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## Solid state studies of the assembly of diionic guanidinium/carboxylate compounds

Wei Wang<sup>a,†</sup>, Jun Gu<sup>b,†</sup>, Xiaoliang Zou<sup>a</sup>, Weiqi Tong<sup>a,\*</sup>, Hegui Gong<sup>a,\*</sup>

<sup>a</sup> Department of Chemistry, Shanghai University, 99 Shang-Da Road, Shanghai 200444, China

<sup>b</sup> College of Materials Science and Engineering, Shanghai University, 99 Shang-Da Road, Shanghai 200444, China

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### ABSTRACT

Reported herein are the solid state studies of guanidinium/carboxylate salts or the zwitterionic species derived from amino acids. It was disclosed that carboxylates tend to bond to the two unsubstituted external guanidine (N–H)s, adopting assembly modes A and C depending on the geometry of the linkers. Rigid linkers that inhibit the guanidine and carboxylate planes parallel or on the same plane tend to give helical tapes. Bonding of carboxylate to the internal (N–H)s was observed (mode D) only when the external (N–H)s are not available as in **5**, suggesting that external bonding modes A and C are possibly energetically more favored than the internal modes B and D. This work may be useful for the development of complex linear particularly helical structures and dimeric structures in polar solvents.

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### Introduction

Neutral hydrogen-bond-mediated self-assembly, although has received tremendous success in the construction of numerous architectures,<sup>1,2</sup> the low binding affinities in high-dielectric media particularly in water often constrain its applications to organic solvents.<sup>1,2</sup> To circumvent these drawbacks, ionic interactions are introduced to enforce the strength of H-bonds by virtue of their strong electrostatic attraction.<sup>3,4</sup> Consequently, ion-pair assisted H-bonding (IPA-H) may possess the features from both ionic interactions and hydrogen bonds, hence satisfying the demand for strength and directionality. Typical IPA-H bonding elements include guanidinium/carboxylate,<sup>5</sup> guanidinium/phosphate,<sup>6</sup> amidinium/carboxylate,<sup>7</sup> and ammonium/carboxylate.<sup>8</sup> Successful development of dimeric complexes such as zwitterion dimers,<sup>5</sup> molecular capsules,<sup>9</sup> and double helices<sup>10</sup> in polar solvents has been achieved. More importantly, recognition of peptides and proteins using guanidinium-based receptors has also received significant attention.<sup>11</sup>

Complexation of guanidinium and carboxylate is particularly intriguing, as it often gives bridged bidentate ion-enforced H-bonding motif (mode A, external).<sup>5</sup> Other typical assembly

modes that have been documented include bridged internal (mode B)<sup>12,6a</sup> and random external (mode C) and internal (mode D)<sup>13</sup> ion-pairing motifs (Fig. 1).

Solution studies have shown that the association affinity between guanidinium and carboxylate ions is rather weak in DMSO.<sup>14</sup> However, double ion pairing interactions in Schmuck's guanidiniocarbonyl pyrrole carboxylate zwitterionic system have been shown to increase the binding strength by a factor of 10<sup>9</sup> relative to simple hydrogen-bonding in DMSO.<sup>5d</sup> The additional H-bond derived from the side arm-modified guanidinium favoured the salt bridge assembly mode B. In contrast to the solution studies, the unique bridge assembly modes of guanidinium and carboxylate render them excellent building blocks in crystal engineering, including Ward's cage and Mak's knit network.<sup>15</sup> However, the solid state studies on the assembly of diguanidinium and dicarboxylate, as well as zwitterionic compounds that are linked by readily available spacers are still rare. This is possibly due to the fact that most guanidinium/carboxylate complexation is conducted using mixtures of guanidinium halides (or pseudo halides) with metal (e.g., sodium) carboxylates, which are difficult to crystallize rather than crashing out metal halide salts. In this Letter, we present the solid state studies of a variety of diionic guanidinium/carboxylate salts and zwitterionic analogs derived from amino acids. While the assembly modes in Figure 1 heavily rely on the substitution patterns on the guanidine moieties, the linkers may also play important roles in IPA-H assembly modes and the aggregation patterns.

\* Corresponding authors. Tel.: +86 21 6613 5108 (W.T.), +86 21 6613 2410 (H.G.).

E-mail addresses: [tongwq@staff.shu.edu.cn](mailto:tongwq@staff.shu.edu.cn) (W. Tong), [Hegui\\_gong@shu.edu.cn](mailto:Hegui_gong@shu.edu.cn) (H. Gong).

† These authors contribute equally.

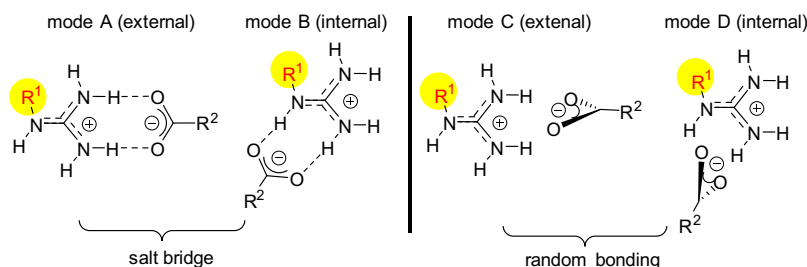
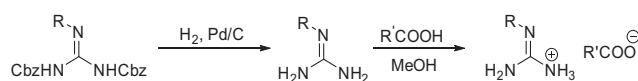


Figure 1. Ion-pair assisted H-bonding modes of guanidinium and carboxylate.

## Results and discussion

Our protocol to guanidinium carboxylate salts **1–2** and **1–3** arises from hydrogenolysis of a Cbz protected guanidine **1** followed by a rapid filtration of **1** to an alcoholic solution of excess carboxylic acid (Scheme 1). The precipitate was collected which gave the salts containing an equimolar mixture of guanidinium and carboxylate. Single crystals of the guanidinium and carboxylate complexes were obtained from the diffusion of methanol to a solution of the salts in water (see the Supporting information).

We first investigated ethyl linked diguanidinium/dicarboxylate salt **1–2** (Fig. 2). X-ray diffraction analysis revealed one-dimensional tapes. Each molecule of **1** is surrounded by six units of **2** through hydrogen-bonding, and vice versa (Fig. 3), making the whole crystal as a grid-like motif. Both **1** and **2** adopt extended conformations wherein the bond angles for N–C–C in **1** and for C–C–C in **2** were determined to be 109.1° and 115.9°, respectively. The two N–H···O hydrogen bonds in the linear motif have bond lengths of 2.78 and 2.86 Å, respectively.



Scheme 1. Preparation of the guanidinium/carboxylate salts.

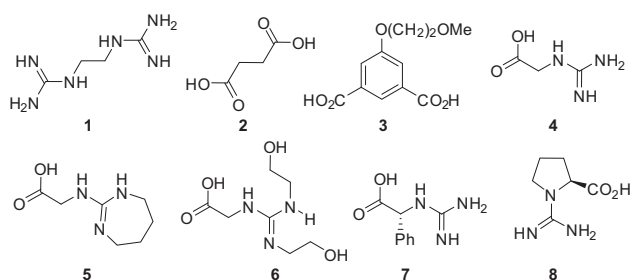


Figure 2. The structures of compounds **1–8**.

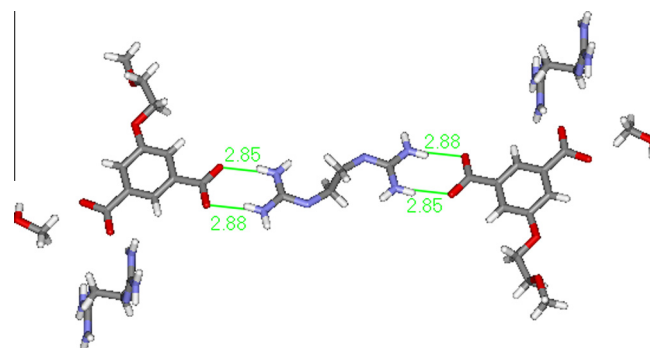


Figure 4. The X-ray crystal structure of **1–3**: a trimolecular structure that is capped with two methanol molecules at the termini of the two carboxyl groups.

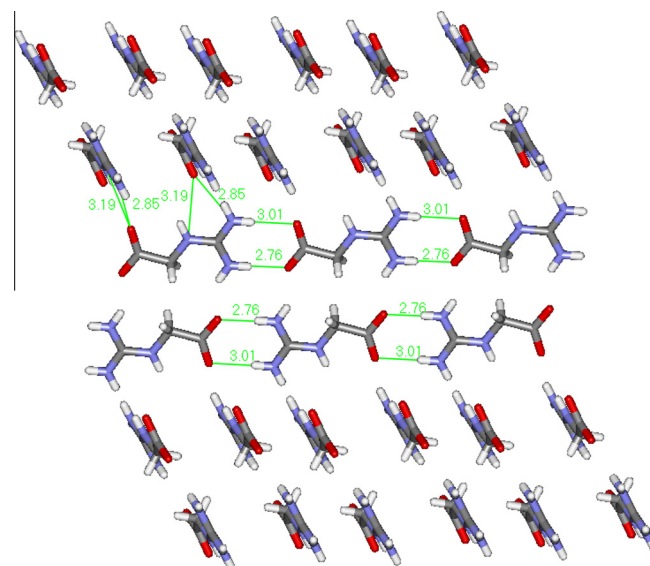


Figure 5. The X-ray crystal structure of **4**.

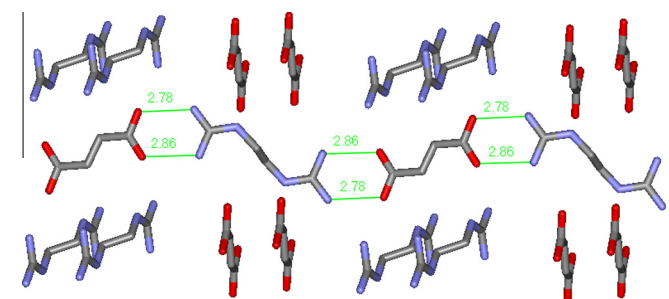


Figure 3. The X-ray crystal structure of **1–2**. Hydrogen atoms are omitted for clarity.

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