^{3+} differing from both of these groups^[7].

In the present work, *i*Q[6] was used as a ligand, and its coordination with alkali cations (M^+) in supramolecular assemblies was investigated in the presence of the structure directing agent $[\text{ZnCl}_4]^{2-}$. Single-crystal X-ray diffraction analysis revealed that the *i*Q[6]- M^+ - $[\text{ZnCl}_4]^{2-}$ -HCl interaction systems consisted of a supramolecular assembly of *i*Q[6]/ M^+ complexes and $[\text{ZnCl}_4]^{2-}$ anions, in which $[\text{ZnCl}_4]^{2-}$ anions are assembled into a honeycomb-like frameworks via outer surface interactions between *i*Q[6]s. The linear coordination polymers of *i*Q[6] hosts coordinated to M^+ cations ($\text{A}=\text{Na}$, K , Rb) fill the pores or channels in the $[\text{ZnCl}_4]^{2-}$ framework^[8-10].

1 Experimental

1.1 Reagents and instrument

All chemicals including alkali metal chlorides (MCl) were of reagent grade and were used without further purification. *i*Q[6] was prepared as described previously^[1]. Elemental analysis was carried out on a EURO EA-3000 elemental analyzer.

1.2 Preparation of titled compounds

A similar process was used to prepare crystals for

all $iQ[6]-M^+-[ZnCl_4]^{2-}-HCl$ systems. Specifically, MCl (0.15 mmol, $M=Na, K, Rb$) and $ZnCl_2$ (14.79 mg, 0.12 mmol) were dissolved in 1 mL H_2O to prepare solution A, and $iQ[6]$ (20 mg, 0.015 mmol) was dissolved in 1 mL $6\text{ mol}\cdot\text{L}^{-1}$ HCl to prepare solution B. Solution B was then slowly added to solution A and stirred. X-ray diffraction-quality crystals were obtained by slowly evaporation after 7 days.

$[Na_2(H_2O)_2(iQ[6])] \cdot [ZnCl_4] \cdot [Zn(H_2O)Cl_3](H_3O) \cdot 7H_2O$ (**1**): Anal. Calcd. for $C_{36}H_{59}N_{24}O_{23}Na_2Zn_2Cl_7$ (%): C, 26.68, H, 3.67, N, 20.74; Found(%): C, 26.87, H, 3.56, N, 21.01.

$\{K_4(H_2O)_8[ZnCl_4](iQ[6])_2\} \cdot [ZnCl_4] \cdot 3[Zn(H_2O)Cl_3](H_3O)_3 \cdot 22H_2O$ (**2**): Anal. Calcd. for $C_{72}H_{147}N_{48}O_{60}K_4Zn_3Cl_{17}$ (%): C, 23.18, H, 3.97, N, 18.02; Found(%): C, 23.28, H, 3.76, N, 18.21.

$[Rb(H_2O)(iQ[6])] \cdot [ZnCl_4] \cdot [Zn(H_2O)Cl_3](H_3O)_2 \cdot 16H_2O$ (**3**): Anal. Calcd. for $C_{36}H_{78}N_{24}O_{32}RbZn_2Cl_7$ (%): C, 23.71, H, 4.31, N, 18.43; Found (%): C, 23.84, H, 4.13, N, 18.77.

1.3 X-ray crystallography

A suitable single crystal ($\sim 0.2\text{ mm} \times 0.2\text{ mm} \times 0.1\text{ mm}$) was embedded in paraffin oil and mounted on a Bruker SMART Apex II CCD diffractometer equipped with a graphite-monochromated $Mo\ K\alpha$ radiation source

($\lambda=0.071\ 07\ 3\text{ nm}$, $\mu=0.828\text{ mm}^{-1}$), which was operated in the ω -scan mode under a nitrogen stream ($-50\text{ }^\circ\text{C}$). Data were corrected for Lorentz and polarization effects using the SAINT program^[11], and semi-empirical absorption corrections based on equivalent reflections were applied using the SADABS program^[12]. The structure was elucidated through direct methods, and full-matrix least-squares refinement of F^2 values was performed using SHELXS-97^[13] and SHELXL-97^[14]. All non-hydrogen atoms were refined anisotropically, and carbon-bound hydrogen atoms were introduced at calculated positions and treated as riding atoms with an isotropic displacement parameter equal to 1.2 times that of the parent atom. Most of the water molecules were omitted using the SQUEEZE option of the PLATON program^[15]. A total of 8, including 1 protonated water molecules, 25, including 3 protonated water molecules and 18, including 2 protonated water molecules were squeezed for compounds **1**, **2**, and **3**, respectively. Analytical expressions for neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. Details of the crystal parameters, data collection conditions, and refinement parameters for the three compounds are summarized in Table 1.

CCDC: 1469246, **1**; 1469247, **2**; 1469248, **3**.

Table 1 Crystal data and structure refinement details of compounds from $iQ[6]-M^+-ZnCl_2-HCl$ systems

Compound	1	2	3
Empirical formula	$C_{36}H_{59}N_{24}O_{23}Na_2Zn_2Cl_7$	$C_{72}H_{147}N_{48}O_{60}K_4Zn_3Cl_{17}$	$C_{36}H_{78}N_{24}O_{32}RbZn_2Cl_7$
Formula weight	1 620.94	3 731.28	1 823.58
Crystal system	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/n$	$P\bar{1}$	$Pna2_1$
a / nm	1.669(9)	1.515 4(16)	2.284(3)
b / nm	1.836(10)	2.037(2)	2.059(3)
c / nm	2.147(11)	2.396(3)	1.503(18)
$\alpha / (^\circ)$	90.00	88.528(4)	90.00
$\beta / (^\circ)$	104.824(2)	87.871(4)	90.00
$\gamma / (^\circ)$	90.00	87.871(4)	90.00
V / nm^3	6 367.4(6)	7 391.5(14)	7 072.5(15)
Z	4	2	4
$D_c / (\text{g}\cdot\text{cm}^{-3})$	1.691	1.676	1.713
μ / mm^{-1}	1.154	1.321	1.727
Unique reflns	14 339	25 657	12 154
Obsd reflns	8 141	15 851	8 857
Parameters	794	1 630	757

Continued Table 1

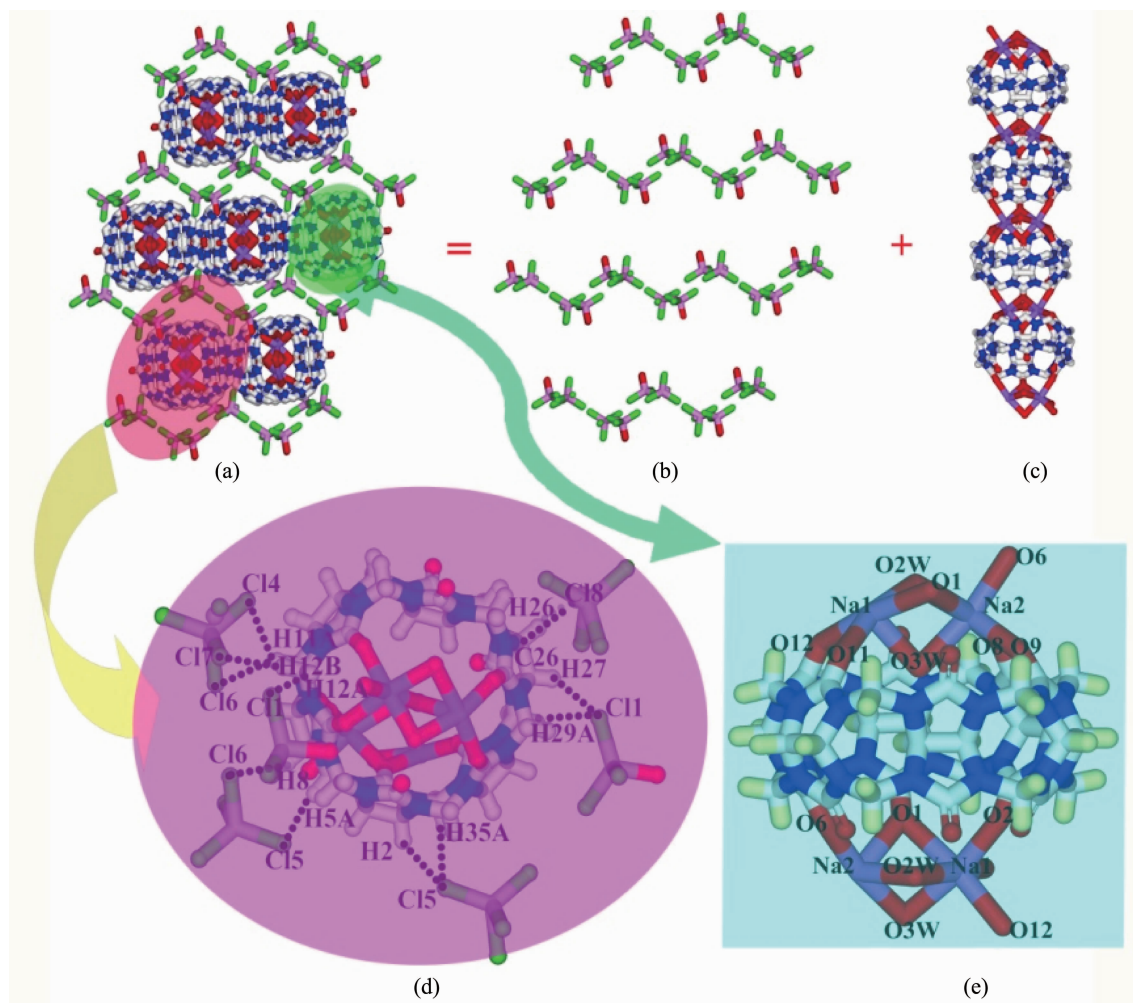
R_{int}	0.049 7	0.045 4	0.047 8
$R [I > 2\sigma(I)]^a$	0.078 3	0.080 6	0.041 9
$wR [I > 2\sigma(I)]^b$	0.251 0	0.239 3	0.103 3
R (all data)	0.120 2	0.110 9	0.062 9
wR (all data)	0.279 6	0.263 2	0.109 8
GOF on F^2	1.038	1.056	0.922

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|, ^b wR_2 = \sum [w(|F_o|^2 - |F_c|^2)] / \sum [w(F_o)^2]^{1/2}, \text{ where } w = 1 / [\sigma^2(F_o^2) + (aP)^2 + bP]; P = (F_o^2 + 2F_c^2) / 3.$$

2 Results and discussion

Fig.2 shows the structure of compound **1**. The supramolecular assembly is based on $[\text{ZnCl}_4]^{2-}$ and $[\text{Zn}(\text{H}_2\text{O})\text{Cl}_3]^-$ anions in which complexes of $i\text{Q}[6]$ and Na^+ cations (Fig.2a) occupy the pores within the

honeycomb-like framework constructed from $[\text{ZnCl}_4]^{2-}$ and $[\text{Zn}(\text{H}_2\text{O})\text{Cl}_3]^-$ anions (Fig.2b). Each hollow in the honeycomb is occupied by one $i\text{Q}[6]\text{-Na}^+$ -based linear coordination polymer (Fig.2a, 2c). Closer inspection of Fig.2a reveals that each $i\text{Q}[6]$ molecule interacts with six Zn-based anions (four $[\text{ZnCl}_4]^{2-}$ anions and two



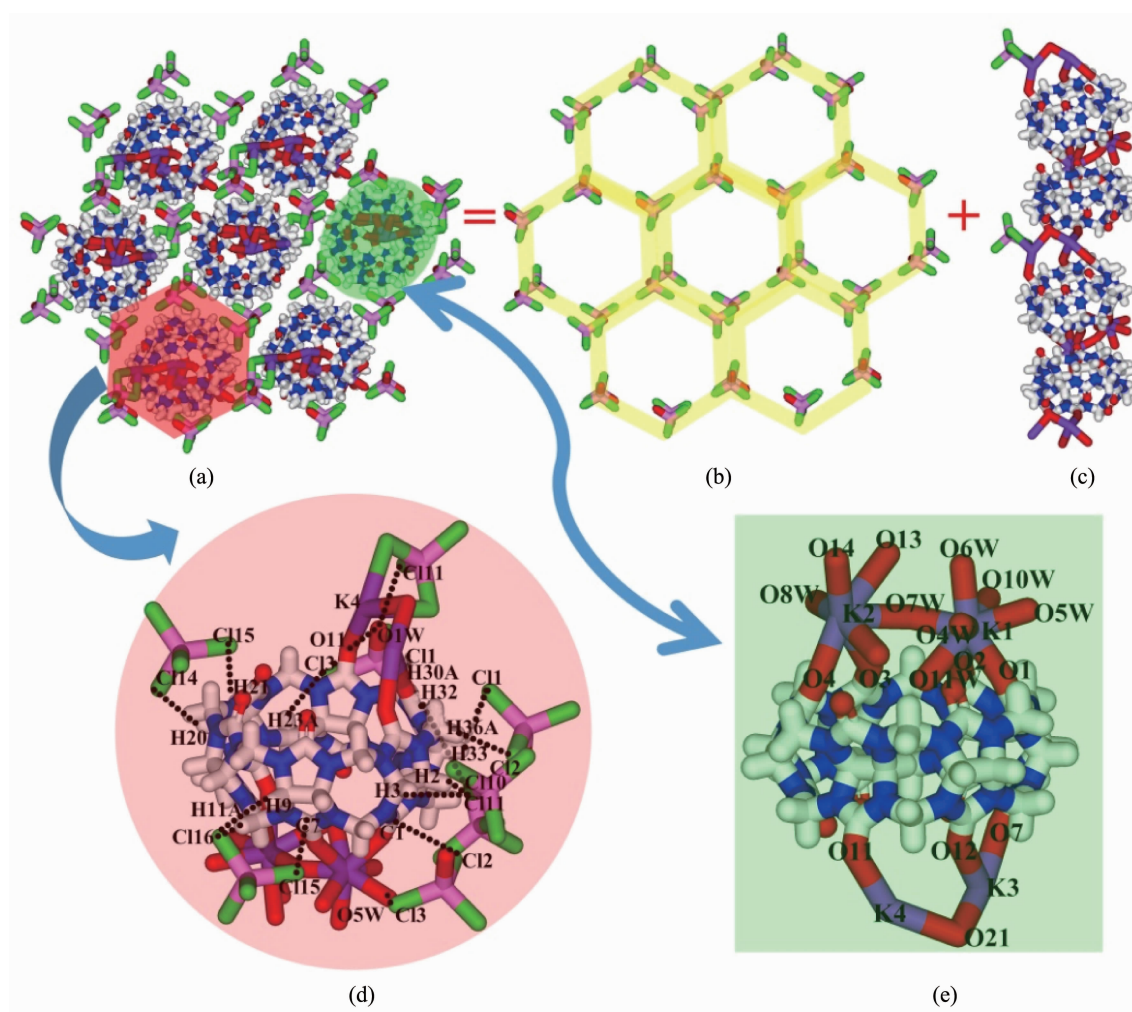
Free water molecules are omitted for clarity

Fig.2 Crystal structure of compound **1**: (a) Overall view of the supramolecular assembly constructed from $i\text{Q}[6]/\text{Na}^+$ complexes and $[\text{ZnCl}_4]^{2-}$ and $[\text{Zn}(\text{H}_2\text{O})\text{Cl}_3]^-$ anions along the b axis; (b) Zn anion-based honeycomb-like framework; (c) Linear $i\text{Q}[6]/\text{Na}^+$ -based coordination polymer; (d) Interaction of $i\text{Q}[6]$ with Zn-based anions; (e) Coordination of $i\text{Q}[6]$ with Na cations

$[\text{Zn}(\text{H}_2\text{O})\text{Cl}_3]^-$ anions) through ion-dipole interactions between Zn-based anions and the electropositive outer surface of $i\text{Q}[6]$. The distance between chlorides from $[\text{ZnCl}_4]^{2-}$ anions and methine or methylene carbons on the outer surface of $i\text{Q}[6]$ ranged between 0.342 4 and 0.388 2 nm, and an additional hydrogen bond is present between a coordinated water molecule (O1W) bound to a $[\text{Zn}(\text{H}_2\text{O})\text{Cl}_3]^-$ anion and a portal carbonyl oxygen (O8) of the $i\text{Q}[6]$ - Na^+ complex, with a O1W - O8 distance of 0.270 5 nm (Fig.2d). Each $i\text{Q}[6]$ molecule coordinates with four sodium cations, and each $i\text{Q}[6]$ portal coordinates two Na1 and Na2 cations. Four carbonyl oxygens (O11 , O12 to Na1 and O8 , O9 to Na2)

form the top portal of $i\text{Q}[6]$ (Fig.2e), and both Na1 and Na2 cations coordinate with water molecules O2W , O3W and a carbonyl oxygen (O1) from a neighboring $i\text{Q}[6]$ molecule. Furthermore, four carbonyl oxygens (O1 , O2 to Na1 and O1 , O6 to Na2) form the bottom portal of the $i\text{Q}[6]$ (Fig.2e), and again both Na1 and Na2 cations coordinate with water molecules O2W , O3W and a carbonyl oxygen (O1) from another neighboring $i\text{Q}[6]$ molecule, with a Na^+ -portal carbonyl oxygen distance of 0.228 6~0.261 7 nm, and a Na^+ - O_{water} distance of 0.237 8~0.243 7 nm.

Fig.3 shows structure of compound **2**. Fig.3a shows a similar supramolecular assembly, comprised of

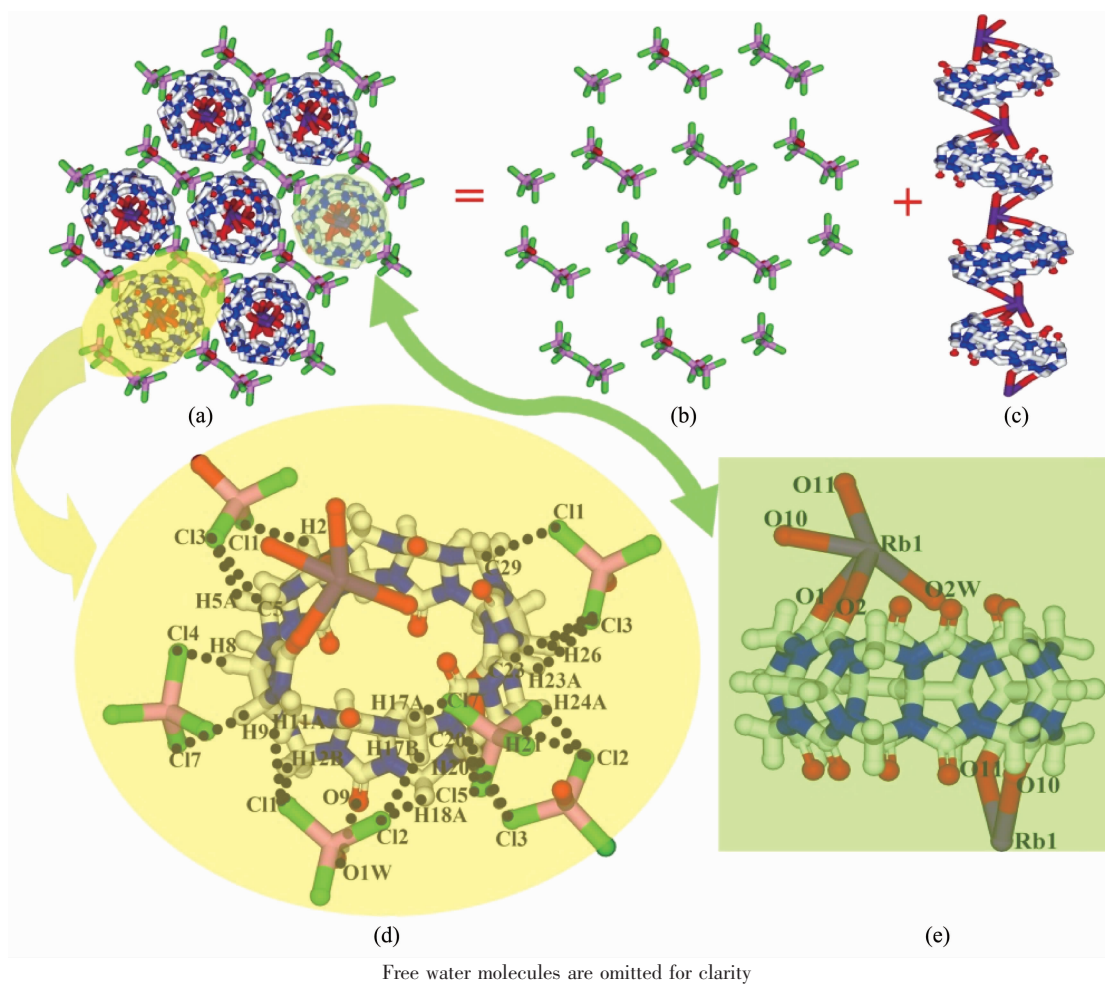


Free water molecules are omitted for clarity

Fig.3 Crystal structure of compound **2**: (a) Overall view of the supramolecular assembly constructed from $i\text{Q}[6]/\text{K}^+$ complexes and $[\text{ZnCl}_4]^{2-}$ and $[\text{Zn}(\text{H}_2\text{O})\text{Cl}_3]^-$ anions along the b axis; (b) $[\text{ZnCl}_4]^{2-}$ -based honeycomb-like framework; (c) Linear $i\text{Q}[6]/\text{K}^+$ -based coordination polymer; (d) Interaction of an $i\text{Q}[6]$ molecule with Zn-based anions; (e) Coordination of an $i\text{Q}[6]$ molecule with K^+ cations

$[\text{ZnCl}_4]^{2-}$ and $[\text{Zn}(\text{H}_2\text{O})\text{Cl}_3]^-$ anions surrounded with $i\text{Q}[6]$ molecules and K^+ cations by non-covalent interaction. Again, the $[\text{ZnCl}_4]^{2-}$ and $[\text{Zn}(\text{H}_2\text{O})\text{Cl}_3]^-$ anions form a honeycomb-like framework (Fig.3b), and the $i\text{Q}[6]$ - K^+ -based linear coordination polymers occupy the pores in this framework via outer surface interactions with the electropositive surface of $\text{Q}[n]$ (Fig.3a, c). Five $[\text{ZnCl}_4]^{2-}$ anions and three $[\text{Zn}(\text{H}_2\text{O})\text{Cl}_3]^-$ anions surround each $i\text{Q}[6]$ molecule in the assembly, and close inspection reveals detailed interactions that include: (1) an ion-dipole interaction between a $[\text{ZnCl}_4]^{2-}$ chloride and a methine or methylene carbon from the outer surface of $i\text{Q}[6]$, with a distance of 0.341 2~0.375 5 nm (dashed lines in Fig.3d); (2) an ion-dipole interaction between a $[\text{ZnCl}_4]^{2-}$ chloride and an electron deficient carbonyl

carbon with a distance of 0.327 6~0.336 2 nm (dashed lines in Fig.3d); (3) a hydrogen bond between a water molecule coordinated to the $[\text{Zn}(\text{H}_2\text{O})\text{Cl}_3]^-$ anion or K^+ cation and a portal carbonyl oxygen or chloride from the $[\text{Zn}(\text{H}_2\text{O})\text{Cl}_3]^-$ anion, with a distance of 0.309 2~0.341 6 nm (dashed lines in Fig.3d). There is an additional interaction between a coordinated K^+ cation (K4) and a $[\text{ZnCl}_4]^{2-}$ anion, with K-Cl distances of 0.325 9 and 0.328 9 nm, respectively (Fig.3d). Each $i\text{Q}[6]$ in compound **2** is also coordinated to four K^+ cations (K1 and K2 from one portal, and K3 and K4 from the other portal). K1 coordinates to eight oxygen atoms, two carbonyl oxygens (O1 , O2), and six water molecules (O4W , O5W , O6W , O7W , O10W and O11W); K2 coordinates to seven oxygen atoms, four carbonyl



oxygens (O3, O4, and O13, O14 from a neighbouring *i*Q[6] molecule), and three water molecules (O9W, O8W and O7W); K3 coordinates only to three carbonyl oxygens (O7, O12 and O21 from another neighbouring *i*Q[6] molecule); K4 coordinates only to two carbonyl oxygens (O11 and O21 from another neighbouring *i*Q[6] molecule). Distances between K^+ and portal carbonyl oxygens are in the range of 0.232 2~0.321 2 nm, and K^+-O_{water} distances are 0.236 2~0.297 4 nm.

Compound **3** has a similar supramolecular assembly to **1** and **2** described above, in which $[ZnCl_4]^{2-}$ and $[Zn(H_2O)Cl_3]^-$ anions form a honeycomb-like framework, and *i*Q[6] molecules coordinated with Rb^+ cations form a linear coordination polymer that is inserted in the cells of the framework (Fig.4a~c). Each *i*Q[6] molecule is surrounded by three $[ZnCl_4]^{2-}$ anions and three $[Zn(H_2O)Cl_3]^-$ anions through ion-dipole interactions between a $[ZnCl_4]^{2-}$ chloride and a methine or methylene carbon on the outer surface of *i*Q[6], with a distance of 0.338 1~0.371 2 nm (Fig.4d). An additional hydrogen bond is present between water molecule (O1W) coordinated to the $[Zn(H_2O)Cl_3]^-$ anion and portal carbonyl

oxygen (O9), with a distance of 0.268 3 nm (dashed lines in Fig.4d). Each *i*Q[6] is also coordinated to rubidium cation Rb1 at both portals. Rb1 coordinates to five oxygen atoms (carbonyl oxygens O1, O2 and O10 and O11 from a neighboring *i*Q[6]), and one water molecule (O2W). The Rb^+ -portal carbonyl oxygen distance is 0.278 4~0.301 9 nm, and the K^+-O_{water} distance is 0.305 6 nm (Fig.4e).

The crystal structures therefore revealed a similar Zn-based honeycomb-like framework filled with linear *i*Q[6]/ M^+ -based coordination polymers for all three compounds (Fig.2a, 3a, 4a). However, closer inspection revealed a slightly different arrangement of the linear *i*Q[6]/ M^+ -based coordination polymers that led to different porous supramolecular assemblies with different alkali metal ions. With Na^+ (compound **1**), *i*Q[6]/ Na^+ -based coordination polymers are arranged tightly, with no obvious free space. In contrast, with K^+ and Rb^+ (compounds **2** and **3**, respectively), the zigzag-like *i*Q[6]/ K^+ and Rb^+ -based coordination polymers are arranged into different porous assemblies (Fig.5).

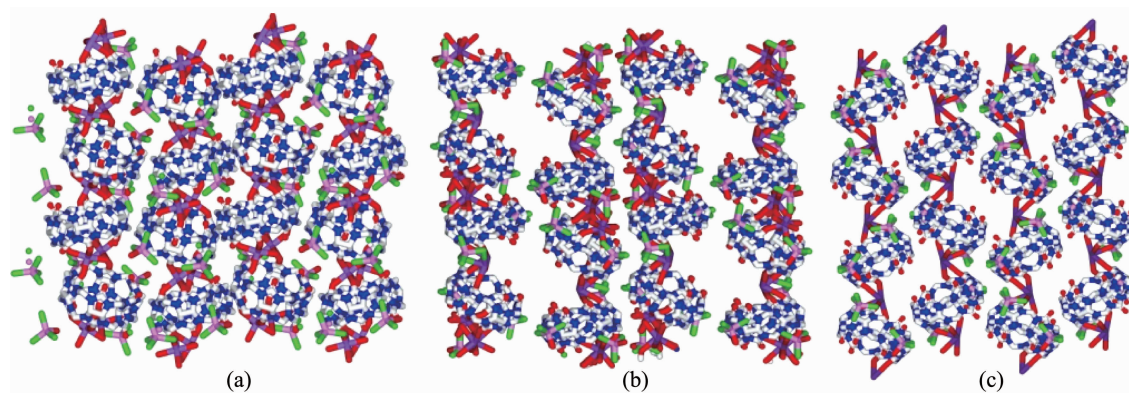


Fig.5 Supramolecular assembly constructed from linear coordination polymers of *i*Q[6]/ Na^+ (a), *i*Q[6]/ K^+ (b) and *i*Q[6]/ Rb^+ (c)

3 Conclusions

In the present study, we discovered that *i*Q[6] forms linear coordination polymers with alkali metal ions (M^+) in the presence of $[ZnCl_4]^{2-}$ anion structure-directing agents. The supramolecular assemblies consist of a $[ZnCl_4]^{2-}$ based honeycomb-like framework that interacts with the electropositive outer surface of *i*Q[6] through ion-dipole interactions. The electrone-

gative environment presumably attracts the M^+ cations to the portals of *i*Q[6], resulting in their coordination and formation of the 1D coordination polymers. Interestingly, different M^+ cations resulted in the formation of different supramolecular assemblies with different structural features. In particular the pore size was dependent on the ionic diameter of the cation. The resultant supramolecular assemblies might give rise to different absorption characteristics, and further

investigation is underway in our laboratory.

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