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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 alklyamide-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).

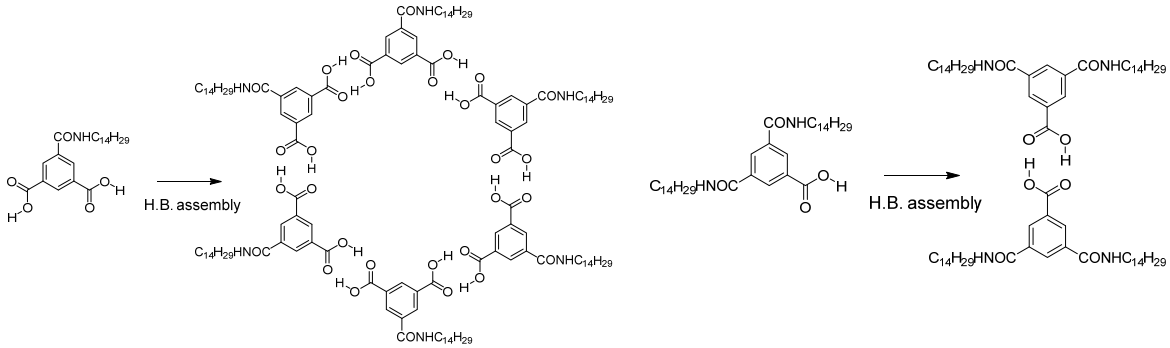

Figure 1. Molecular structure of **1** (left) and possible hydrogen-bonding assembly structure of hexamer $(\mathbf{1})_6$ and molecular structure **2** (right) and possible dimer structure $(\mathbf{2})_2$.

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 in different solvent system. For example, the molecules **1** and/or **2** form organogels in the mixed solvents of H_2O-CH_3OH and/or H_2O-C_2H_5OH. Morphologies and properties of these assemblies were characterized and discussed below.

Results and discussion.

From the TG analysis of **1** (Figure 2), organogel from H_2O-CH_3OH showed a weight-loss of 2.35 % at 100 ^oC and of 8.8 % at 150 ^oC, whereas organogel from H_2O-C_2H_5OH showed a weight-loss of 4.88 % at 120 ^oC. Pore size of hexamer of molecular assembly of $(\mathbf{1})_6$ is 285 Å, and van der Waals volume of H_2O is almost 30 Å. The water-loss from organogel was consistent with possible formula of $(\mathbf{1})_6 \cdot 9(H_2O)$, where weight of 8.77 % could be assigned to H_2O molecules.

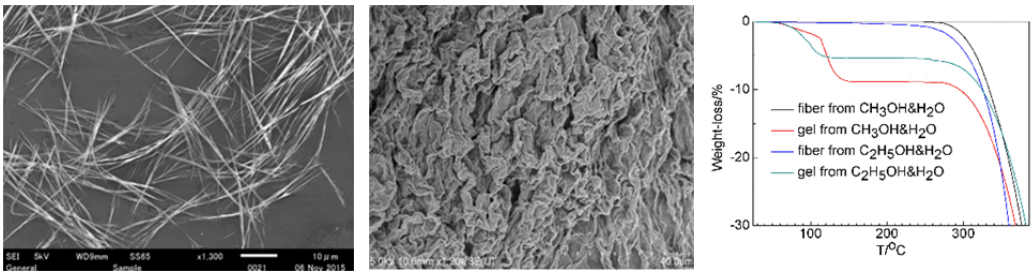

Figure 2. SEM images of fibrous microcrystals (left) and xerogel (middle) of **1** on HOPG. TG charts of **1** obtained by different solvent system (right).

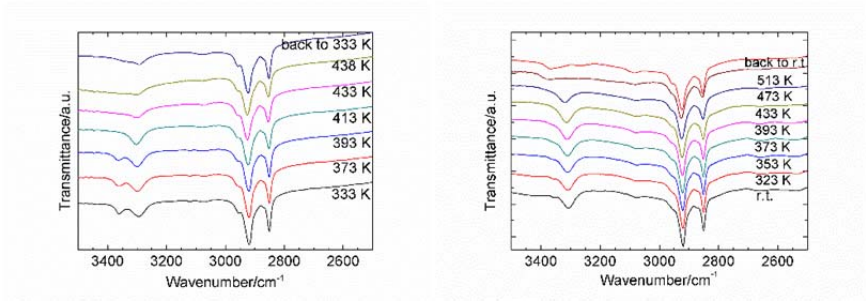

Figure 3. Temperature dependent IR spectra of molecule **1** (left) and of molecule **2** (right) on KBr pellets.

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 ν_{NH} and ν_{OH} mode, and the heating process kept the peak position of ν_{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 ν_{NH} and ν_{OH} bands, respectively, and the ν_{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 maicrocrystals or organogel according to the solvent system. The formula of (**1**)•$(H_2O)_{9\sim12}$ 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

[1] Y. Shishido, H. Anetai, T. Takeda, N. Hoshino, S. Noro, T. Nakamura, T. Akutagawa, *J. Phys. Chem. C*. **2014**, *118*, 21204-21214.

[2] H. Anetai, Y. Wada, T. Takeda, N. Hoshino, S. Yamamoto, M. Mitsuishi, T. Takenobu, and T. Akutagawa, *J. Phys. Chem. Lett.* **2015**, *6*, 1813.