

Video Article

Construction and Systematical Symmetric Studies of a Series of Supramolecular Clusters with Binary or Ternary Ammonium Triphenylacetates

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Abstract

Functions of clusters in nano or sub-nano scale significantly depend on not only kinds of their components but also arrangements, or symmetry, of their components. Therefore, the arrangements in the clusters have been precisely characterized, especially for metal complexes. Contrary to this, characterizations of molecular arrangements in supramolecular clusters composed of organic molecules are limited to a few cases. This is because construction of the supramolecular clusters, especially obtaining a series of the supramolecular clusters, is difficult due to low stability of non-covalent bonds compare to covalent bonds. From this viewpoint, utilization of organic salts is one of the most useful strategies. A series of the supramolecules could be constructed by combinations of a specific organic molecule with various counter ions. Especially, primary ammonium carboxylates are suitable as typical examples of supramolecules because various kinds of carboxylic acids and primary amines are commercially available, and it is easy to change their combinations. Previously, it was demonstrated that primary ammonium triphenylacetates using various kinds of primary amines specifically construct supramolecular clusters, which are composed of four ammoniums and four triphenylacetates assembled by charge-assisted hydrogen bonds, in crystals obtained from non-polar solvents. This study demonstrates an application of the specific construction of the supramolecular clusters as a strategy to conduct systematical symmetric study for clarification of correlations between molecular arrangements in supramolecules and kinds and numbers of their components. In the same way with binary salts composed of triphenylacetates and one kind of primary ammoniums, ternary organic salts composed of triphenylacetates and two kinds of ammoniums construct the supramolecular clusters, affording a series of the supramolecular clusters with various kinds and numbers of the components.

Video Link

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Introduction

Supramolecules are fascinating and important research targets because of their unique functions, such as construction of supramolecular architectures, sensing of ions and/or molecules, and chiral separations, originated from their molecular recognition abilities using flexible non-covalent bonds¹⁻¹¹. In molecular recognitions, symmetry of supramolecular assemblies is one of the most important factors. Despite the importance, it is still difficult to design supramolecules with desired symmetries due to flexibility in numbers and kinds of the components as well as angles and distances of non-covalent bonds.

Clarification of correlations between symmetries of supramolecules and their components based on systematical studies is useful strategy to achieve construction of desired supramolecules. For this purpose, supramolecular clusters were selected as research targets because they are composed of limited number of components and are evaluable theoretically¹²⁻¹⁴. However, contrary to metal complexes, there are a limited number of reports constructing supramolecular clusters due to low stability of non-covalent bonds for sustaining the supramolecular structures^{15,16}. This low stability also becomes a problem in obtaining a series of supramolecular assemblies which have the same kinds of structures. In this study, charge-assisted hydrogen bonds of organic salts, which are one of the most robust non-covalent bonds¹⁷⁻²⁰, are mainly employed to construct specific supramolecular assemblies preferentially²¹⁻³². It is also noteworthy that organic salts are composed of acids and bases, and thus numerous kinds of organic salts are easily obtained just by mixing different combinations of acids and bases. Especially, organic salts are useful for systematic studies because combinations of a specific component with various kinds of counter ions result in the same types of supramolecular assemblies. Therefore, it is possible to compare structural differences of supramolecular assemblies based on kinds of counter ions.

In previous works, supramolecules with 0-dimensional (0-D), 1-dimensional (1-D), and 2-dimensional (2-D) hydrogen-bonding networks by primary ammonium carboxylates were confirmed and characterized from a viewpoint of chirality³². These multi-dimensional supramolecules are important research targets in hierarchical crystal design²⁷ as well as applications exploiting their dimensionality. In addition, characterization of the hydrogen-bonding networks would give important knowledge about roles of biological molecules because all of amino acids have ammonium and carboxylic groups. Providing guidelines to obtain these supramolecules separately gives them further opportunities in applications. In these

supramolecules, construction of supramolecular clusters with 0-D hydrogen-bonding networks is relatively difficult as demonstrated in statistical study²⁸. However, after clarification of factors for constructing the supramolecular clusters, they were selectively constructed, and a series of the supramolecular clusters was obtained^{21-25,32}. These works make it possible to conduct systematical symmetric study on the supramolecular clusters to clarify component-dependent symmetric characteristics of the supramolecular clusters. For this purpose, the supramolecular clusters of primary ammonium triphenylacetates have interesting features, that is, their topological variety in hydrogen-bonding networks^{24,32}, which would reflect their symmetric features as well as chiral conformations of the component trityl groups (**Figure 1a** and **1b**). Here methodologies for constructing a series of supramolecular clusters using primary ammonium triphenylacetates and for characterizing symmetric features of the supramolecular clusters are demonstrated. Keys for the construction of the supramolecular clusters are introduction of bulky trityl groups and recrystallization of the organic salts from non-polar solvents. Binary and ternary primary ammonium triphenylacetates were prepared for the construction of the supramolecular clusters. Crystallographic studies from viewpoints of topologies of the hydrogen-bonding networks^{24,32}, topographies (conformations) of trityl groups^{33,34}, and molecular arrangements as analogues of octacoordinated polyhedrons¹² (**Figure 1c**) revealed component-dependent symmetric characteristics of the supramolecular clusters²⁵.

Protocol

1. Preparation of Single Crystals Composed of Primary Ammonium Triphenylacetates

1. Prepare organic salts, primary ammonium triphenylacetates (**Figure 1a**).
 1. Dissolve triphenylacetic acid (TPAA, 0.10 g, 0.35 mmol) and primary amine: *n*-butylamine (*n*Bu, 2.5×10^{-2} g, 0.35 mmol), isobutylamine (isoBu, 2.5×10^{-2} g, 0.35 mmol), *t*-butylamine (*t*Bu, 2.5×10^{-2} g, 0.35 mmol), or *t*-amylamine (*t*Am, 3.0×10^{-2} g, 0.35 mmol), together in methanol (20 ml) in TPAA : amine = 1:1 molar ratio for preparation of binary organic salts.
 2. In the case of ternary organic salts, dissolve TPAA (0.10 g, 0.35 mmol) and two kinds of primary amines: *n*Bu (1.3×10^{-2} g, 0.17 mmol)-*t*Bu (1.3×10^{-2} g, 0.17 mmol), *n*Bu (1.3×10^{-2} g, 0.17 mmol)-*t*Am (1.5×10^{-2} g, 0.17 mmol), isoBu (1.3×10^{-2} g, 0.17 mmol)-*t*Bu (1.3×10^{-2} g, 0.17 mmol), or isoBu (1.3×10^{-2} g, 0.17 mmol)-*t*Am (1.5×10^{-2} g, 0.17 mmol), together in methanol (20 ml) in TPAA : amine-1 : amine-2 = 2:1:1.
 3. Evaporate all of the solutions by rotary evaporators (40 °C, 200 Torr), affording organic salts: TPAA-*n*Bu, TPAA-isoBu, TPAA-*t*Bu, TPAA-*t*Am, TPAA-*n*Bu-*t*Bu, TPAA-*n*Bu-*t*Am, TPAA-isoBu-*t*Bu, and TPAA-isoBu-*t*Am.
2. Prepare single crystals composed of supramolecular clusters.
 1. Dissolve each of the organic salts (5.0 mg) in a glass vial in toluene (0.30 ml) as a non-polar good solvent, which was selected because the supramolecular clusters are preferably constructed in non-polar environment. For the organic salts TPAA-*t*Bu, TPAA-*t*Am, TPAA-isoBu-*t*Bu, and TPAA-isoBu-*t*Am, heat toluene up to 40 °C to dissolve them.
 2. Add hexane: 0.5 ml, 0.5 ml, 0.5 ml, 2 ml, 2 ml, 1 ml, and 0.5 ml, to the solution of the organic salts of TPAA-*n*Bu, TPAA-isoBu, TPAA-*t*Am, TPAA-*n*Bu-*t*Bu, TPAA-*n*Bu-*t*Am, TPAA-isoBu-*t*Bu, and TPAA-isoBu-*t*Am, respectively, as a poor solvent to decrease solubility of the organic salt, except for the solution of the organic salt TPAA-*t*Bu.
 3. Keep the solution stable at room temperature in the glass vial, affording single crystals within a day.
3. Confirm the organic salt formation by Fourier transform infrared (FT-IR) spectra^{35,36}.
 1. Mix the single crystals of the organic salt with potassium bromide (KBr) in 1:100 weight ratio.
 2. Grind the mixture by an agate mortar until it becomes homogeneous powdered mixture.
 3. Fill up a round die (diameter: 5 mm) with the powdered mixture and make a pellet by pressing it with a pellet press.
 4. Put the pellet into a FT-IR spectrometer, and perform measurements (cumulative number: 16, resolution: 1 cm^{-1}).

2. Crystallographic Studies

1. Pick up a high quality single crystal of the organic salt TPAA-*t*Am from the glass vial into paraffin on a glass plate. The crystal looks uniform under a stereomicroscope, meaning the crystal is not assemblies of multiple crystals but a single crystal, and has a crystal size around 0.3 to 1 mm without cracks.
2. Put the single crystal on a loop.
3. Set the loop with the single crystal in single crystal X-ray diffraction equipment.
4. Select a collimator: 0.3, 0.5, 0.8, or 1 mm, depending on the maximum size of the single crystal.
5. Start a preparatory measurement of single crystal X-ray diffraction to collect X-ray diffraction patterns^{37,38} from the single crystal using the single crystal X-ray diffraction equipment (radiation source: graphite monochromated $\text{CuK}\alpha$ ($\lambda = 1.54187 \text{ \AA}$), exposure time: 30 sec (determine based on the crystal size), detector: e.g. imaging plate, crystal-to-detector distance: 127.40 mm, temperature: 213.1 K, number of frames: 3).
6. Determine possible crystal parameters and set conditions: exposure time, angles of X-ray exposure: ω , χ , and ϕ , and number of frames, for following measurement based on the result of the above preparatory measurement.
7. Start a regular measurement of single crystal X-ray diffraction to collect X-ray diffraction patterns^{37,38} from the single crystals using the single crystal X-ray diffraction equipment under the conditions (radiation source: graphite monochromated $\text{CuK}\alpha$ ($\lambda = 1.54187 \text{ \AA}$), detector: e.g. imaging plate, crystal-to-detector distance: 127.40 mm, temperature: 213.1 K).
8. Solve a crystal structure from the diffraction patterns by direct methods, SIR2004³⁹ or SHELXS97⁴⁰, and refine by a full-matrix least-squares procedure using all the observed reflections based on F^2 . Refine all the non-hydrogen atoms with anisotropic displacement parameters, and place the hydrogen atoms in idealized positions with isotropic displacement parameters relative to the connected non-hydrogen atoms and not refined. Perform these calculations using a software such as the CrystalStructure⁴¹.
9. Repeat the procedures from steps 2.1 to 2.8 with some modifications of the conditions: collimator size, exposure time of X-ray for preparatory measurements and regular measurements, and angles of X-ray exposure: ω , χ , and ϕ , and number of frames, for the single crystals of organic salts: TPAA-*n*Bu-*t*Bu, TPAA-*n*Bu-*t*Am, TPAA-isoBu-*t*Bu, and TPAA-isoBu-*t*Am to reveal their crystal structures.

10. Retrieve crystal structures of the organic salts: TPAA-*n*Bu (refcode: MIBTOH)²², TPAA-isoBu (refcode: GIVFEX)²⁴, and TPAA-*t*Bu (refcode: GIVFIB)²³, from Cambridge Structural Database⁴² using a software, Conquest⁴³, or a request form⁴⁴.
11. Investigate the supramolecular clusters in the crystal structures by computer graphics using software such as Mercury⁴⁵⁻⁴⁸ and Pymol⁴⁹; Determine point group symmetries of hydrogen-bonding patterns in the supramolecular clusters by comparing the obtained patterns with the previously classified ones (**Figure 1b**) and chiral conformations of the trityl groups as Λ or Δ (**Figure 1a**).
12. Characterize polyhedral features of the supramolecular clusters in each of the crystal structures of the organic salts.
 1. Delete all of the atoms in the supramolecular clusters except for carbon and nitrogen atoms of the component carboxylate anions and ammonium cations.
 2. Make bonds between the carbon and nitrogen atoms of which original carboxylate and ammonium cations are connected by hydrogen bonds.
 3. Measure distances between carbon-carbon and nitrogen-nitrogen atoms, and set boundaries for making further bonds (5.3 and 4.1 Å for carbon-carbon and nitrogen-nitrogen distances, respectively, in this study).
 4. Make further bonds between carbon-carbon and nitrogen-nitrogen atoms of which distances are less than 5.4 and 4.2 Å, respectively.
 5. Determine the resulting polyhedrons of the organic salts: TPAA-isoBu, TPAA-*t*Bu, TPAA-*t*Am, TPAA-isoBu-*t*Bu, and TPAA-isoBu-*t*Am, as *trans*-bicapped octahedron (*tbo*), triangular dodecahedron (*td*), *td*, *td*, and *td*, respectively, by considering rotational axis (C_3 or C_2) as well as numbers of sides of the polyhedrons.
 6. Make additional bonds to the resulting polyhedrons of the organic salts: TPAA-*n*Bu, TPAA-*n*Bu-*t*Bu, and TPAA-*n*Bu-*t*Am, by considering number of sides, symmetry elements, and intermolecular interactions in the supramolecular clusters because they have less sides than ideal ones: *td*, *tbo*, and square antiprism (*sa*).
 7. Determine the polyhedron of the TPAA-*n*Bu salt as *sa* by making two addition bonds due to its C_2 symmetry and 14 original bonds. Determine the other polyhedrons of the organic salts TPAA-*n*Bu-*t*Bu and TPAA-*n*Bu-*t*Am as *td* based on their C_2 symmetry and "bands" of the trityl groups around the supramolecular cluster. Namely, the trityl groups in the supramolecular clusters of the ternary organic salts form "bands" by intermeshing their three phenyl rings and the polyhedron *td* has sides connecting four acids (**Figure 1c(ii)**), meaning they have similar structural features.

Representative Results

Organic salt formation of TPAA and primary amines were confirmed by FT-IR measurements. Crystal structures of the organic salts were analyzed by single crystal X-ray diffraction measurements. As a result, the same kinds of the supramolecular clusters, which are composed of four ammoniums and four triphenylacetates by charge-assisted hydrogen bonds (**Figure 1a**), were confirmed in all of the single crystals of the organic salts regardless of kinds and numbers of the component ammoniums (**Table 1**, **Figure 2**). This result is applicable to systematical symmetric study to clarify component-dependent symmetric varieties of the supramolecular clusters.

According to systematical symmetric studies on the supramolecular clusters, it was found that chirality and polyhedral features of the supramolecular clusters (**Figure 1b** and **1c**) depend on kinds and numbers of the component primary ammoniums. The binary supramolecular cluster of TPAA-*n*Bu has an achiral D_{2d} hydrogen-bonding network from a topological viewpoint. The D_{2d} is a symbol of the Schönflies notation and denotes that there are three two-fold axes which are perpendicular to each other as well as two vertical mirror planes which pass between two of the two-fold axes. In the supramolecular cluster, its components are arranged in a square antiprism (*sa*) manner with two-fold rotational axes or C_2 symmetry (**Figure 3a**). This polyhedral feature is clarified by replacing the component molecules with representative atoms: carbon atoms of the carboxylate anions and nitrogen atoms of the ammonium cations, and making new connections between carbon-carbon, carbon-nitrogen, and nitrogen-nitrogen atoms depending on distances of the atoms. The supramolecular cluster has racemic, $\Lambda : \Delta = 2 : 2$, trityl groups. The binary supramolecular clusters of TPAA-*t*Bu and TPAA-*t*Am, which have achiral S_4 hydrogen-bonding networks, also have racemic, $\Lambda : \Delta = 2 : 2$, trityl groups (**Figure 3c** and **3d**). In these cases, their components are arranged in triangular dodecahedron (*td*) manners which have C_2 symmetry according to the same analysis with the case of the TPAA-*n*Bu supramolecular cluster. Contrary to these cases, the binary supramolecular cluster of TPAA-isoBu has an achiral C_3 hydrogen-bonding network, which has not a two-fold rotational axis but a pseudo-three-fold rotational axis (**Figure 3b**). This symmetry results in chiral trityl groups as $\Lambda : \Delta = 1 : 3$ (and *vice versa*). Namely, when the trityl group with Λ conformation is on the pseudo-three-fold rotational axis, the other trityl groups with Δ conformation are around the axis (and *vice versa*). In addition, the molecular arrangement in the supramolecular cluster belongs to a *trans*-bicapped octahedron (*tbo*) manner with a three-fold rotational axis, or C_3 symmetry. From these investigations, it can be said that if the hydrogen-bonding network (or the polyhedron) has C_2 or (pseudo)- C_3 symmetry, the trityl groups prefer to form racemic $\Lambda : \Delta = 2 : 2$, or chiral $\Lambda : \Delta = 1 : 3$ (and *vice versa*) conformations, respectively, in the binary supramolecular cluster.

Contrary to the case of the binary supramolecular clusters, the ternary supramolecular clusters of TPAA-*n*Bu-*t*Bu, TPAA-*n*Bu-*t*Am, TPAA-isoBu-*t*Bu, and TPAA-isoBu-*t*Am, which have C_2/C_2' , D_{2d} , D_{2d} , and D_{2d} hydrogen-bonding networks, respectively, have different characteristics (**Figure 4**). All of them have two-fold rotational axes, or C_2 symmetries, in hydrogen-bonding network, but the trityl groups have chirality as $\Lambda : \Delta = 0 : 4$ (and *vice versa*). This result indicates that introduction of the third component leads to symmetry reduction in the supramolecular clusters, demonstrating usefulness of organic salts for inducing chirality. It should be noted that chirality of the trityl groups are used in chiral columns^{33,34}. Further investigations on the ternary supramolecular clusters revealed that the trityl groups were intermeshed each other in the supramolecular clusters (**Figure 5**). This intermesh could be one of the main factor to form chiral $\Lambda : \Delta = 0 : 4$ (and *vice versa*) conformations by delivering chirality of one of the trityl group to the others. This connectivity among four TPAA anions are similar with a structural feature of the *td* (**Figure 5b**), and thus the polyhedrons of the ternary supramolecular clusters are easily determined as the *td* by combination of the same analysis with the case of the binary supramolecular cluster.

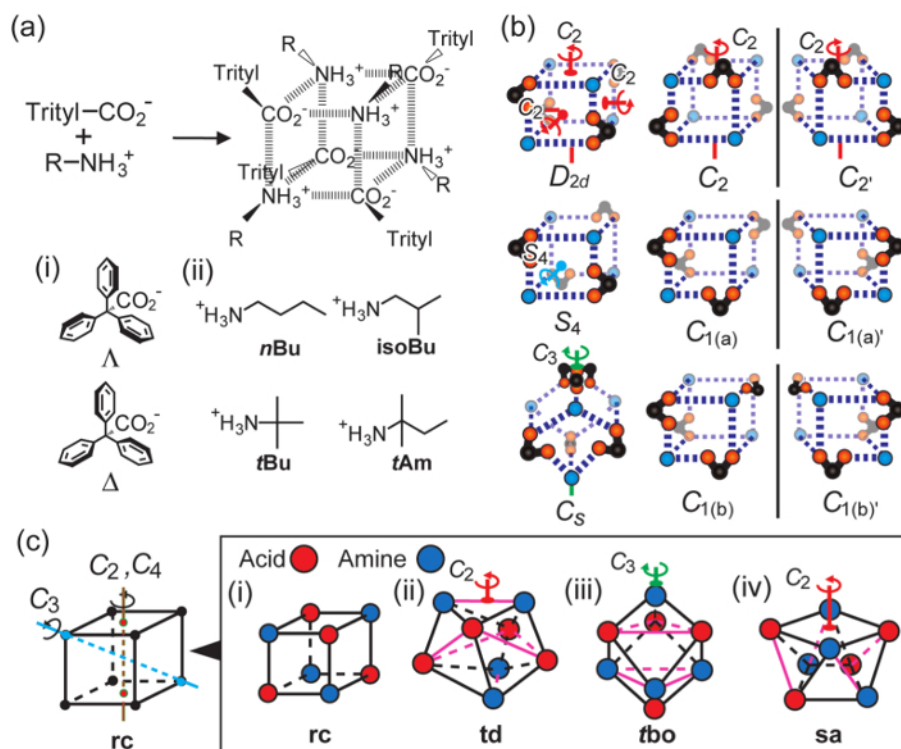


Figure 1: Characteristics of hydrogen-bonding supramolecular clusters. (a) Formation of the hydrogen-bonding supramolecular clusters. Chemical structures of (i) triphenylacetates with chiral trityl conformations: left- (Λ) and right-handed (Δ), and (ii) primary ammoniums employed in this study. (b) Topological classification of the hydrogen-bonding networks of supramolecular clusters. Point group symmetries are described by Schönflies notation. (c) Polyhedral arrangements: (i) regular cube (rc) (ii) triangular dodecahedron (td) (iii) *trans*-bicapped octahedron (tbo), and (iv) square antiprism (sa). This figure has been modified and adapted with permission from *Cryst. Growth Des.* **15** (2), 658 - 665, doi: 10.1021/cg5013445 (2015). Copyright (2015) American Chemical Society.

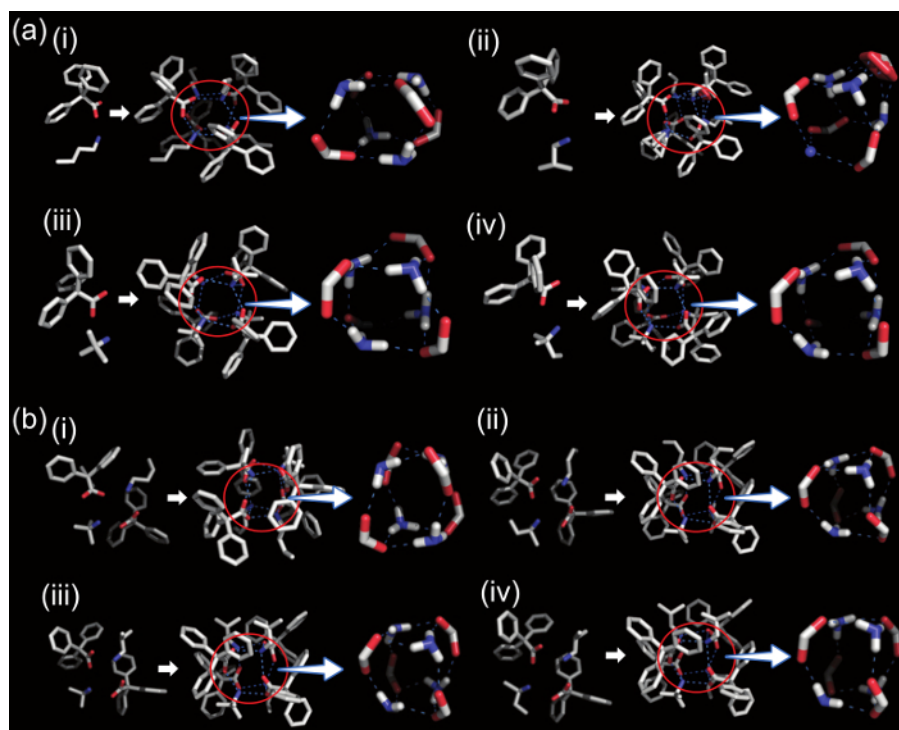


Figure 2: Structures of supramolecular clusters. Structures of supramolecular clusters of (a) binary organic salts: (i) TPAA-*n*Bu (ii) TPAA-isoBu (iii) TPAA-*t*Bu, and (iv) TPAA-*t*Am, and (b) ternary organic salts: (i) TPAA-*n*Bu-*t*Bu (ii) TPAA-*n*Bu-*t*Am (iii) TPAA-isoBu-*t*Bu, and (iv) TPAA-isoBu-*t*Am. All of the supramolecular clusters are constructed by ion pairs of the TPAA anions and the primary ammonium cations. Hydrogen bonds are represented in light blue by dotted lines. This figure has been modified and adapted with permission from *Cryst. Growth Des.* **15** (2), 658 - 665, doi: 10.1021/cg5013445 (2015). Copyright (2015) American Chemical Society.

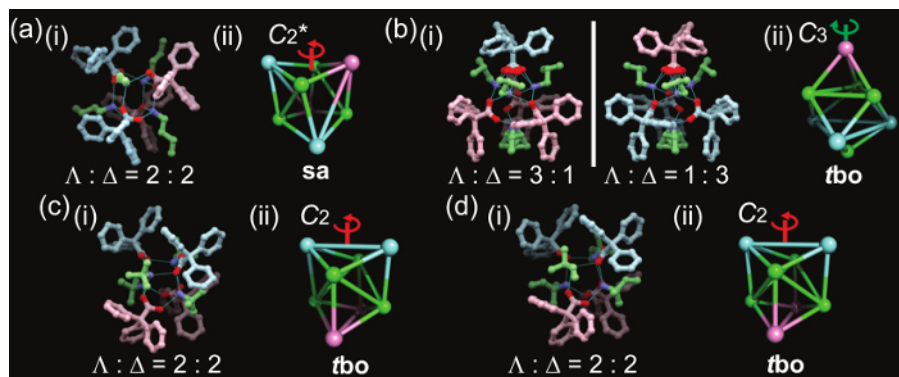


Figure 3: Polyhedral supramolecular clusters of binary organic salts. Structures of polyhedral supramolecular clusters of binary organic salts (a) TPAA-*n*Bu (sa) (b) TPAA-isoBu (tbo) (c) TPAA-*t*Bu (td), and (d) TPAA-*t*Am (td). (i) The full structure of the supramolecular cluster and (ii) polyhedral arrangement of the components, which is represented by carbon atoms of the carboxylate groups and nitrogen atoms of the ammonium groups, in the supramolecular cluster. Trityl groups with Λ or Δ conformations are colored in light pink or light blue, respectively. A symbol ' C_2^* ' means that the two-fold rotational axis is pseudo symmetry. Ammoniums are colored in green. Hydrogen atoms are omitted for clarity. This figure has been modified and adapted with permission from *Cryst. Growth Des.* **15** (2), 658 - 665, doi: 10.1021/cg5013445 (2015). Copyright (2015) American Chemical Society.

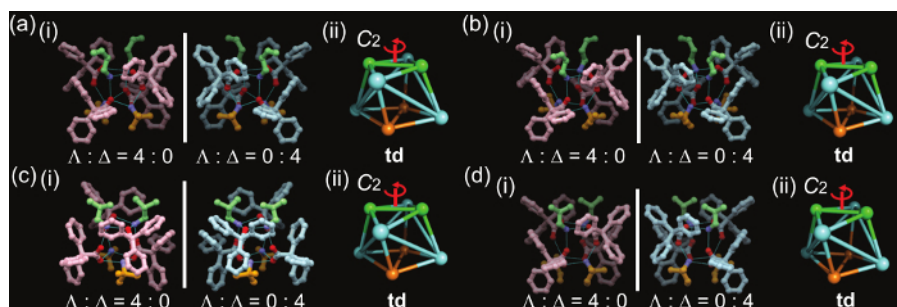


Figure 4: Polyhedral supramolecular clusters of ternary organic salts. Structures of polyhedral supramolecular clusters of ternary organic salts (a) TPAAnBu-tBu (td) (b) TPAAnBu-tAm (td) (c) TPAAisoBu-tBu (td), and (d) TPAAisoBu-tAm (td). (i) The full structure of the supramolecular cluster and (ii) polyhedral arrangement of the components, which is represented by carbon atoms of the carboxylate anions and nitrogen atoms of the ammonium cations, in the supramolecular cluster. Trityl groups with Λ or Δ conformations are colored in light pink or light blue, respectively. Ammoniums are colored in green for *n*Bu and isoBu and orange for *t*Bu and *t*Am. Hydrogen atoms are omitted for clarity. This figure has been modified and adapted with permission from *Cryst. Growth Des.* **15** (2), 658 - 665, doi: 10.1021/cg5013445 (2015). Copyright (2015) American Chemical Society.

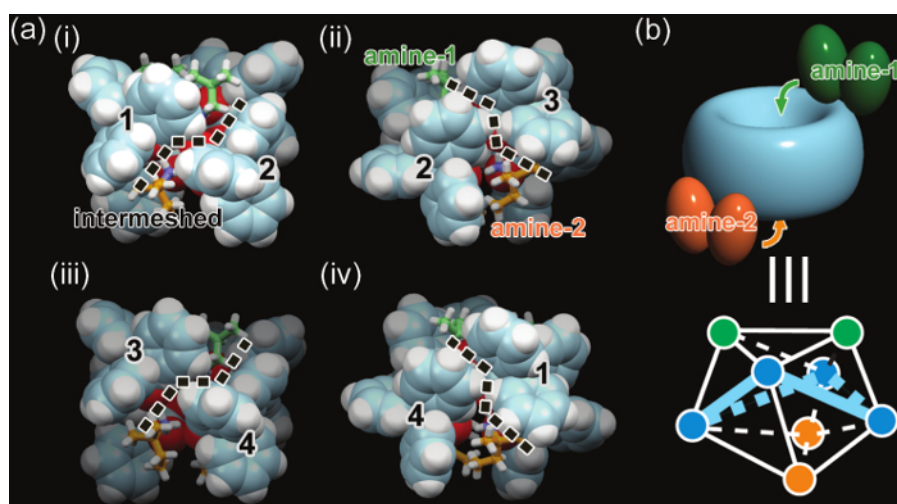


Figure 5: Arrangements of trityl groups in the ternary supramolecular clusters (TPAAisoBu-tAm). Manners of intermesh between two out of four trityl groups (numbered from 1 to 4): (i) 1 and 2, (ii) 2 and 3, (iii) 3 and 4, and (iv) 4 and 1. (b) Schematic representation of a 'band' structure composed of the intermeshing trityl groups and that in a triangular dodecahedron. The trityl groups with Δ conformation are colored in light blue. The ammoniums: isoBu and *t*Am, are colored in green and orange, respectively. This figure has been modified and adapted with permission from *Cryst. Growth Des.* **15** (2), 658 - 665, doi: 10.1021/cg5013445 (2015). Copyright (2015) American Chemical Society.

Entries	Topology	Trityl chirality	Polyhedron	Ref. code or CCDC no.
TPAA- <i>n</i> Bu	D_{2d}	$\Lambda : \Delta = 2 : 2$	sa	MIBTOH ^[a]
TPAA-isoBu	C_s	$\Lambda : \Delta = 1 : 3$ $\Lambda : \Delta = 3 : 1$	fbo	GIVFEX ^[b]
TPAA- <i>t</i> Bu	S_4	$\Lambda : \Delta = 2 : 2$	td	GIVFIB ^[c]
TPAA- <i>t</i> Am	S_4	$\Lambda : \Delta = 2 : 2$	td	973395 ^[d]
TPAA- <i>n</i> Bu- <i>t</i> Bu	$C_{2v}/C_{2'}$	$\Lambda : \Delta = 4 : 0$ $\Lambda : \Delta = 0 : 4$	td	973399 ^[d]
TPAA- <i>n</i> Bu- <i>t</i> Am	D_{2d}	$\Lambda : \Delta = 4 : 0$ $\Lambda : \Delta = 0 : 4$	td	973398 ^[d]
TPAA-isoBu- <i>t</i> Bu	D_{2d}	$\Lambda : \Delta = 4 : 0$ $\Lambda : \Delta = 0 : 4$	td	973397 ^[d]
TPAA-isoBu- <i>t</i> Am	D_{2d}	$\Lambda : \Delta = 4 : 0$ $\Lambda : \Delta = 0 : 4$	td	973396 ^[d]

Table 1: Characteristics of the supramolecular clusters. [a]-[d]: See refs. 22, 24, 23 and 25, respectively. This table has been modified and adapted with permission from *Cryst. Growth Des.* **15** (2), 658 - 665, doi: 10.1021/cg5013445 (2015). Copyright (2015) American Chemical Society.

Discussion

A series of supramolecular clusters with closed hydrogen-bonding networks was successfully constructed and characterized from viewpoints of chirality and polyhedral features using organic salts of TPAA, which has a trityl group, and various kinds and combinations of primary amines. In this method, the critical steps are introduction of a molecule with a bulky trityl group and recrystallization of organic salts composed of the molecule and counter ions from non-polar solvents. This is because the supramolecular cluster has an inverted-micellar structure, that is, ionic hydrogen bonds and hydrophobic hydrocarbons are inside and outside, respectively. Therefore, the supramolecular cluster is stable and is selectively constructed in non-polar environments.

Although the supramolecular cluster always has four ammoniums and four triphenylacetates, it is possible to introduce two kinds of ammoniums as well as a kind of ammonium, giving the supramolecular clusters variety by forming ternary supramolecular clusters in addition to binary ones. This flexibility in forming the supramolecular clusters leads to effective systematical symmetric studies for clarifying dependence of not only kinds but also numbers of components and suggests a potential to achieve multi-functionalization of the supramolecular clusters. It is also noteworthy that high quality single crystals of the organic salts are easily obtained, and thus their crystal structures were revealed by single crystal X-ray analysis. On the contrary, only a few structures of octameric water clusters, of which hydrogen-bonding networks are similar to those of the supramolecular clusters and their topology was classified theoretically¹³, have been confirmed experimentally^{50,51}. This advantage is attributable to facts that the supramolecular clusters are stable due to robust charge-assisted hydrogen bonds and are packed effectively in crystalline states due to their cube-like shapes.

A method using organic salts is one of the most useful approaches to achieve prediction and/or control of supramolecular and crystal structures based on systematical studies. In this study, it is demonstrated that introduction of trityl groups results in selective construction of supramolecular clusters. The supramolecular clusters with specific symmetric properties can be constructed after clarification of their counter ion-dependent symmetric features. For example, it is reported that supramolecular clusters composed of triphenylmethylammonium sulfonates construct diamondoid porous organic salts⁵². The results obtained in this study show a possibility to control construction of the diamondoid and another unknown types of porous structures by changing components. In addition, introduction of another specific moieties (e.g. linear long alkyl chains) can lead to construction of another unique supramolecules (e.g. supramolecular layers)²⁹⁻³¹. Systematical symmetric studies on these supramolecules can contribute to achieve component-based symmetry control of the supramolecules and crystals. Furthermore, although the supramolecular clusters composed of carboxylates and ammoniums are limited to clusters with eight components: four ammoniums and four carboxylates, it is possible to tune the component numbers by using phosphonic acids instead of carboxylic acids. This is because phosphonic acids have two acidic protons, and thus they can form more diverse hydrogen-bonding networks than carboxylic acids, which have only one acidic proton. Discoveries and systematical symmetric studies of further new and functional supramolecular clusters will bring an exciting future in material sciences as well as crystal engineering.

Disclosures

The authors have nothing to disclose.

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