Supporting Information

Chlorine-assisted fabrication of hybrid supramolecular structures

via electrostatic interactions

Lei Xie, Yuanqi Ding, Xinyi Wang and Wei Xu*

Interdisciplinary Materials Research Center, College of Materials Science and

Engineering, Tongji University, Shanghai 201804, P. R. China

*Correspondence: xuwei@tongji.edu.cn

1. Thermal dynamic stability of C self-assembled structure

After thermal treatment, the self-assembled structure of cytosine molecules remains the same as "glassy state" without structural transformation on surface until total desorption as shown in Figure S1.



Figure S1. Large STM image obtained after annealing at 390 K for 10 min, showing glassy state phase.

2. Determination of molecular chirality and structural model

The chirality of the molecules is hard to recognize due to the limited molecular size and the lack of large chemical groups like methyl embedded. As the amino group is a protrusion of the molecule, we assign it to the tiny sharp end of the molecular configuration. While the amino groups are not always distinguishable, we then assign them according to the principle of the electrostatic interaction formation as a supplementary means (i. e. oxygen atoms should point to Na⁺ ions and hydrogen atoms should interact with Cl⁻ ions). Once the amino groups and direction of oxygen atoms are confirmed, the chirality can be verified. Hydrogen bonds formed between molecules can be considered as a testing method to further verify the accuracy of the assignment of the model. It is shown in the Figure S2 that different colors represent different chiralities of molecules and the sharp end indicates the amino group.



Figure S2. Close-up STM image with contours in blue and green colors representing different chiralities of molecules (R and L, respectively) and the sharp end indicates the amino group.

3. Geometric parameters for C=O···Na⁺ and NH···Cl⁻ interactions

Firstly, we summarize the parameters for the C=O···Na⁺ interactions within C₆Na₂ motifs. As shown in the Figure S3, we label the comprising molecules as C1 (short for Cytosine1), C2 and C3 and the adjacent Na ion to Na⁺(1). According to the rotational symmetry within the motif, the other components can be labeled as C1', C2', C3' and Na⁺(1').



Figure S3. DFT-optimized gas-phase model of C_6Na_2 motif with labels of all the species namely C1, C2, C3 and Na⁺(1), as well as C1', C2', C3' and Na⁺(1') the with rotational symmetry. The C=O···Na⁺ interaction are depicted in pink dashed lines.

As is shown, for instance, the C=O···Na⁺ interaction between C1 and Na⁺(1) has a corresponding one between C1' and Na⁺(1'). Thus we compare them together in the Table S1 and find that they have similar properties both in distance and angle. One thing to note that, for C3 and C3' molecules, they interact with Na⁺(1) and Na⁺(1') simultaneously and these interactions are also states in the table.

Relevant geometric parameters for electrostatic interactions involving Na ⁺		
	Distance (Å)	Angle (degrees)
(C1) C=O···Na ⁺ (1)/(C1') C=O···Na ⁺ (1')	2.750/2.753	149/149
(C2) C=O···Na+ (1)/(C2') C=O···Na+ (1')	2.219/2.221	173/173
(C3) C=O···Na ⁺ (1)/(C3') C=O···Na ⁺ (1')	2.465/2.464	106/106
(C3) C=O···Na ⁺ (1')/(C3') C=O···Na ⁺ (1)	2.310/2.309	143/143

Table S1. The relevant geometric parameters (distance and angle) for all the C=O \cdots Na⁺ interactions.

Secondly, we summarize the parameters for the NH···Cl⁻ hydrogen bond interactions. The gasphase optimized model for the Cl ions connecting both C_6Na_2 motifs and C_4 motifs is shown in Figure S4a below. Based on the nomenclature and rotational symmetry mentioned above, we label the molecules which have interactions with Cl ions as C1, C2, C4 and C1', C2', C4' as shown in the enlarged Figure S4b below (C3 and C3' don't have interaction with Cl ions). The side Cl ions are labeled as Cl⁻(1) and Cl⁻(1'), and the middle one as Cl⁻(2).



Figure S4. (a) DFT-optimized gas-phase model of a cluster involving C_6Na_2 motifs and C_4 motifs connected by Cl ions. (b) Enlarged image of the model in black rectangle in (a) with labels of components, namely C1, C2, C4, Cl⁻(1) and C1', C2', C4', Cl⁻(1') according to with rotational symmetry, as well as the middle Cl⁻(2). The NH^{...}Cl⁻ interactions are depicted in green dashed lines.

Therefore, the relevant geometric parameters for the interactions involving Cl⁻ are listed in the Table S2 below. For example, the interaction of NH···Cl⁻ between C1 and Cl⁻(1), and between C1' and Cl⁻(1') are comparable. As a result, we can find out that the corresponding bonds are similar in both distance and angels except for the hydrogen bonds involving Cl⁻(2), whose distances are 3.6 Å and 2.6 Å, respectively. This may due to the relatively large size of the cavity where Cl⁻(2) locates in and also the weak electrostatic interactions of CH···Cl⁻ generated in the system stabilizing the whole structure. So that the middle Cl ion is relatively flexible in the cavity and the disappearance of Cl⁻(2) will result in defect type II (discussed in Figure 4).

Relevant geometric parameters for electrostatic interactions involving CI-			
	Distance (Å)	Angle (degrees)	
(C1) NH…Cl- (1)/(C1') NH…Cl- (1')	2.333/2.439	170/167	
(C2) NH…Cl ⁻ (1')/(C2') NH…Cl ⁻ (1)	2.943/2.483	173/174	
(C4) NH…Cl- (1')/(C4') NH…Cl- (1)	2.287/2.373	176/175	
(C1) NH…Cl ⁻ (2)/(C1') NH…Cl ⁻ (2)	3.576/2.573	136/139	

Table S2. The relevant geometric parameters (distance and angle) for all the $NH \cdots Cl^{-1}$ interactions.

4. Distance between Na⁺···Na⁺ and Cl⁻···Cl⁻

The distance between $Na^+ Na^+$ in the optimized C_6Na_2 model is calculated to be 3.925 Å, which is in accordance with the distance between Na^+ ions in the previous study about $1mC_4Na_2$ motif which is calculated to be 3.959 Å. Moreover, the distance between the adjacent two Cl⁻ ions is calculated to be 5.185 Å and 5.723 Å. As discussed above, the middle Cl ion has larger degree of freedom in the cavity, resulting in a relatively large difference in the distances with two side Cl ions. Because Na^+ and Cl⁻ ions are separated by C molecules in the structure, that

is to say that they don't have direct interactions with each other, it is meaningless to calculate the distance between them.

It may be expected that if we increase the size of the anions (i.e. iodine ions), the cavity formed by molecules and two side anions might be too small for the residence of the middle anion, which may result in the generation more defects of type II. Moreover, if we change the charge of the cations (i.e. Ca^{2+}) which will also have electrostatic interaction with oxygen atoms, the binding mode and the final structure may remain the same according to the study of G4-M which can be formed by either Na⁺ or Ca²⁺.

5. More examples of overview STM image showing connections



Figure S5. More examples of the regions in the sample showing different connection types. (a) A defect free region where only type I and type II are found. (b) Another example where only two type III connections are displayed.