Hydrogen-Bonding Molecular Assemblies of Alkylamide-Substituted Isophthalic Acid Derivative

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Introduction

Bottom-up molecular assembly using non-covalent intermolecular interactions such as hydrogen-bonding, π-π stacking, and amphiphilic interactions to produce supramolecular assemblies has attracted broad research interests because of its potential applications for future devices. We have designed ferroelectric hydrogen-bonding assemblies of alkylamide-substituted benzene derivative and fluorescent ferroelectric hydrogen-bonding pyrene derivative, where the dynamic motion of hydrogen-bonding interaction plays an important role to show the ferroelectric response.[1, 2] In this study, we focused on alkylamide-substituted benzene carboxylic acids derivatives of 1 and 2 for developing novel hydrogen-bonding molecular assemblies and new functions (Figure 1).

Experimental section. Alkylamide-substituted benzene carboxylic acids of 1 and 2 were prepared. Self-assembly properties of hydrogen-bonding molecules of 1 and 2 were examined in different solvent systems. For example, the molecules 1 and/or 2 form organogels in the mixed solvents of H2O-CH3OH and/or H2O-C2H5OH. Morphologies and properties of these assemblies were characterized and discussed below.

Results and discussion.

From the TG analysis of 1 (Figure 2), organogel from H2O-CH3OH showed a weight-loss of 2.35 % at 100 °C and of 8.8 % at 150 °C, whereas organogel from H2O-C2H5OH showed a weight-loss of 4.88 % at 120 °C. Pore size of hexamer of molecular assembly of (1)₆ is 285 Å, and van der Waals volume of H2O is almost 30 Å. The water-loss from organogel was consistent with possible formula of (1)₆·9(H2O), where weight of 8.77 % could be assigned to H2O molecules.
According to the IR spectra of molecule 1 (left in Figure 3), the vibrational peaks at 3294 and 3361 cm\(^{-1}\) were assigned to the \(\nu_{\text{NH}}\) and \(\nu_{\text{OH}}\) mode, and the heating process kept the peak position of \(\nu_{\text{NH}}\), which indicated that the intermolecular N–H–O= hydrogen-bonding interactions remained even after heating. On the contrary, the vibration peaks at 3307 and 3361 cm\(^{-1}\) of molecule 2 were assigned to the \(\nu_{\text{NH}}\) and \(\nu_{\text{OH}}\) bands, respectively, and the \(\nu_{\text{NH}}\) one showed a blue-shift by increasing in the temperature, corresponding to decrease of the magnitude of intermolecular N–H–O= hydrogen-bonding interactions after heating.

In this study, alkylamide-substituted isophthalic acid derivative was assembled to different structures of fibrous microcrystals or organogel according to the solvent system. The formula of (1)•(H\(_2\)O)\(_{9\sim12}\) was confirmed in the molecular assembly of 1, which could be assigned to the ring-shaped hydrogen-bonding tubular molecular assembly. From the FT-IR spectra, the intermolecular hydrogen-bonding interactions of 2 should be stronger than that of 1 due to twice of the number of alkylamide group. Detail in assembly structures and dielectric responses of these two hydrogen-bonding molecules will be presented.

References