

## Construction of Supramolecular Self-Assembled Frameworks Comprised of *p*-Nitrophenol and Four Modified Cucurbit[*n*]urils

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Herein, we report the supramolecular self-assembly of fully substituted cyclopentyl-derived cucurbit[5]uril (CyP<sub>5</sub>Q[5]), cucurbit[6]uril (CyP<sub>6</sub>Q[6]), symmetrical dicyclopentyl-substituted cucurbit[6]uril (CyP<sub>2</sub>Q[6]) and fully substituted cyclobutyl-derived cucurbit[5]uril (CyB<sub>5</sub>Q[5]) with *p*-nitrophenol (**G**). Single-crystal X-ray diffraction was employed to characterize these supramolecular complexes [C<sub>81</sub>H<sub>81</sub>CaCl<sub>2</sub>N<sub>26</sub>O<sub>29</sub> (**1**), C<sub>60</sub>H<sub>85</sub>Ca<sub>2</sub>Cd<sub>2</sub>Cl<sub>8</sub>N<sub>25</sub>O<sub>25</sub> (**2**), C<sub>27</sub>H<sub>37</sub>CaCl<sub>4</sub>N<sub>13</sub>O<sub>14</sub>Zn (**3**) and C<sub>58</sub>H<sub>63</sub>CaCl<sub>4</sub>N<sub>23</sub>O<sub>23</sub>Zn (**4**)]. In these four systems, calcium ions were introduced to coordinate with the cucurbit[*n*]uril and **G** was enriched on the outer surface of the cucurbit[*n*]uril to construct four supramolecular frameworks.

**Keywords:** *p*-Nitrophenol, calcium ion, modified cucurbit[*n*]uril, supramolecular self-assembled frameworks.

## Конструирование супрамолекулярных самособирающихся каркасов, состоящих из *p*-нитрофенола и четырех модифицированных кукурбит[*n*]урилов

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Сообщается о супрамолекулярной самосборке полностью замещенного циклопентильного производного кукурбит[5]урила (CyP<sub>5</sub>Q[5]), кукурбит[6]урила (CyP<sub>6</sub>Q[6]), симметричного дициклопентилзамещенного кукурбит[6]урила (CyP<sub>2</sub>Q[6]) и полностью замещенного циклобутильного кукурбит[5]урила (CyB<sub>5</sub>Q[5]) с *p*-нитрофенолом (**G**). Образующиеся супрамолекулярные комплексы [C<sub>81</sub>H<sub>81</sub>CaCl<sub>2</sub>N<sub>26</sub>O<sub>29</sub> (**1**), C<sub>60</sub>H<sub>85</sub>Ca<sub>2</sub>Cd<sub>2</sub>Cl<sub>8</sub>N<sub>25</sub>O<sub>25</sub> (**2**), C<sub>27</sub>H<sub>37</sub>CaCl<sub>4</sub>N<sub>13</sub>O<sub>14</sub>Zn (**3**) и C<sub>58</sub>H<sub>63</sub>CaCl<sub>4</sub>N<sub>23</sub>O<sub>23</sub>Zn (**4**)] были охарактеризованы методом рентгеноструктурного анализа. Для построения четырех супрамолекулярных каркасов были введены ионы кальция для координации с кукурбит[*n*]урилами, дополненными по периферии фрагментами **G**.

**Ключевые слова:** *p*-Нитрофенол, ион кальция, модифицированный кукурбит[*n*]урил, супрамолекулярные самособирающиеся каркасы.

## Introduction

Cucurbit[n]uril (CB[n] or Q[n]) is a new generation of supramolecular macrocyclic compounds following crown ethers, cyclodextrins and calixarenes. Cucurbit[6]uril (Q[6]) was the first compound reported in the Q[n] family.<sup>[1]</sup> Ordinary Q[n] range from the smallest Q[4]<sup>[2,3]</sup> to the largest twisted Q[15],<sup>[4]</sup> and a series of modified Q[n] have been subsequently reported, including methyl-,<sup>[5]</sup> cyclohexyl-,<sup>[6]</sup> cyclopentyl-,<sup>[7,8]</sup> hydroxyl-,<sup>[9]</sup> phenyl-<sup>[10]</sup> and cyclobutyl-modified cucurbit[n]urils.<sup>[11]</sup> The discovery of these modified Q[n]s has greatly changed the solubility of cucurbit[n]urils, providing favorable conditions for Q[n] compounds in the fields of coordination chemistry, host-guest chemistry and nanomaterials. Consequently, several supramolecular compounds have been constructed by studying the interaction of the carbonyl portal of Q[n]s with metal ions<sup>[12-17]</sup> and the host-guest interaction between the hydrophobic cavity of Q[n]s and organic guest molecules.<sup>[18-24]</sup> In addition, supramolecular frameworks have also been constructed by studying the interactions formed between the outer surface of Q[n]s and negatively charged molecules or anions.<sup>[25-27]</sup>

Recent studies have shown that there were weak interactions formed between Q[n]s, such as hydrogen bonding,  $\pi \cdots \pi$  stacking, C-H $\cdots\pi$  interactions, and ion-dipole interactions.<sup>[28-31]</sup> There is an ion-dipole interaction formed between the [CdCl<sub>4</sub>]<sup>2-</sup> or [ZnCl<sub>4</sub>]<sup>2-</sup> anion and the positive potential outer surface of the Q[n], which is conducive to the construction of supramolecular self-assembled complexes based on the Q[n] and small organic molecules, which is considered to be effective structure inducer.<sup>[17, 26]</sup> In this paper, *p*-nitrophenol (G) was selected as the guest molecule and fully-substituted cyclopentyl-derived cucurbit[5]uril (CyP<sub>5</sub>Q[5]) and cucurbit[6]uril (CyP<sub>6</sub>Q[6]), symmetrical dicyclopentyl-substituted cucurbit[6]uril (CyP<sub>2</sub>Q[6]) and fully-substituted cyclobutyl-derived cucurbit[5]uril (CyB<sub>5</sub>Q[5]) used as hosts, and the supramolecular framework constructed. The structures of *p*-nitrophenol and the four modified Q[n]s are shown in Figure 1.

## Experimental

### General materials

All materials were reagent grade and used without any further purification. CyP<sub>5</sub>Q[5], CyP<sub>2</sub>Q[6], CyP<sub>6</sub>Q[6] and CyB<sub>5</sub>Q[5] (purity  $\geq 97\%$ ) were prepared in the Key Laboratory of Macrocyclic and Supramolecular Chemistry of Guizhou Province, China.

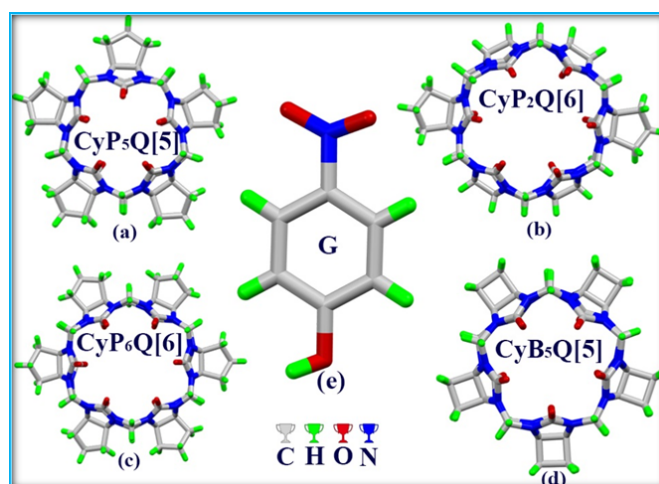
### Synthesis of the complexes 1-4

A mixture of CyP<sub>5</sub>Q[5] (10 mg, 9.73  $\mu\text{mol}$ ), *p*-nitrophenol (10 mg, 71.89  $\mu\text{mol}$ ) and CaCl<sub>2</sub> in 3 mL of 3 mol/L aqueous hydrochloric acid was heated until dissolution. Then, the solution was heated and stirred for 7–10 min in a water bath at 50 °C. Finally, the solution was allowed to stand at room temperature for 10–15 days to obtain single crystals of C<sub>81</sub>H<sub>81</sub>CaCl<sub>2</sub>N<sub>26</sub>O<sub>29</sub> (1) (33.8% yield). A mixture of CyP<sub>6</sub>Q[6] (10 mg, 8.08  $\mu\text{mol}$ ), *p*-nitrophenol (10 mg, 71.89  $\mu\text{mol}$ ), CdCl<sub>2</sub> (5 mg, 27.28  $\mu\text{mol}$ ) and CaCl<sub>2</sub> (5 mg, 45.05  $\mu\text{mol}$ ) in 3 mL of 3 mol/L aqueous

hydrochloric acid was heated until dissolution. Then, the solution was heated and stirred for 7–10 min in a water bath at 50 °C. Finally, the solution was allowed to stand at room temperature for 10–15 days to obtain single crystals of C<sub>60</sub>H<sub>85</sub>Ca<sub>2</sub>Cd<sub>2</sub>Cl<sub>8</sub>N<sub>25</sub>O<sub>25</sub> (2) (35.4% yield). A mixture of CyP<sub>2</sub>Q[6] (10 mg, 9.29  $\mu\text{mol}$ ), *p*-nitrophenol (10 mg, 71.89  $\mu\text{mol}$ ), ZnCl<sub>2</sub> (10 mg, 73.38  $\mu\text{mol}$ ) and CaCl<sub>2</sub> (5 mg, 45.05  $\mu\text{mol}$ ) in 3 mL of 3 mol/L aqueous hydrochloric acid was heated until dissolution. Then, the solution was heated and stirred for 7–10 min in a water bath at 50 °C. Finally, the solution was allowed to stand at room temperature for 10–15 days to obtain single crystals of C<sub>27</sub>H<sub>37</sub>CaCl<sub>4</sub>N<sub>13</sub>O<sub>14</sub>Zn (3) (37.3% yield) and a mixture of CyB<sub>5</sub>Q[5] (10 mg, 10.41  $\mu\text{mol}$ ), *p*-nitrophenol (10 mg, 71.89  $\mu\text{mol}$ ), ZnCl<sub>2</sub> (10 mg, 73.38  $\mu\text{mol}$ ) and CaCl<sub>2</sub> (5 mg, 45.05  $\mu\text{mol}$ ) in 3 mL of 3 mol/L aqueous hydrochloric acid was heated until dissolution. Then, the solution was heated and stirred for 7–10 min in a water bath at 50 °C. Finally, the solution was allowed to stand at room temperature for 10–15 days to obtain single crystals of C<sub>58</sub>H<sub>63</sub>CaCl<sub>4</sub>N<sub>23</sub>O<sub>23</sub>Zn (4) (41.5% yield).

### Crystal structure determination

A crystal with the appropriate size and transparency was selected and fixed on a glass probe with using petroleum jelly for X-ray single crystal diffraction analysis on a Bruker D8 Venture X-ray single crystal diffractometer in  $\omega$ -scan mode using graphite to monochromatize the Mo-K $\alpha$  rays ( $\lambda = 0.71073 \text{ \AA}$ ,  $\mu = 0.828 \text{ mm}^{-1}$ ). The crystal data were collected and Lorentz polarization and absorption correction carried out. SHELXT-14 and SHELXL-14 program packages were used for structural analysis and full matrix least squares refinement. All non-hydrogen atoms were anisotropically refined using the analytical expression of the neutral atom scattering factor and combined with anomalous dispersion correction. The SQUEEZE program in the PLATON package was used to delete some of the disordered solvent molecules. The X-ray crystallographic data for structures reported in this study have been deposited in the Cambridge Crystallographic Data Center under accession numbers CCDC: 2031927 (1), 2023194 (2), 2156026 (3) and 2156027 (4). These data can be obtained free of charge via [http://www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif). The crystal parameters, data acquisition conditions, and parameters of the complexes 1–4 are listed in Table 1.



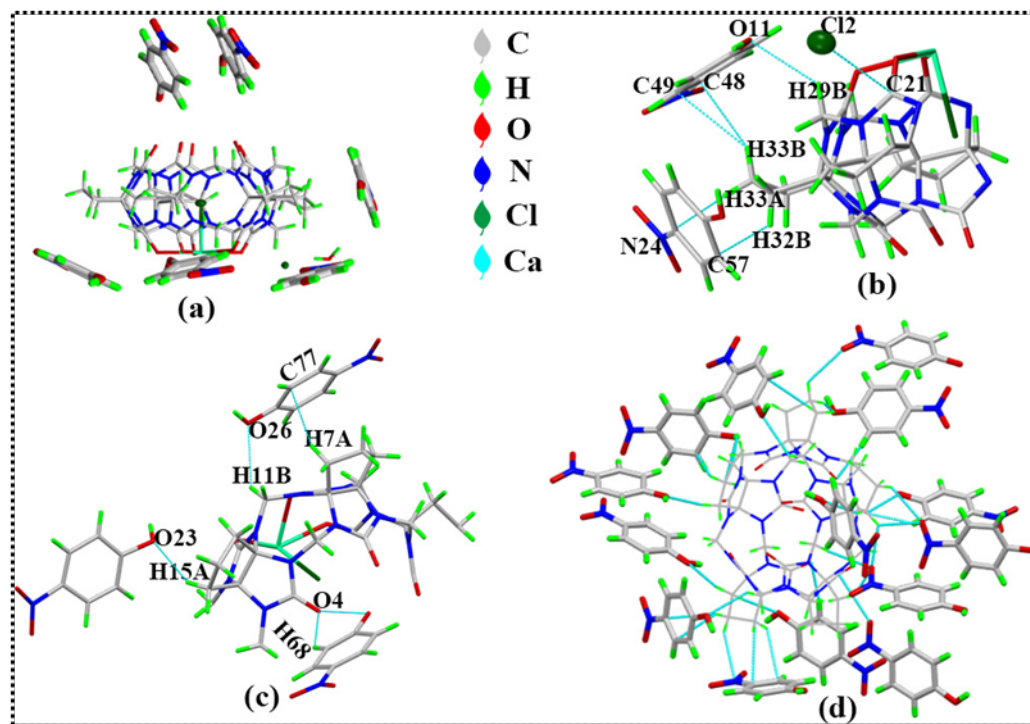
**Figure 1.** The structures of *p*-nitrophenol and four modified Q[n]s: (a) CyP<sub>5</sub>Q[5], (b) CyP<sub>2</sub>Q[6], (c) CyP<sub>6</sub>Q[6], (d) CyB<sub>5</sub>Q[5] and (e) *p*-nitrophenol (G).

**Table 1.** Crystallographic data for complexes 1–4.

Complex	1	2	3	4
Empirical formula	C <sub>81</sub> H <sub>81</sub> CaCl <sub>2</sub> N <sub>26</sub> O <sub>29</sub>	C <sub>60</sub> H <sub>85</sub> Ca <sub>2</sub> Cd <sub>2</sub> Cl <sub>8</sub> N <sub>25</sub> O <sub>25</sub>	C <sub>27</sub> H <sub>37</sub> CaCl <sub>4</sub> N <sub>13</sub> O <sub>14</sub> Zn	C <sub>58</sub> H <sub>63</sub> CaCl <sub>4</sub> N <sub>23</sub> O <sub>23</sub> Zn
<i>M<sub>r</sub></i>	1993.69	2145.08	1014.94	1697.56
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> -1	<i>P</i> -1	<i>P</i> -1
<i>a</i> (Å)	25.3747(16)	10.396(3)	10.458(2)	10.6771(18)
<i>b</i> (Å)	20.3378(15)	15.684(4)	14.957(3)	15.343(2)
<i>c</i> (Å)	17.3896(11)	16.552(4)	15.260(3)	23.040(4)
<i>α</i> (deg)	90	115.720(8)	117.530(5)	102.675(5)
<i>β</i> (deg)	90.087(2)	99.619(10)	98.114(6)	94.198(5)
<i>γ</i> (deg)	90	96.034(10)	96.867(6)	99.900(5)
<i>V</i> [Å <sup>3</sup> ]	8974.2(10)	2348.7(11)	2048.6(7)	3603.5(10)
<i>Z</i>	4	1	2	2
<i>D<sub>c</sub></i> (g cm <sup>-3</sup> )	1.476	1.517	1.645	1.565
<i>F</i> (000)	4140	1092	1040	1748
<i>μ</i> (mm <sup>-1</sup> )	0.226	0.869	1.065	0.653
Date/Params	15757/1264	11588/620	6925/546	12553/935
<i>θ</i> (deg)	2.23–26.70	2.49–28.25	2.55–27.87	2.31–28.05
<i>R</i> <sub>int</sub>	0.0785	0.0552	0.0890	0.1470
<i>R</i> [ <i>I</i> > 2σ( <i>I</i> )] <sup>[a]</sup>	0.1861	0.0533	0.0847	0.1330
<i>wR</i> [ <i>I</i> > 2σ( <i>I</i> )] <sup>[b]</sup>	0.4383	0.1567	0.2437	0.3622
<i>R</i> (all data)	0.1995	0.0650	0.1196	0.1559
<i>wR</i> (all data)	0.4430	0.1680	0.2565	0.3776
GOF ( <i>F</i> <sup>2</sup> )	1.102	1.034	1.046	1.448

<sup>[a]</sup>Conventional *R* on *Fhkl*:  $\sum||F_o| - |F_c|| / \sum|F_o|$ .

<sup>[b]</sup>Weighted *R* on  $|Fhkl|^2$ :  $\sum[w(F_o^2 - F_c^2)^2] / \sum[w(F_o^2)^2]^{1/2}$ .

**Figure 2.** Crystal structure of complex 1: (a) Asymmetric unit; (b, c, d) intermolecular interaction.

## Results and Discussion

### Description of the crystal structure of complex

The asymmetric unit of supramolecular self-assembly complex **1** contained one CyP<sub>5</sub>Q[5] molecule, six *p*-nitrophenol (**G**) molecules, two chloride ions, and one Ca<sup>2+</sup>

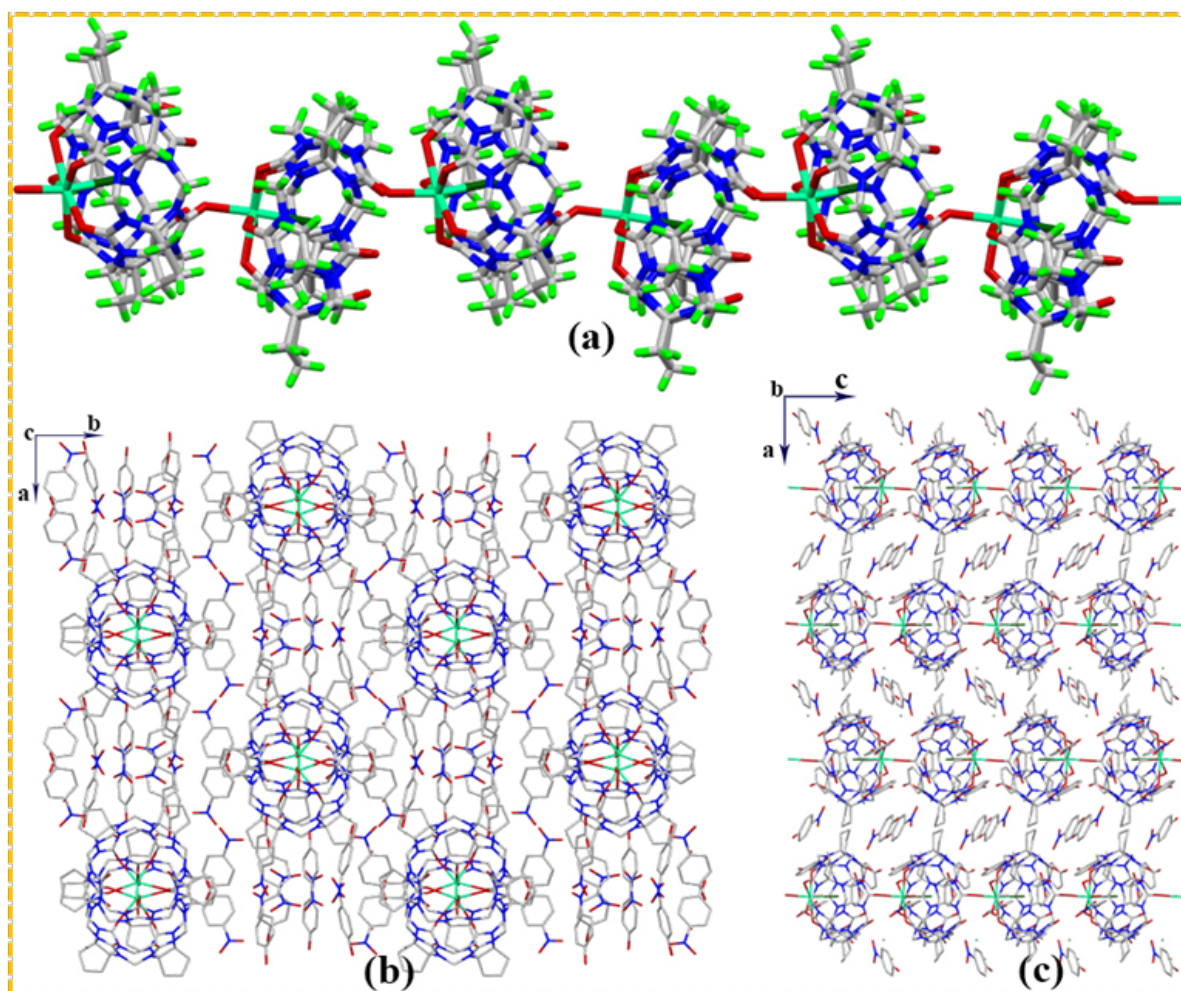
ion (Figure 2(a)). One chloride ion was directly coordinated to the calcium ion and the other is free. Figure 2(b and c) show the surrounding **G** molecules of CyP<sub>5</sub>Q[5] interact through C-H...π bonds C48-H33B, C49-H33B, C57-H32B and C77-H7A with the distances between them being 2.791, 2.754, 2.843 and 2.886 Å, respectively. In addition, there were C-H...O and C-H...N interactions formed

between CyP<sub>5</sub>Q[5] and **G** (O11-H29B, N24-H33A, O26-H11B, O23-H15A and O4-H68) with the distances between them being 2.555, 2.700, 2.646, 2.614 and 2.589 Å, respectively. The chloride ion interacted with the outer surface of the CyP<sub>5</sub>Q[5] (C21) via an ionic dipole interaction. Due to the coordination of the Ca<sup>2+</sup> ions with the carbonyl oxygen atoms at the portal of CyP<sub>5</sub>Q[5], the outer surface of CyP<sub>5</sub>Q[5] had more positive charges, so **G** was enriched around CyP<sub>5</sub>Q[5], as shown in Figure 2d, which clearly showed CyP<sub>5</sub>Q[5] had fourteen **G** molecules bound to its outer surface via weak interactions.

Figure 3(a) shows the calcium ions act as a bridge connecting two CyP<sub>5</sub>Q[5] molecules, thereby forming a one-dimensional supramolecular chain. Figure 3(b and c) are the packing diagrams of the crystal structures of supramolecular self-assembled complex **1** viewed along two different directions. It can be seen that **G** was enriched around CyP<sub>5</sub>Q[5] and presents a regular arrangement (Figure 3(b)). Figure 3(c) shows **G** was embedded in the large pores formed between the CyP<sub>5</sub>Q[5] molecules. It was

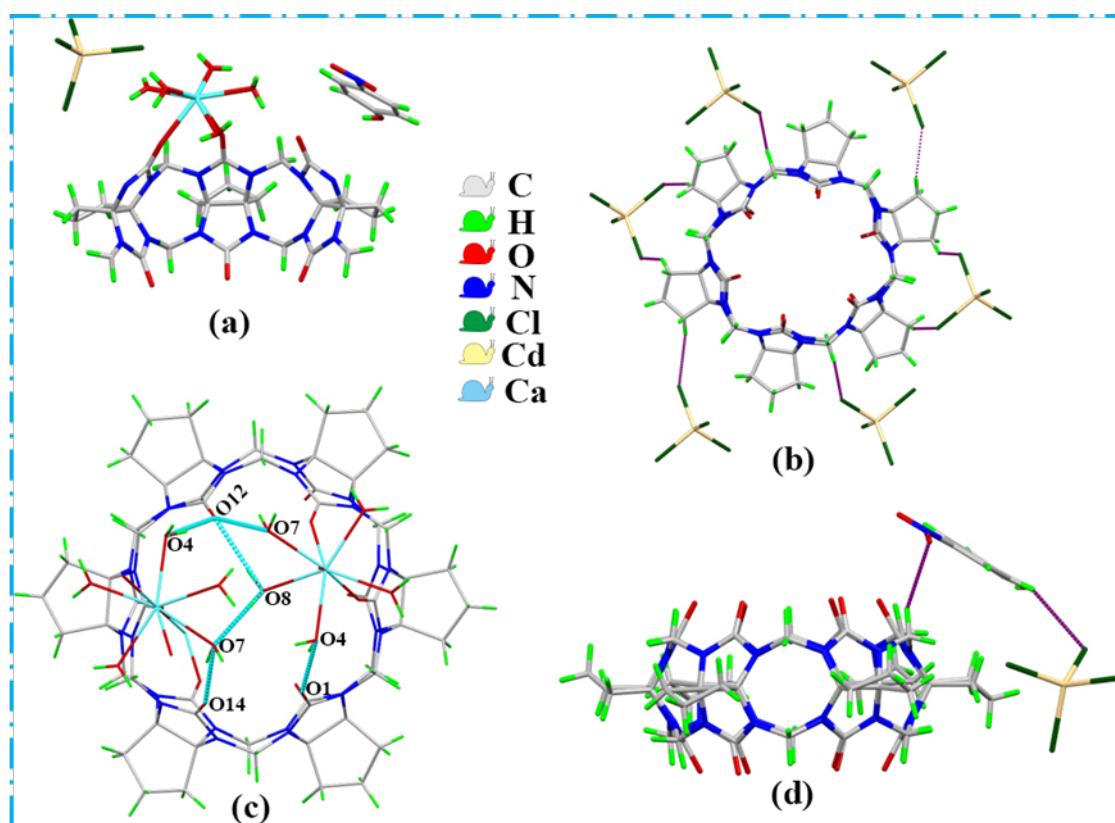
further demonstrated that there was enough space around the CyP<sub>5</sub>Q[5] host for guest molecules to enter.

The asymmetric unit of supramolecular self-assembly complex **2** contained one CyP<sub>6</sub>Q[6] molecule, one *p*-nitrophenol (**G**) molecule, one [CdCl<sub>4</sub>]<sup>2-</sup> counter ion, one Ca<sup>2+</sup> ion and five coordinated water molecules (Figure 4(a)). Figure 4(b and d) show that an ion-dipole interaction was formed between the [CdCl<sub>4</sub>]<sup>2-</sup> counter ion and CyP<sub>6</sub>Q[6]. Each CyP<sub>6</sub>Q[6] was surrounded by six [CdCl<sub>4</sub>]<sup>2-</sup> counter ion that interacted with it (Figure 4(b)), the **G** molecule not only formed a C-H... $\pi$  interaction with the outer surface of CyP<sub>6</sub>Q[6], but also had an C-H...Cl interaction with the [CdCl<sub>4</sub>]<sup>2-</sup> counter ion (Figure 4(d)). The calcium ions not only coordinated with the carbonyl oxygen atom of CyP<sub>6</sub>Q[6], but also coordinated with free water molecules; the coordinated water molecule formed a hydrogen bond with the carbonyl oxygen atom of CyP<sub>6</sub>Q[6] (O12-O8, O12-O4, O12-O7, O4-O1, O7-O14, O7-O8), the distances between them were 2.959, 2.801, 2.851, 2.836 Å, 2.716 and 2.924 Å, respectively.

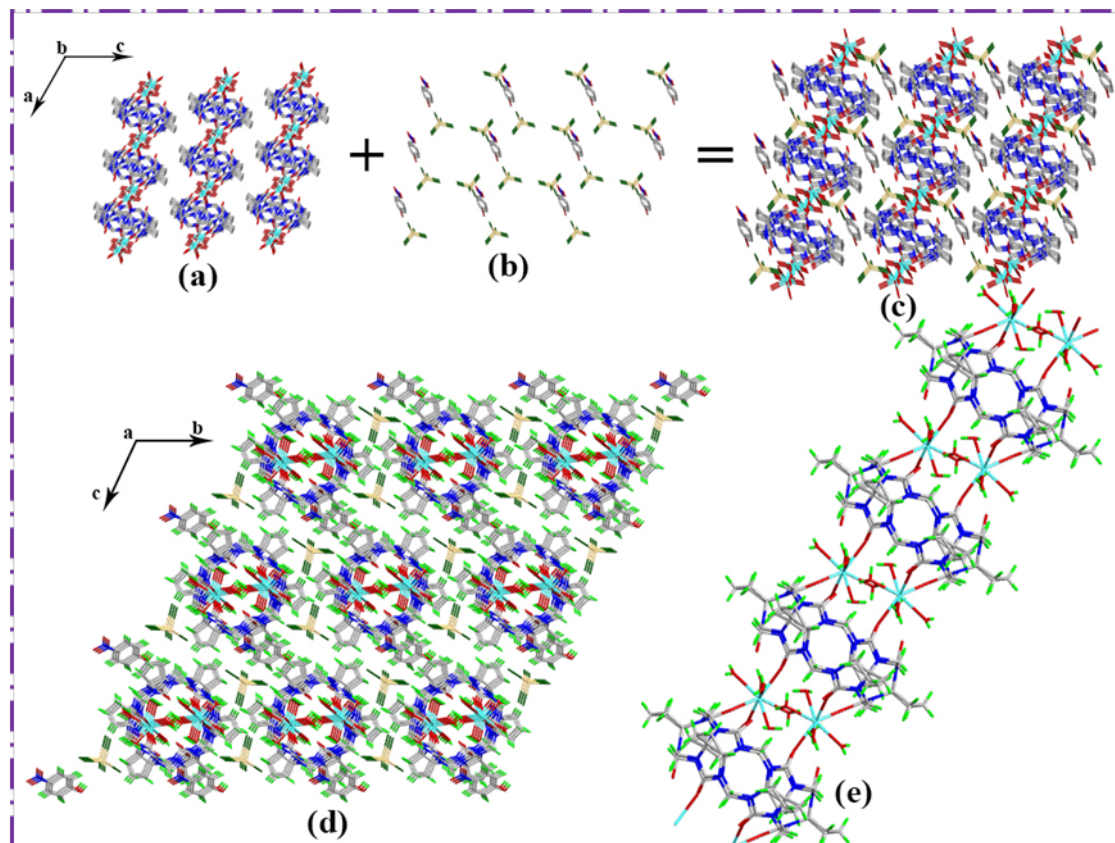


**Figure 3.** Crystal structure of complex **1**: (a) One-dimensional supramolecular chain; (b) and (c) Stacking diagram viewed along the c and b-axis.

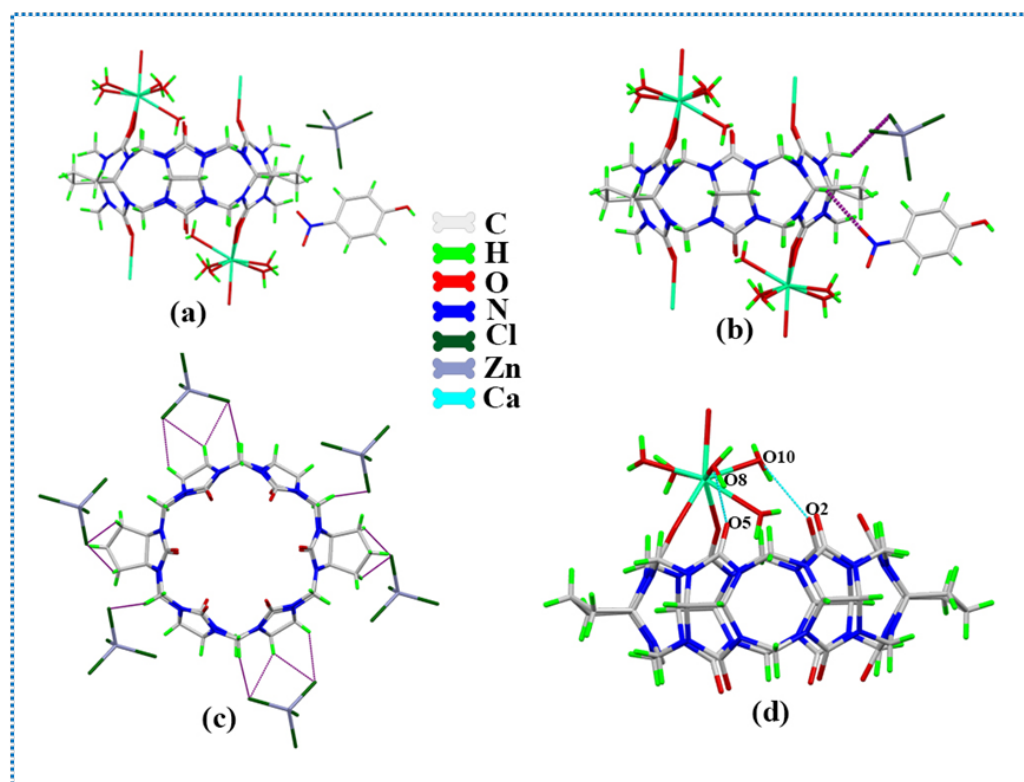




**Figure 4.** Crystal structure of complex 2: (a) Asymmetric unit; (b, d) Ion-dipole interaction; (c) Hydrogen bond interaction.



**Figure 5.** Crystal structure of complex 2: (a), (b) and (c) Stacking diagram viewed along the b-axis; (d) Stacking diagram viewed along the a-axis; (e) One-dimensional supramolecular chain.



**Figure 6.** Crystal structure of complex **3**: (a) Asymmetric unit; (b, c) Ion-dipole interaction; (d) Hydrogen bond interaction.

Figure 5(a, b and c) show the stacking diagram of the crystal structure viewed along the *b*-axis. Many holes were formed between the **G** molecules and the complexes of CyP<sub>6</sub>Q[6] and calcium ions were embedded in them. Figure 5(d) shows the stacking diagram of the crystal structure of the complex viewed along the *a*-axis and Figure 5(e) shows the one-dimensional supramolecular chain of the complex **2** with two CyP<sub>6</sub>Q[6] coordinated with two calcium ions.

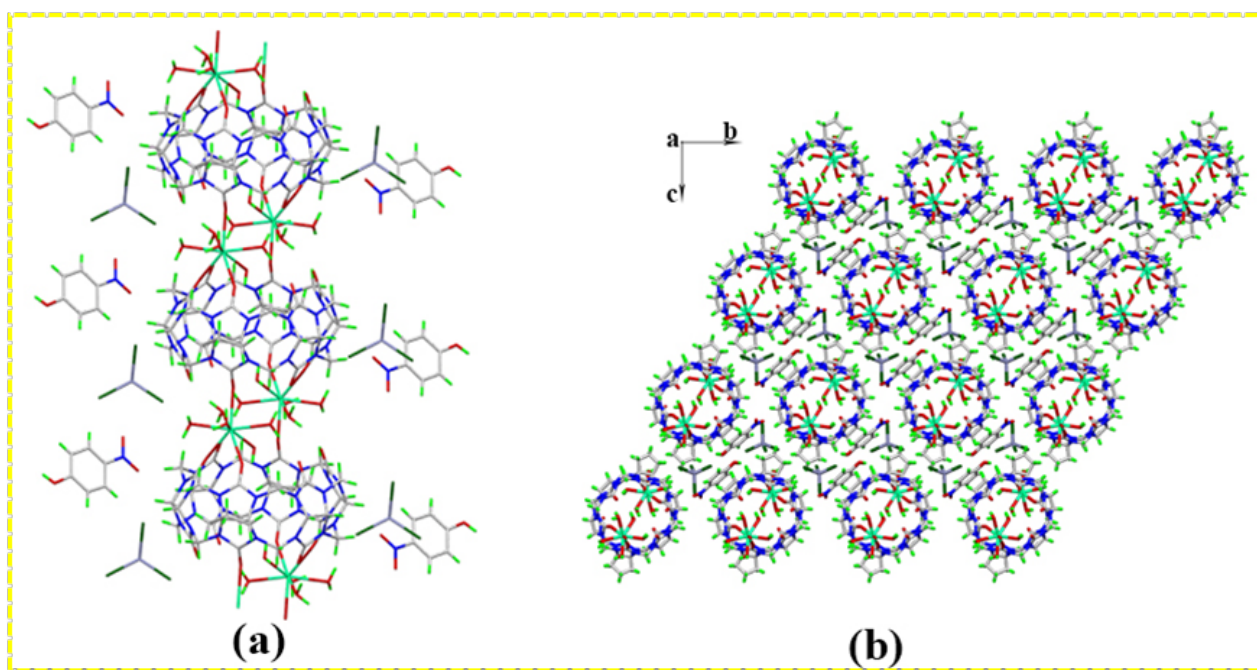
The asymmetric unit of supramolecular self-assembly complex **3** contained one molecule of CyP<sub>2</sub>Q[6], one molecule of *p*-nitrophenol (**G**), and one [ZnCl<sub>4</sub>]<sup>2-</sup> counter ion (Figure 6(a)). Figure 6(b) shows the [ZnCl<sub>4</sub>]<sup>2-</sup> counter interacts with CyP<sub>2</sub>Q[6] via a C-H⋯Cl interaction and *p*-nitrophenol interacts with CyP<sub>2</sub>Q[6] via a C-H⋯O interaction. Figure 6(c) shows that there were six [ZnCl<sub>4</sub>]<sup>2-</sup> ions around each CyP<sub>2</sub>Q[6] bonded via ion-dipole interactions (shown by the purple curve in Figure 6(c)). Interestingly, in addition to the Ca<sup>2+</sup> ion forming a coordination bond with the carbonyl oxygen atom at the portal of the CyP<sub>2</sub>Q[6], there was a hydrogen bond (O8-O5, O10-O2) formed between the coordination water molecule interacting with Ca<sup>2+</sup> and the carbonyl oxygen atom, as shown by the blue curve in Figure 6(d), and the distances between them are 2.802 and 2.902 Å, respectively.

Figure 7(a) shows the one-dimensional supramolecular chain of complex **3**, in which two CyP<sub>2</sub>Q[6] were connected via Ca<sup>2+</sup> coordination to form a one-dimensional chain supramolecular. The specific form was the coordination of the portal carbonyl oxygen atoms of the two CyP<sub>2</sub>Q[6] molecules surrounded by [ZnCl<sub>4</sub>]<sup>2-</sup> counter ions and inlaid with **G** molecules. Figure 7(b) shows the crystal structure stacking diagram of the complex viewed

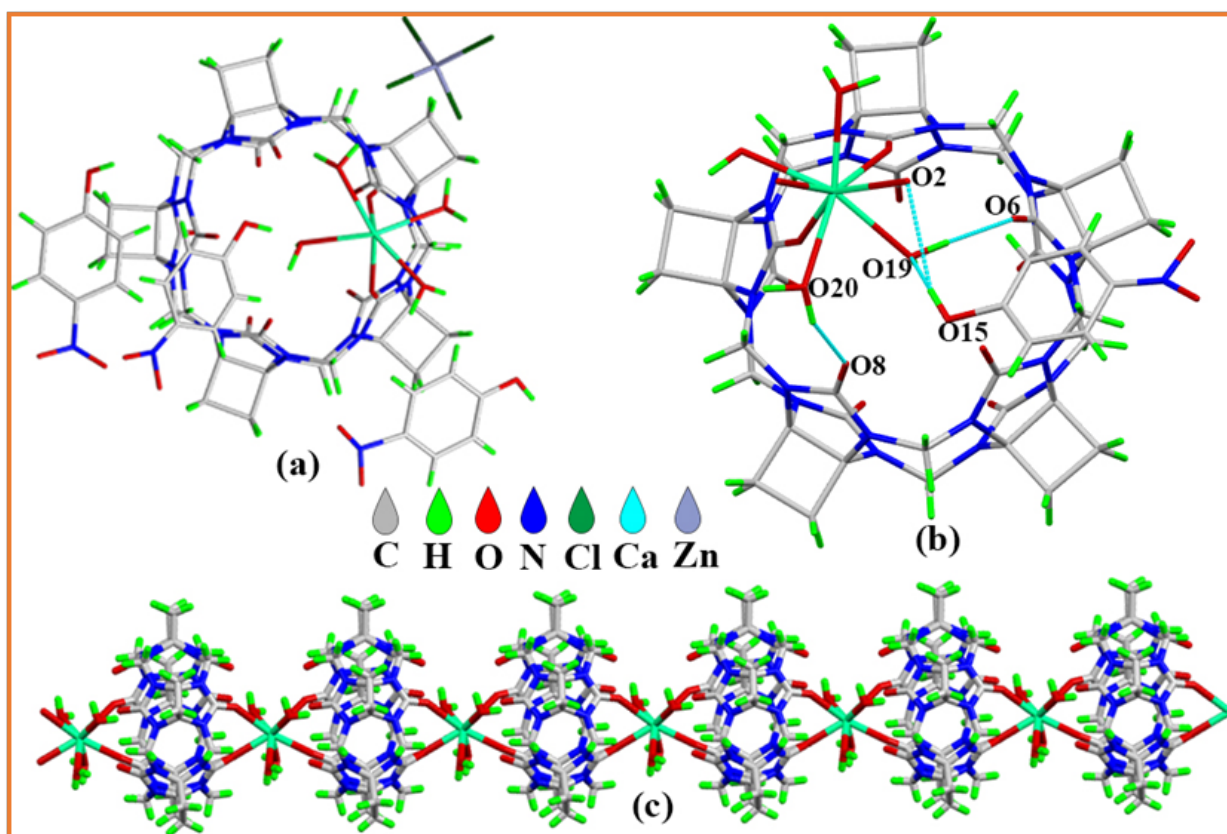
along the *a*-axis. It can be clearly seen that the **G** molecule was embedded in the pores of the CyP<sub>2</sub>Q[6] molecule, forming a supramolecular complex framework.

The asymmetric unit of supramolecular self-assembly complex **4** contained one molecule of CyB<sub>5</sub>Q[5], three molecules of *p*-nitrophenol (**G**), one Ca<sup>2+</sup> ion and one [ZnCl<sub>4</sub>]<sup>2-</sup> counter ion (Figure 8(a)). Figure 8(b) shows the calcium ions not only coordinated with the carbonyl oxygen atom of CyB<sub>5</sub>Q[5], but also coordinated with the free water molecules; the coordinated water molecule formed a hydrogen bond with the carbonyl oxygen atom of CyB<sub>5</sub>Q[5] (O19-O6, O20-O8) and the distances between them were 2.816 and 2.773 Å, respectively. The coordination water molecule formed a hydrogen bond with **G** (O15-O19, O15-O2) and the distances between them were 2.843 and 3.385 Å, respectively. Figure 8(c) shows the one-dimensional supramolecular chain of the complex **4** had two CyB<sub>5</sub>Q[5] coordinated with one calcium ion.

Figure 9(a) shows there are five **G** molecules and four [ZnCl<sub>4</sub>]<sup>2-</sup> counter ions around each CyB<sub>5</sub>Q[5] molecule and the [ZnCl<sub>4</sub>]<sup>2-</sup> counter ions form C-H⋯Cl interactions with the outer surface of CyB<sub>5</sub>Q[5]. **G** formed weak C-H⋯π and C-H⋯O interactions with the outer surface and portal of CyB<sub>5</sub>Q[5]. There were three CyB<sub>5</sub>Q[5] molecules around each metal ion forming a C-H⋯Cl interaction connecting the CyB<sub>5</sub>Q[5] molecules. At the same time, there was a dipole-dipole interaction formed between the CyB<sub>5</sub>Q[5] (Figure 9(a)). Figure 9(c) is the crystal structure stacking diagram of complex **4** viewed along the *a*-axis. It can be clearly seen that holes were formed between the CyB<sub>5</sub>Q[5] molecules and the **G** molecules were embedded in these holes, thereby forming a supramolecular self-assembly.

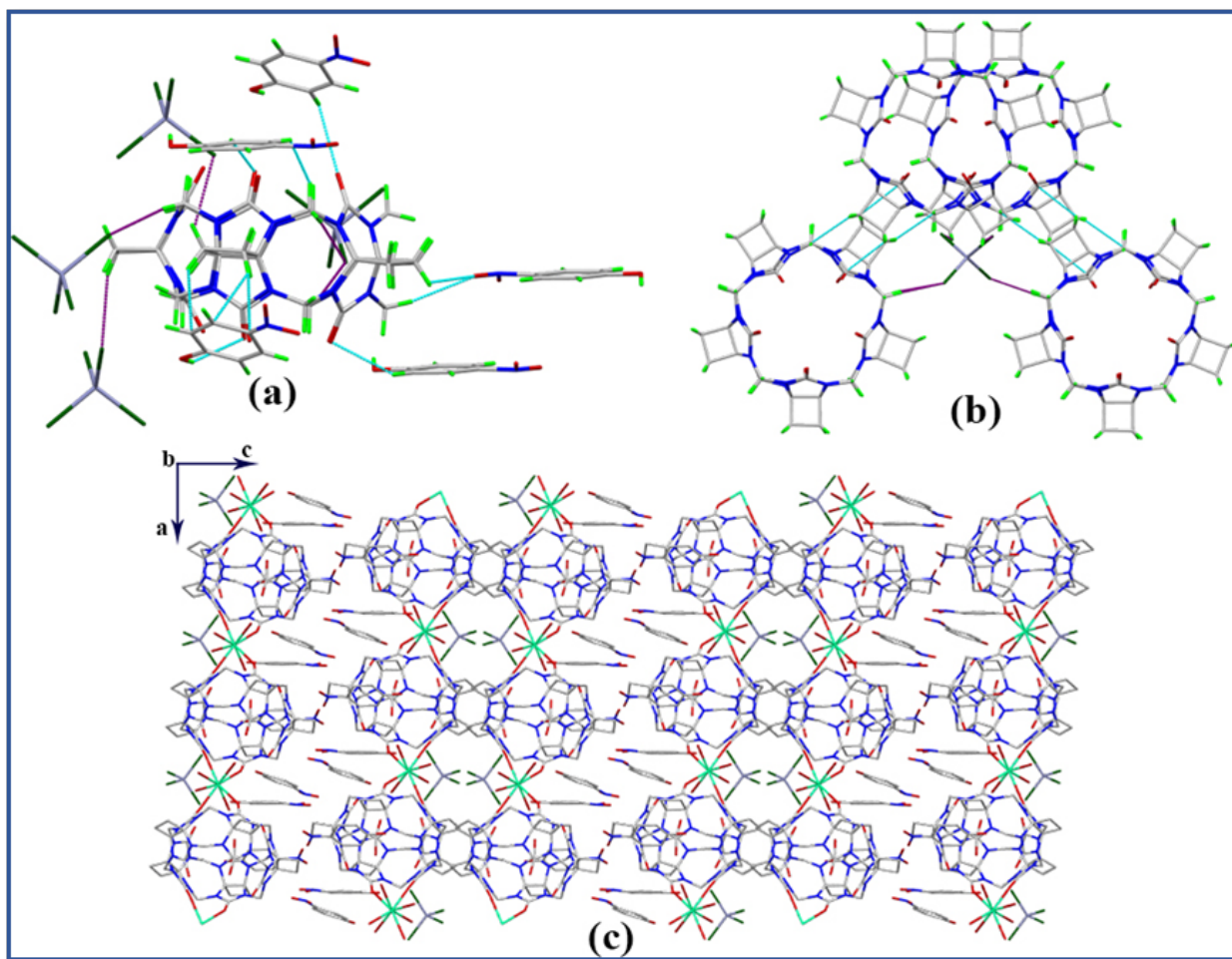


**Figure 7.** Crystal structure of complex 3: (a) One-dimensional supramolecular chain; (b) Stacking diagram viewed along the a-axis.



**Figure 8.** Crystal structure of complex 4: (a) Asymmetric unit; (b) Hydrogen bond interaction; (c) One-dimensional supramolecular chain.





**Figure 9.** Crystal structure of complex 4: (a, b) Intermolecular interaction; (c) Stacking diagram viewed along the a-axis.

## Conclusions

In this paper, the supramolecular self-assembly of *p*-nitrophenol and four modified cucurbit[*n*]urils was designed and carried out. A quaternary supramolecular complex using cucurbit[*n*]uril as the host, calcium ion as the bridge connecting the supramolecular chain of the cucurbit[*n*]uril,  $[\text{ZnCl}_4]^{2-}$  or  $[\text{CdCl}_4]^{2-}$  as the structure inducer and **G** as the guest was formed. In these four systems, the  $\text{Ca}^{2+}$  ions were introduced to coordinate with the cucurbit[*n*]uril and *p*-nitrophenol was enriched on the outer surface of the cucurbit[*n*]urils to construct four supramolecular frameworks. Through the study of the crystal structures of the four complexes, the research scope of cucurbit[*n*]urils has been further expanded and research on phenolic compounds has been further developed in the field of cucurbit[*n*]urils.

**Supplementary information.** The experimental sections and crystal data are listed in the supporting materials.

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**Conflict of interests.** The authors declare no conflict of interests.

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