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Separation of dimethylcyclohexane stereoisomers by selective guest inclusion of host compound of guanidinium *o*-terphenyl-4,4′-disulfonate

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ABSTRACT

Using the molecular recognizability of guanidinium *o*-terphenyl-4,4′-disulfonate (G_2*o*-TPDS) host compound to guests, the stereoisomers of dimethylcyclohexane (DMCH) were separated. In a binary competition of *cis*- and *trans*-isomers of 1,2-, 1,3- and 1,4-DMCH, it was found that the equatorial, equatorial (e,e) conformers (*trans*-1,2-, *cis*-1,3- and *trans*-1,4-DMCH) were predominantly selected as guests to the host inclusion against the axial, equatorial (a,e) conformers (*cis*-1,2-, *trans*-1,3- and *cis*-1,4-DMCH) due to the spatial configuration of the nano-cavity in the host frame. Furthermore, among the three e,e-conformers, *trans*-1,2- and *trans*-1,4-DMCH were preferentially accommodated to the host frame rather than *cis*-1,3-DMCH. However, there was little guest selectivity of the host frame between *trans*-1,2- and *trans*-1,4-DMCH. From powder X-ray diffraction and differential scanning calorimetry of the host–guest inclusion compounds, it was revealed that *trans*-1,2- and *trans*-1,4-DMCH were guest templates for stronger G_2*o*-TPDS host-frame structure than other isomers, resulting in the more stable host–guest inclusion compounds of G_2*o*-TPDS (*trans*-1,2-DMCH) and G_2*o*-TPDS (*trans*-1,4-DMCH). So, they required higher energy and onset temperature to release guest molecules from the host frames than other inclusion compounds. This thermal analysis of the host–guest inclusion compounds was consistent with the guest selectivity of the host frame in the binary mixture, implying the potential method to predict the selective guest in the inclusion compound in the guest mixture.

1. Introduction

Traditional techniques to separate a particular component from a mixture were generally based on difference of the physical properties, as such, distillation, extraction and adsorption exploiting the difference of vapor pressure, solubility and affinity of the components, respectively [1–4]. However, those techniques were hardly applicable to the separation of isomer mixture having similar physical properties [5,6]. Therefore, a new approach of selective host–guest inclusion based on molecular recognition has drawn a great attention to achieve the isomer isolation.

Although some approaches based on the recognition of molecular shape and size such as molecular sieve and molecular imprinted polymer were of partial success in the separation of isomers [7–10], they still had a high limitation in wide application to separation of isomers due to their rigidity of host structures. That is, the meso-porous zeolite for molecular sieve was formed by the ionic bonding and the molecular imprinted polymer depended mainly on the covalent bonding. Thus, their structures were so rigid that it was hardly possible to adjust their inner cavity space to a broad range of guest molecule shape and size. The organic clathrates formed by the hydrogen bonding between the host and target molecules were flexible in adjusting their structures to various isomers [6,11–17]. However, this method is only applicable for separating guest molecules with a lone pair electron for hydrogen bonding.

By recent studies of Ward group [18,26], alternatively, the guanidinium organosulfonate host–guest system was first suggested for the separation of xylene isomers by exploiting the recognizability of the inner cavity of host frame to the guest molecules in size and shape. In the host compound of the guanidinium organosulfonate, N-H moieties of the guanidinium cation (G) and the sulfonate moieties of the organosulfonate anion (S) were hydrogen-bonded, forming quasi-hexagonal lamellar motif in two dimensions (called as GS sheet), and the organic residues of the organosulfonate anions extruded in the third dimension (called as organic pillar) created a cavity space to include the guest molecules during the self assembly process [18–22,26]. Here, the recognizability of the

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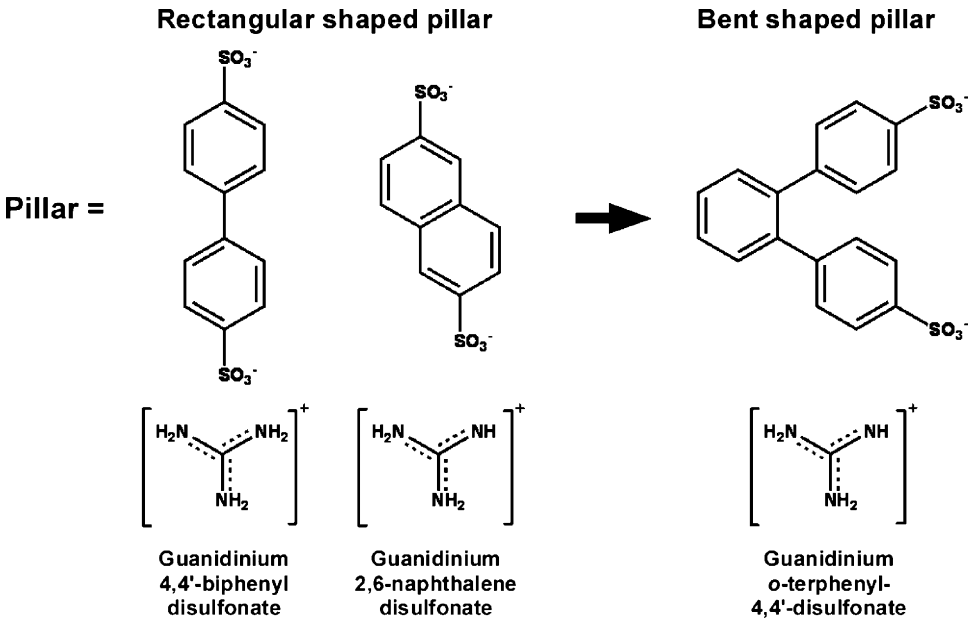


Scheme 1.

host frame was originated from the configuration of cavity space designed by the organic residues (organic pillar). The architecture of the host frame was templeted by the guest molecules for the stable inclusion. That is, the guest molecule shape determined the host frame as bilayer, brick and tubular structures, and then GS sheet of the host frame was puckered and the organic pillar tilted for the best accommodation of the guest molecules. So, in the host–guest inclusion compound of guanidinium-*xylene*-2,6-naphthalenedisulfonate (G_2-*xylene*-NDS), the bilayer host structure was template by the *p*-xylene guest and the brick host structure by the *o*-xylene.

Such a self-adjustment of the host frame to a given guest molecule was to self-optimize the interaction between the host compound and guest molecule, inducing the self-assembly of stable host–guest inclusion compound. By Kim et al. [26], a differential scanning calorimetry was used to analyze the thermal stability of the host–guest inclusion compound and to predict the guest selectivity of the host frame in the guest mixture.

In addition, the GS host compounds of an inorganic–organic salt form were so chemically stable as to be reusable after the retrieval of the guest molecules from the inclusion compounds. It might be another advantage of the GS host compounds to the practical application of separation process [18].

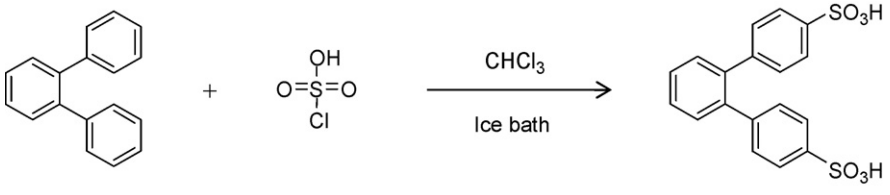
In the previous studies, constitutional isomers of xylene and dimethylnaphthalene (DMN) were separated using host frames of guanidinium 2,6-naphthalenedisulfonate (G_2NDS), guanidinium 4,4′-biphenyldisulfonate (G_2BPDS) and guanidinium *p*-toluenesulfonate (GTS) [18,26]. In the present study, however, the separation of the stereoisomers of dimethylcyclohexane (DMCH) is first attempted using guest selectivity of a new host compound of guanidinium 4,4′-*o*-terphenyldisulfonate (G_2*o*-TPDS) (Scheme 1). Also, the prediction of the guest selectivity of the host frame is studied by the thermal analysis of the inclusion compound.

2. Experiments

2.1. Preparation of guanidinium 4,4′-o-terphenyldisulfonate

For preparation of the host compound of guanidinium 4,4′-*o*-terphenyldisulfonate (G_2*o*-TPDS), the chemical reagents of *o*-terphenyl, chlorosulfonic acid, guanidine carbonate salt (99%), and tetrafluroboric acid solution (48 wt.% in water) were purchased from Sigma–Aldrich Co. (U.S.A.) and dimethylcyclohexane isomers for the guests were purchased from TCI Co. (Japan). Those reagents were used without further purification.

First, the intermediate reagent of guanidinium tetrafluroborate (GTFB) was prepared by reaction of guanidine carbonate salt (0.5 mol, 22.5 g) with a tetrafluroboric acid solution (1 mol, 182.9 g) for 2 h. Then, the solid of GTFB was obtained by drying the product solution with a rotary evaporator. Secondly, the *o*-terphenyl-4,4′-disulfonic acid (*o*-TPDSA) was prepared by the reaction of *o*-terphenyl (8mmol, 2.24 g) with chlorosulfonic acid (16 mmol, 2 g) in chloroform solution (10 ml) under nitrogen gas atmosphere in ice bath. After stirring for 2 h, the oily *o*-TPDSA was isolated from the product solution by phase separation and washed several times with pure chloroform. Then, it was dried to the solid with the rotary evaporator.



o-terphenyl Chlorosulfonic acid *o*-TPDSA

The guanidinium 4,4′-*o*-terphenyldisulfonate (G_2*o*-TPDS) was obtained by reaction of GTFB and *o*-TPDSA in acetone for 2 h.