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Multicomponent Organic Alloys Based on Organic Layered Crystals**

Kazuki Sada, Katsunari Inoue, Tomoyuki Tanaka, Attila Epergyes, Akira Tanaka, Norimitsu Tohnai, Akikazu Matsumoto, and Mikiji Miyata**

Inorganic mixed crystals or solid solutions such as metal alloys and intermetallic compounds are composed of two or more kinds of atoms or ions homogeneously mixed in the crystal.[1–3] They have been widely prepared and utilized as structural materials for daily life since ancient times. Formation of mixed crystals has been extensively investigated in the search for new functional materials with optical, electrical, and magnetic properties. Integration and fine-tuning of the functions have been often carried out by varying combinations of the components and the mixing ratios,[4] since the atoms and ions are easily mixed in the inorganic materials due to their spherical structures.

On the other hand, recrystallization from solution or crystallization from the melt is generally used for purification of crystalline organic compounds. Studies on organic mixed crystals have focused chiefly on well-defined molecular complexes in the crystalline state, such as inclusion crystals,[4] hydrogen-bonded cocrystals,[5] and charge-transfer complexes.[6] Less attention has been paid to formation of organic solid solutions or alloys that are composed of many kinds of organic molecules. Kitaigorodsky pointed out that similarity of molecular structures plays a crucial role in formation of organic solid solutions,[1] and some examples such as *n*-paraffins,[7] dicarboxylic acids,[8] naphthalene derivatives,[9]

[*] Dr. K. Sada
Department of Chemistry & Biochemistry
Graduate School of Engineering, Kyushu University
744 Motooka, Nishi-ku, Fukuoka 819-0395 (Japan)
Fax: (+81) 92-802-2820
E-mail: sadatcm@mbox.nc.kyushu-u.ac.jp

K. Inoue, T. Tanaka, A. Epergyes, A. Tanaka, Dr. N. Tohnai, Prof. Dr. M. Miyata
Department of Material & Life Science
Graduate School of Engineering, Osaka University, and
Handai FRC, 2-1 Yamadaoka, Suita 565-0871 (Japan)
Fax: (+81) 6-6879-7404
E-mail: miyata@mls.eng.osaka-u.ac.jp

Prof. Dr. A. Matsumoto
Department of Applied Chemistry
Graduate School of Engineering, Osaka City University
Sugimoto, Sumiyoshi-ku, Osaka 558-8585 (Japan)

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and metal complexes[10] have already been reported. However, multicomponent organic solid solutions prepared from three or more organic molecules are quite rare,[11] because their sizes and shapes are incompatible for forming homogeneous solid solutions, and they recrystallize separately to form eutectic mixtures of the pure components. No other strategy to prepare multicomponent organic solid solutions has ever been reported. Herein, we report novel organic solid solutions based on a robust layered structure and a new strategy to construct multicomponent solid solutions composed of organic molecules with different sizes and shapes. Exploration of design and control of multicomponent organic solid solutions should allow functions of the organic molecules to be accumulated by the same strategy as employed with inorganic molecules.

Carboxylate salts of amines have been widely used for screening of functional organic crystalline materials. For example, they are used for optical resolution of racemic acids or bases,[12–14] crystalline-state reactions,[15] topochemical polymerizations,[16] host–guest crystals,[17] and so on. Salt formation has some advantages for crystal engineering: easy preparation, various combinations, and strong intermolecular interactions between the ion pairs, such as hydrogen bonds and electrostatic interactions. We previously reported that 1-naphthylmethylammonium (NMA) *n*-aliphatic carboxylates from acetate (**C2**) to triacontanate (**C30**) have the same layer structure independent of the length of the alkyl group (Figure 1 a).[18] This phenomenon is ubiquitous for inorganic layered structures such as zeolites and smectite clays.[19] This prompted us to prepare organic solid solutions from mixtures of two or more NMA carboxylate salts, just like inorganic substitutional alloys.

Equimolar mixtures of two or more carboxylic acids were treated with NMA in methanol (Figure 1 b), and removal of the solvent by an evaporator yielded white solids. They were characterized by XRD (Figure 2 a). The sample prepared from a 1:1 mixture of propanoic acid (**C3**) and butanoic acid (**C4**) had an XRD pattern similar to those of the pure crystals (**C3s** and **C4s**), but it was not identical to their sum.

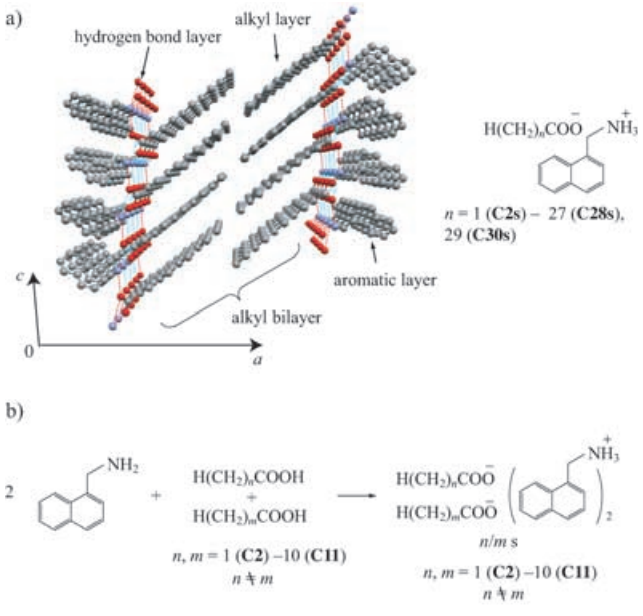

Figure 1. a) Bilayer structure in the crystalline state of **C9s**,[17] and b) the reaction scheme of the solid solutions.

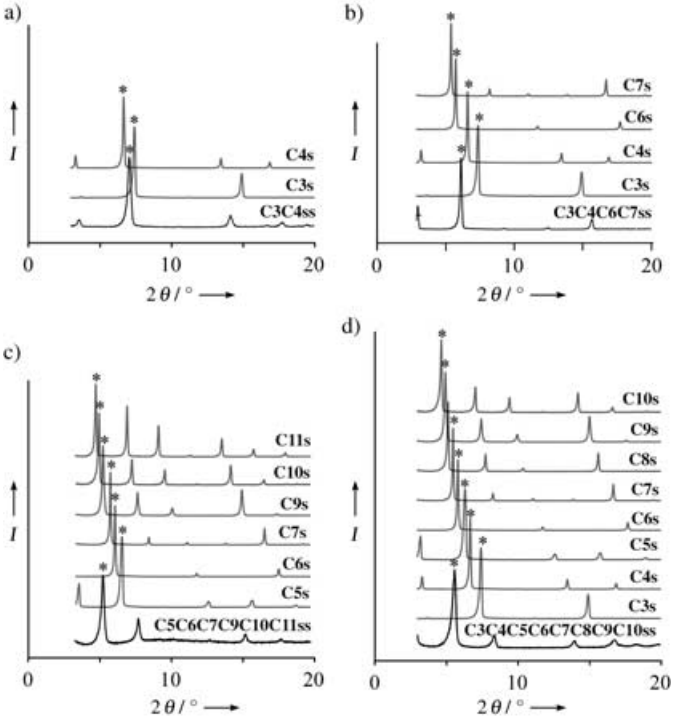

Figure 2. XRD patterns of solid solutions. a) Homogeneous solid solution from **C3** and **C4** (1:1) and the reference single-component salts **C3s** and **C4s**. b) Homogeneous solid solution from **C3**, **C4**, **C6**, and **C7** (1:1:1:1) and the reference single-component salts **C3s**, **C4s**, **C6s**, and **C7s**. c) Homogeneous solid solution from **C5**, **C6**, **C7**, **C9**, **C10**, and **C11** (1:1:1:1:1:1) and the reference single-component salts **C5s**, **C6s**, **C7s**, **C9s**, **C10s**, and **C11s**. d) Homogeneous solid solution from **C3**, **C4**, **C5**, **C6**, **C7**, **C8**, **C9**, and **C10** (1:1:1:1:1:1:1:1) and the reference single-component salts **C3s**, **C4s**, **C5s**, **C6s**, **C7s**, **C8s**, **C9s**, and **C10s**. Asterisks indicate 002 diffractions.

Differential scanning calorimetry (DSC) revealed that the melting point is 124.6 °C, which is lower than that of each pure salt (130.0 °C for **C3s** and 130.9 °C for **C4s**). From these results, we conclude that the white solid is a homogeneous solid solution of the two components (**C3C4ss**), rather than a eutectic mixture (**C3s** + **C4s**) of the individual crystals. The similarity in the XRD patterns suggested that the crystal structure of the solid solution **C3C4ss** resembles those of the pure salts. The FTIR spectrum of **C3C4ss** indicates the presence of the same hydrogen bonds as in the pure salts (carbonyl stretching bands of **C3C4ss**, **C3s**, and **C4s**: 1623, 1623, and 1623 cm^{-1}, respectively). The sharp 002 diffraction peak of the solid solution was observed at $d = 12.48$ Å, between those of **C3s** ($d = 11.87$ Å) and **C4s** ($d = 13.22$ Å). The interlayer distance of the solid solution was intermediate between those of the pure salts.[20]

Furthermore, we tried to prepare multicomponent solid solutions by mixing various carboxylate salts. We first investigated formation of a quaternary solid solution from

C3, **C4**, **C6**, and **C7** (1:1:1:1). The XRD pattern (Figure 2b) showed a single sharp profile, and the *d* spacing was 14.20 Å, which corresponds to **C5s** ($d = 13.97$ Å). This indicates that the quaternary mixtures gave the solid solution (**C3C4C6C7ss**) of these four components, and not their eutectic mixture (**C3s** + **C4s** + **C6s** + **C7s**). Six- and eight-component solid solutions also gave similar XRD results (Figure 2c and d). The *d* spacing from the single peak of the six-component solid solution **C5C6C7C9C10C11ss** was 17.66 Å, which corresponds to **C8s** ($d = 17.18$ Å). The *d* spacing from the peak of **C3C4C5C6C7C8C9C10ss** was 15.77 Å, which corresponds to the average value of **C6s** and **C7s** ($d = 15.17$ and 16.31 Å, respectively). These results provide insight into the structure and mechanism of formation of the solid solution. Mixing the four components can give the following ten possible *d* spacings (probabilities in parentheses): **C3s** (1/16), **C3C4ss** (1/8), **C4s** (1/16), **C3C6ss** (1/8), **C3C7ss** (1/4), **C4C6ss** (1/4), **C4C7ss** (1/8), **C6s** (1/16), **C6C7ss** (1/8), and **C7s** (1/16). However, the single peak around **C5s** ($d = 13.97$ Å) indicates that the bilayer is selectively composed of two sets of the alkyl chain pairs, namely, **C3**/**C7** and **C4**/**C6**. Otherwise, the peak should be much broader or split into several peaks due to the various layer distances. Indeed, as shown in Figure 3, a mixture

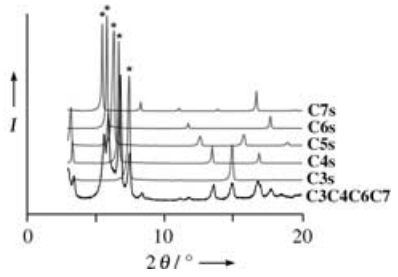

Figure 3. XRD patterns of a ground eutectic mixture of crystals of **C3s**, **C4s**, **C6s**, and **C7s** (black line), together with those of **C3s**, **C4s**, **C5s**, **C6s**, and **C7s** (grey lines). Asterisks indicate 002 diffractions.

prepared by grinding the pure salts shows corresponding peaks in each individual XRD pattern. Moreover, the six- and eight-component solid solutions have more possible *d* spacings, but they converged to averages among the mixtures. They should be composed of the following sets of alkyl-chain pairs: **C5**/**C11**, **C6**/**C10**, and **C7**/**C9** for **C5C6C7C9C10C11ss** and **C3**/**C10**, **C4**/**C9**, **C5**/**C8**, and **C6**/**C7** for **C3C4C5C6C7C8C9C10ss**. Each carboxylate anion recognized the sterically complementary partner. The sterically complementary pairs, for example, **C3**/**C7** and **C4**/**C6** for **C3C4C6C7ss**, have the same width in the alkyl bilayer structure, which provided the closest packing in the alkyl bilayer structure, and made them flat to form the two-dimensional hydrogen-bond network among the ion pairs and CH–π/π–π interactions between the naphthalene rings.[14] Furthermore, these results suggested random arrangement of the pairs. There are two hypothetical models to provide the averaged *d* spacing: a random model[20d] and a staged model[20d] (Figure 4). In staged model, a segregated layer is composed of one single carboxylate of the four carboxylates present, and the layer is paired with the specific partner.

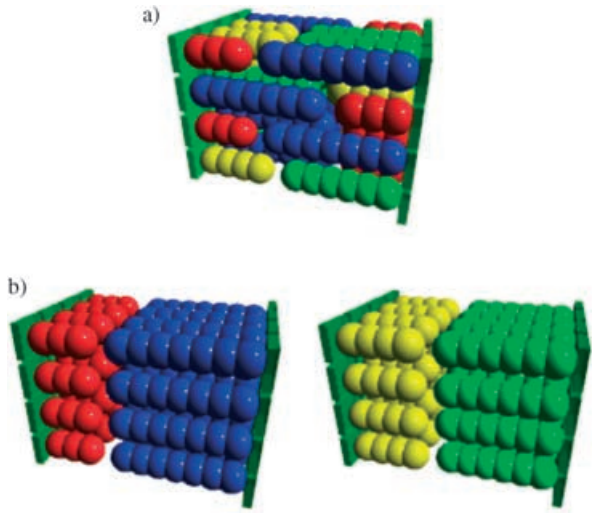

Figure 4. Schematic representations of the layer structures of the four-component homogeneous mixed salt a) with a random arrangement and b) with a staged arrangement.

There is no reason for selective stacking of these staged layers to afford layer structures with constant averaged *d* spacing. Therefore, the random layer is more likely. Thus, formation of the multicomponent solid solutions from more than two kinds of carboxylates was ascribed to specific pairing of the sterically complementary alkyl groups and their randomly disordered arrangement in the alkyl bilayer structure. During crystallization, the most probable pairs (e.g., **C3**/**C7** and **C4**/**C6** in **C3**, **C4**, **C6**, and **C7**) excluded the others by replacement of the counter alkyl group in the alkyl bilayer structure to keep the CH–π/π–π stacking and the two-dimensional hydrogen-bond networks parallel, and afforded the averaged layer distances.

The robust frameworks of NMA salts that accommodate isosteric pairs between their layers play a key role in formation of the solid solutions. These results indicate that robust structural motifs act as template for organic solid solutions and expand Kitaigorodsky's requirement for formation of binary organic solid solutions. Furthermore we could prepare the organic solid solutions from many components with different size and shape.[1] This strategy should be useful for designing wide ranges of the organic solid solutions. To our knowledge, the solid solution composed of eight organic molecules **C3C4C5C6C7C8C9C10ss** has the largest number of mixed components. Finally, introduction of functional groups into the isosteric pairs should provide integration of functions by a similar methodology to inorganic alloys.

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