

Crystal structures and phase transition behaviors of pillar[n]arene crystals

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Various types of guest molecules have been included into the host frameworks, in which the guest molecules are constructed by the weak non-covalent intermolecular interactions within the cavity and the host molecule has a guest selectivity according to the cavity size. A large number of host molecules has been designed from the viewpoint of its application for ion sensor, gas sensor, drug delivery system, and so on. Recently, a new interesting host molecules of pillar[n]arene was synthesized by Ogoshi et al [1]. Highly symmetrical macrocyclic host molecule of pillar[n]arenes can be facile synthesized with multi-functionality.

Although a large number of host complexing pillar[n]arenes have been reported at present, phase transition and dielectric responses of pillar[n]arenes including polar host-molecules have not examined enough. Dynamic behavior of the molecules within the molecular assemblies has a potential to achieve new functionality such as molecular rotator, ferroelectrics, ferroelastics, and so on [2, 3].

Herein, we investigated host-guest complexes of 1,4-diethoxypillar[5]arene (DE[5]) and 1,4-diethoxypillar[6]arene (DE[6]) with size-matching polar guest molecules such as $\text{CF}_3(\text{CF}_2)_3\text{COOH}$, $\text{CF}_3(\text{CF}_2)_3\text{CH}_2\text{OH}$, $\text{CHF}_2(\text{CF}_2)_3\text{CH}_2\text{OH}$, $\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$, $\text{CHF}_2\text{CF}_2\text{OCH}_2\text{CF}_3$, $\text{CHF}_2\text{CF}_2\text{OCH}_2\text{CF}_2\text{CHF}_2$, and CH_3I for DE[5] and pyrrole, tetrahydrofuran, quinuclidine, thiazole, thiophene, and furan for DE[6]. These host-guest complexes were prepared in solution phase by mixing of DE[5] or DE[6].

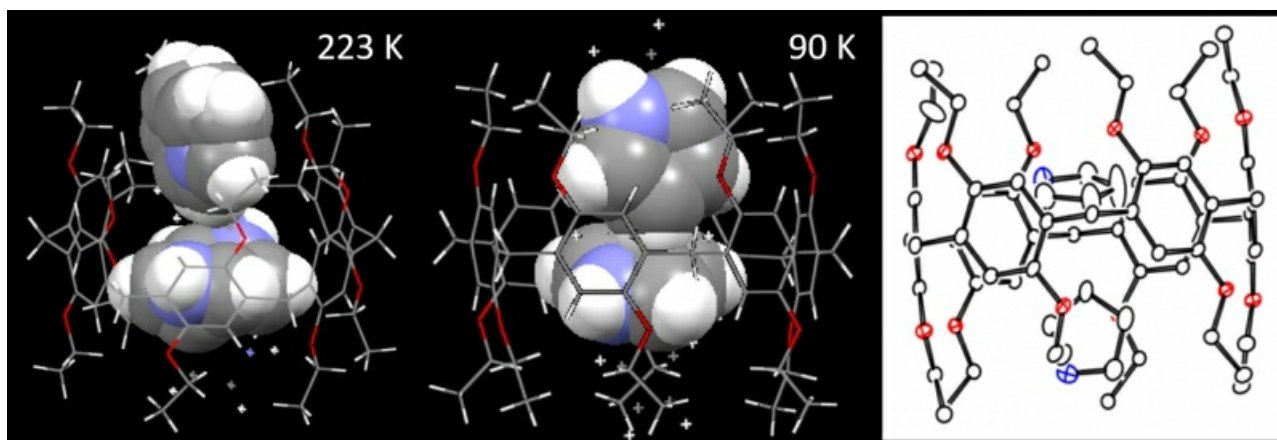
The formation of host-guest complexes was confirmed by ¹H NMR spectra. The host framework of DE[6] showed the host complexation behavior with all the guest molecules, whereas only the two kinds of complexes with $\text{CF}_3\text{CF}_2\text{CH}_2\text{CH}_2\text{I}$ and CH_3I could be obtained in DE[5] with much smaller cavity size than that of DE[6]. Single crystal X-ray structural analyses of these host-guest complexes clearly revealed the inclusion state of the guest molecules within the host cavity. Two molar of polar CH_3I molecules was existed into the inner of DE[5] molecule, forming single crystal of $\text{DE}[5] \cdot 2(\text{CH}_3\text{I})$. Similarly, two molar of pyrrole was observed in the cavity of DE[6], forming single crystal of $\text{DE}[6] \cdot 2(\text{Pyrrole})$. From the ¹H NMR spectra, stoichiometry of the other host-guest complexes were also 2:1 of $\text{DE}[5] \cdot 2(\text{guest})$ and $\text{DE}[6] \cdot 2(\text{guest})$.

Temperature dependent structural change and phase transition behavior of $\text{DE}[6] \cdot 2(\text{Pyrrole})$ were examined by single crystal X-ray analyses and DSC measurements, which showed the phase transition behavior around 205 K. The low-temperature phase I and high temperature phase II had different environment of the guest pyrrole molecules (Figure 1). The molecular structures of pyrrole showed highly disordered state at high temperature phase II at 223 K, whereas those was ordered state at low temperature phase at 90 K. The dielectric phase transition behavior of $\text{DE}[6] \cdot 2(\text{Pyrrole})$ as well as the other host-guest complexes will be discussed.

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