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Supramolecular assembly based on π–π stacking and π-cation interactions between thiacalix[6]arene and DMF

Fumio Hamada,[a,*] Yutaka Higuchi,[a] Yoshihiko Kondo,[a]
Chizuko Kabuto[b] and Nobuhiko Iki[c]

[a] *Department of Material-Process Engineering and Applied Chemistry for Environments, Faculty of Engineering and Resource Science, Akita University, Tegata, Akita 010-8502, Japan*
[b] *Instrumental Analysis Center for Chemistry, Graduate School of Science, Tohoku University, Aramaki-Aoba, Aoba-ku, Sendai 980-8578, Japan*
[c] *Department of Environmental Studies, Graduate School of Environmental Studies, Tohoku University, Aobaku, Sendai 980-8578, Japan*

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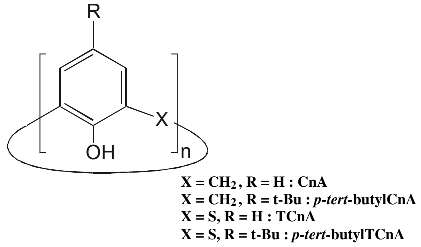
Abstract—The molecular assembly of thiacalix[6]arene was formed by π–π stacking and π–DMF interactions between thiacalix[6]arene and adjoining thiacalix[6]arene and between thiacalix[6]arene and DMF, respectively. The X-ray crystal analysis also revealed that hydroxyl groups of thiacalix[6]arene adopted novel two sets of hydrogen bond with two DMF and intramolecular hydrogen bond between phenolic units, which cause to make 1,2,3-alternate configuration structure of thiacalix[6]arene.

Non-covalent interactions such as π–π stacking interaction, hydrophobic interaction, hydrogen bond and metal coordination play an important role to make self assembly and molecular recognition system in a variety of supramolecular functionality.[1] The calixarenes (CAs) and thiacalixarenes (TCAs) as a counterpart of CAs (Scheme 1) are versatile materials that have been studied extensively as a host molecular and scaffold to form a concave recognition surface.[2] Considerable attention has been recently focused on TCAs because there are many features that are not presented in the chemistry of CAs. Recently, we have reported the crystal structure of mono-, di-, and tri-(*p*-*tert*-butyl)thiacalix[4]arenas which form dimeric self-inclusion complexes.[3] In those cases, we found that π–π stacking interaction of self-inclusion dimeric units of thiacalix[4]arenes. We also have reported the crystal structure of the complex of *p*-*tert*-butylthiacalix[6]arene (*p*-*tert*-butylTC6A) with MeOH molecules and potassium cations.[4] It was shown that the structure of the complex was built from continuous S···K···(O,S) coordination between neighboring *p*-*tert*-butylTC6A and hydrophobic interaction between adjoining *p*-*tert*-butyl groups to make supramolecular structure. However, to our best knowledge, there are few reports that have shown possible to make a supramolecular assembly of thiacalix[n]arenes. In this letter, we would like to report de-*tert*-butylation of *p*-*tert*-butylTC6A and the crystal structure of complex TC6A and DMF. In the crystal structure, two different kinds of sheet structures are formed by intermolecular π–π interaction of phenolic units between neighboring TC6A and π-cation interaction between the aromatic ring and the positively charged group such as nitrogen of DMF included in the neighboring TC6A, which contributed to make a supramolecular assembly.



Scheme 1. Structures of CA and TCA.

Keywords: Crystal structure; π–π Stacking interaction; π–DMF interaction; Thiacalixarenes; Hydrogen bond.

[*] Corresponding author. Tel.: +81 18 889 2440; fax: +81 18 837 0404; e-mail: hamada@ipc.akita-u.ac.jp

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TC6A was synthesized from *p*-*tert*-butylTC6A in the presence of phenol and $AlCl_3$.[5] It was realized that the reaction temperature must be lower than that of TC4A.[6] The reaction condition was carried out at 80 °C for 3 h under nitrogen atmosphere, which was much milder than that of TC4A. When a reaction temperature was raised up over 110° which was the same condition for de-*tert*-butylation of *p*-*tert*-TC4A, only no identifiable material was obtained. The crystal as colorless prism (monoclinic, space group: *P*121/*c*1) suitable for X-ray study is formed by liquid–liquid slow diffusion of acetonitrile into DMF solution of TC6A at room temperature.[7] In the crystal, there are two fashions such as sheet A and sheet B consisted with two kinds of different conformation of TC6A, which are abbreviated as Mol. A and Mol. B, respectively. Basically, those structures like a chair form are very similar as shown in Figure 1. In those molecules, the angles formed between adjoining phenolic unit are 103.35, 102.80° for Mol. A and 103.23, 102.46° for Mol. B, respectively. The different points are one angle between ring C and D which is 103.85° for Mol. A and 101.86° for Mol. B, respectively. In the case of Mol. B, the angle of 101.86° is very narrow than those of other angles. Mol. A and Mol. B include two DMF molecules in their cavities by hydrogen bond. The distance between the hydroxyl groups of host and carbonyl oxygen of guest are 2.78, 2.63 for Mol. A and 2.77, 2.62 Å for Mol. B, which are very similar. In Figure 2, it was found that π–π stacking interaction of which the distance is 3.90 Å between E ring of the Mol. A and C ring of Mol. B, also causes to make molecular assembly. In the crystal, such π–π stacking interaction between Mol. A and Mol. B were located as [0 1 0] direction. However, the configuration of these two benzene ring is not completely face-to-face configuration, the dihedral angle between two benzene rings was 23.0°. It was reported that deformed π–π stacking such as displaced π–π stacking in the CA system.[8] We found some interaction such as the π–DMF interaction in Mol. B as shown in Figure 3. To our best knowledge, it is the first example to detect such an interaction between aromatic ring and DMF. The position of DMF and phenolic unit of ring B in the Mol. B is located as face to face configuration and the distance between nitrogen of DMF and phenolic unit of ring C is 3.56 Å. It was suggested that DMF molecular could be localized by hydrogen bond between carbonyl oxygen of DMF and neighboring hydroxyl group of TC6A as shown in Figure 4. The nitrogen moiety of DMF would be positively charged, which resulted to give binding force such as π-cation interaction.[9] The crystal was formed by layers with sheet A and B in layer along [1 0 0], which constructed the supramolecular assembly as shown in Figure 5.

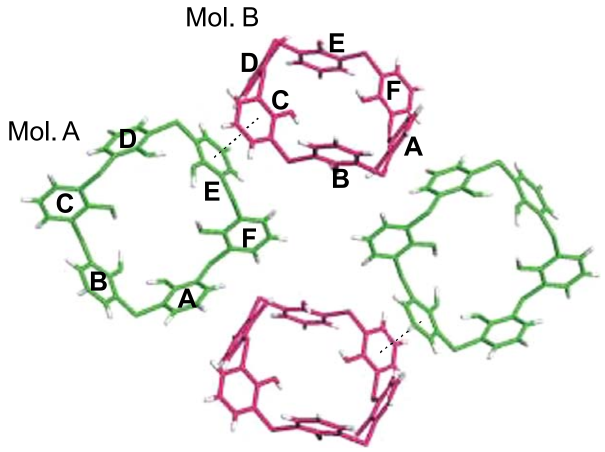

Figure 2. Structure of molecular sheet with π–π stacking interaction between Mol. A and Mol. B in parallel with *ac* plane. The Mol. A and Mol. B are in green and pink, respectively.

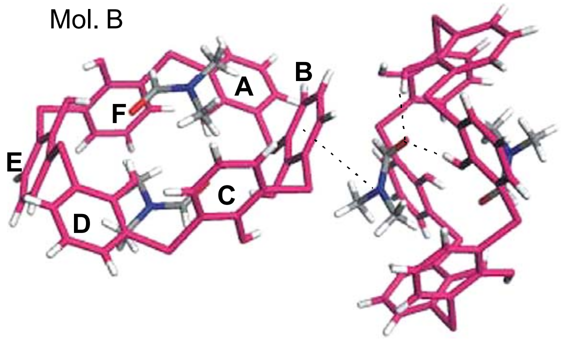

Figure 3. π–DMF interaction and hydrogen bond between Mol. B and DMF.

In conclusion, we achieved de-*tert* butylation of *p*-*tert*-butylTC6A under much more milder condition than

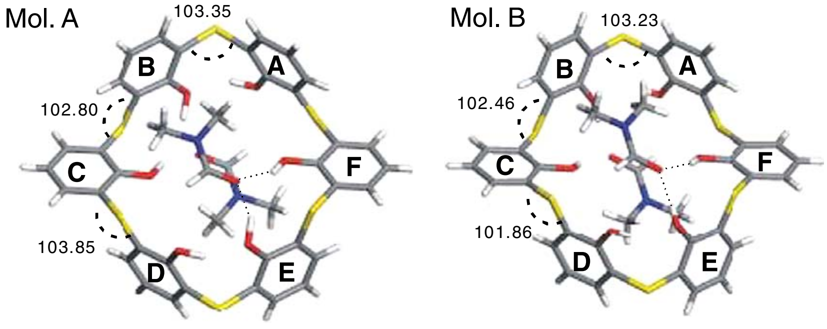

Figure 1. X-ray crystal structures of Mol. A and Mol. B. The carbons, oxygens, sulfurs, nitrogens, and hydrogens in the Mol. A and Mol. B are in gray, red, yellow, blue, and white, respectively.

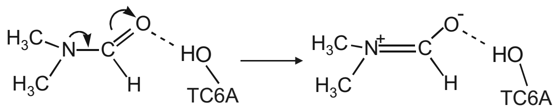

Figure 4. The model of localizing of DMF by hydrogen bond in the Mol. B.

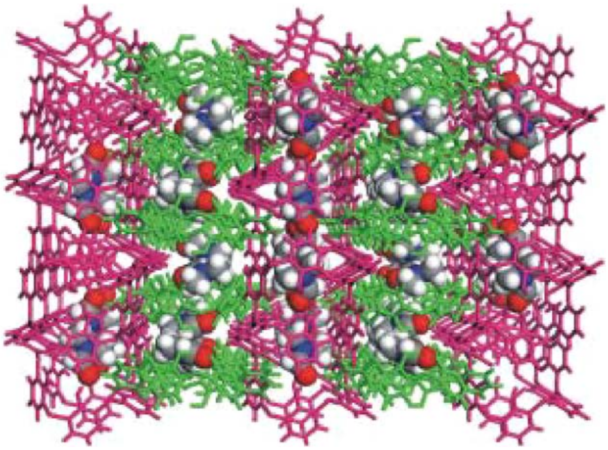

Figure 5. Structure of supramolecular assembly of the TC6A complex with DMF molecules along *c* axis. The Mol. A and Mol. B are shown as stick models in green and pink, respectively, and guest molecules are presented as a CPK model.

that of TC4A. X-ray crystallographic measurement of the crystal structure of TC6A revealed that two DMF molecules were included in the cavity of TC6A based on hydrogen bond between two phenolic hydroxyl and carbonyl group of DMF. The inter molecular π–π interaction between neighboring TC6A and π-cation interaction between DMF and TC6A were also observed. The intramolecular hydrogen bond between phenolic groups were also recognized.

Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2006.05.055.

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5. A suspension of *p*-*tert*-butylTC6A (500 mg, 0.462 mmol) in 25 ml in toluene was heated until clearly solution was obtained and then phenol (261 mg, 2.77 mmol) and $AlCl_3$ anhydride (2.59 g, 19.4 mmol) were added to the reaction mixture. The mixture was heated at 80 °C for 3 h under nitrogen atmosphere. After cooling to a room temperature, the reaction mixture was poured into ice cold water. The organic layer was separated and then washed with 1 N HCl aqueous solution. The organic layer was dried over Na_2SO_4 and filtered, which was evaporated in vacuo to yield precipitates. The precipitates were washed with acetone and then chloroform to yield pure de-*tert*-butylTC6A (220 mg, 64% yield). ^1H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ 8.89 (s, 6H, –OH), 7.62 (d, $J = 7.8$ Hz, 12H, aromatic-H), 6.78 (t, $J = 7.5$ Hz, aromatic-H), MALDI-TOFMS *m*/*z* 766.83 $[M+Na]^+$, calcd for $C_{36}H_{24}O_6S_6Na$, 766.98.
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7. Crystal Data: $C_{40}H_{38}O_8S_6N_2$, $M = 877.11$, Colorless prism, Crystal dimensions $0.3 \times 0.15 \times 0.10$ mm, Monoclinic, space group $P121/c1$ (No. 14), $a = 19.336(5)$ Å, $b = 13.478(3)$ Å, $c = 15.614(4)$ Å, $\beta = 93.217(1)°$, $V = 4062(1)$ Å^3, $Z = 4$, Mo-$K\alpha$ radiation ($\lambda = 0.71070$ Å), $D_{calcd} = 1.417$ g cm^{-3}, $T = 173$ K, μ(Mo-Kα) = 3.19 cm^{-1}, Rigaku/MSC Mercury CCD diffractometer, 28,968 measured reflections, 7691 unique reflections ($R_{int} = 0.018$), 5800 observed reflections ($I > 3.00\sigma(I)$), 545 parameters, $R = 0.040$, $R_w = 0.040$, refined against $|F|$, GOF = 1.07. The structure was solved by direct methods with the SIR-92 program. Crystallographic data for this crystal has been deposited with the Cambridge Crystallographic Data Center as supplementary publication no. CCDC 291613, Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road Cambridge CB2, 1EZ, UK (Fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).
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