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Tunable Organic Clay Mimic Structures with Di(Primary Ammonium) Dicarboxylates

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Design of supramolecular architectures as intended is one of the ultimate goals of supramolecular chemistry. To achieve the worthwhile goal, design of crystal structures are a promising approach because X-ray single crystallographic analysis is the only way for precise elucidation of molecular arrangements and intermolecular interactions at a molecular level. One of the approaches to design supramolecular architectures, organic salts is useful tool. The organic salts have the following excellent advantages; i) robust supramolecular synthons are formed with charge-assisted hydrogen bonds, ii) a wide variety of cations or anions are able to be arranged on the clays by just changing combinations of the salts. In previous work, we showed the control of interlayer distance of organic clay mimic structures composed of 1-naphthylmethylammonium carboxylates [1] by just varying the carbon numbers of the n-alkanoate. The clays are formed with robust two-dimensional hydrogen bond network, and the anions between layers are arranged at invariable intervals. Consequently, the clays have difficulties to control and vary intervals of molecules. Here we show the tunable organic clay mimic structures, which are designed and constructed with tert-amylammonium dicarboxylates [2]. The tunability takes important roles in association with various points: configurations of inclusion spaces, possibilities of topochemical reactions, solid-state physical properties, etc. The resulting structures give us a powerful and useful key to solve the conventional difficulties. To design the 2D motif with a tunable axle, a robust one-dimensional hydrogen bond network and tectons as a link are necessary. For this purpose, we adopted a robust supramolecular synthon composed of primary ammonium carboxylates. Many kinds of crystal structures composed of primary ammonium carboxylates have been analyzed and 287 salts are found in Cambridge Structural Database (CSD) (queried on components that contain at least two molecules, one primary amine and one carboxylic acid, except any other extra acids, bases and metals). And 173 (60.3%) of them form the specified one-dimensional hydrogen bond network with directionality. The same network formed when several types of dicarboxylic acids, such as terephthalic acid, biphenyl-4,4'-dicarboxylic acid and isophthalic acid, were employed as a tecton. X-ray analysis revealed that most of the organic salts formed the layer structures with interdigitated arrangements of primary ammonium cations. By varying the tecton, intervals of the cations on the layer and polarity of the layer are tunable. This design mentioned above is widely applicable to construct the predictable organic crystals.

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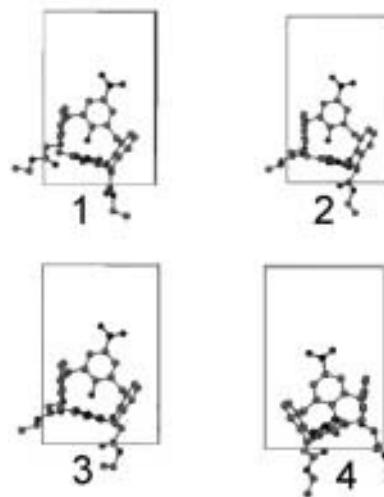
Isostructurality of co-crystals of an ester substituted dinitro calixarene host

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Upper rim dinitro substituted and lower rim ethyl ester annexed calix[4]arene molecule was synthesised and crystallized from selected polar protic and aprotic solvents. Four inclusion crystals, containing acetone (**1**), DMF (**2**), DMSO (**3**) and n-BuOH (**4**) as guest, respectively, were investigated using X-ray diffraction on single crystals [1]. The co-crystals exhibit pronounced similarities, but also distinct differences. The cell similarity, isostructurality and molecular homostructurality indices were calculated. All four inclusion compounds have similar cell parameters, but only three of them are homostructural, the fourth one differs. The non-protic guests are included with 1:1 host-guest stoichiometry in **1**, **2** and **3**, whereas the host-guest ratio is 2:1 in crystal **4**. Butanol, but not the other guests, is located on an inversion center, and also the cone conformation of the host in **4** is more distorted than it is in the other three co-crystals. Accordingly, the guest recognition modes seem to seriously affect the molecular conformation and placement of the host molecule. Inclusion of the n-BuOH leads to a supramolecular morphotropism [2], the first ever described by our knowledge, in which the calixarene molecule in **4** is related to the host molecules in the other three compounds (**1**, **2** and **3**) by a non-crystallographic virtual rotation of 180° within the unit cell.



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