COMMUNICATION

ChemComm
www.rsc.org/chemcomm

Self-assembled calix[6]pyrrole capsules: solid-state encapsulation of different guests in preorganized calix[6]pyrrole capsules

Boaz Turner,[a] Alexander Shterenberg,[a] Moshe Kapon,[a] Mark Botoshansky,[a] Kinga Suwinska[b] and Yoav Eichen*[ac]

[a] *Department of Chemistry and [c]Solid-State Institute, Technion – Israel Institute of Technology, Technion City, 32000, Haifa, Israel. E-mail: chryoav@tx.technion.ac.il; Fax: 972-4-8233735; Tel: 972-4-8293708*
[b] *Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, PL-01 224, Warszawa, Poland. E-mail: kinga@ichf.edu.pl; Fax: 8-22-6325276; Tel: 48-22-6323221*
[c] *Solid-State Institute, Technion – Israel Institute of Technology, Technion City, 32000, Haifa, Israel*

Received (in Columbia, MO, USA) 10th December 2001, Accepted 2nd February 2002
First published as an Advance Article on the web 6th March 2002

***meso*-hexamethyl-*meso*-hexaphenyl calix[6]pyrrole assembles into well-defined dimeric capsules in the crystalline state; the preorganized capsule serves as an efficient host for different organic guests as well as for solvent molecules.**

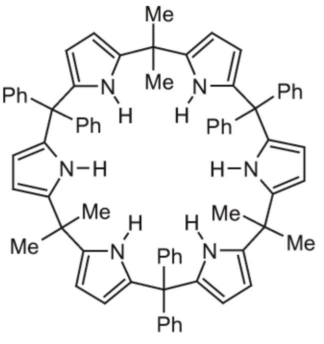
Self-assembled hosts capable of entirely encapsulating their guests are amongst the most efficient building blocks for selective and effective tools capable of molecular recognition and supramolecular manipulation. In recent years, different approaches towards the preparation of capsules were investigated.[1–3] Of particular interest are capsules that are formed by self-assembly of simple molecular building blocks, mainly due to the more convenient synthesis and resulting applicability. Different supramolecular capsule systems were reported in the last years, most of them based on assembly of molecular fragments through hydrogen bonding. These molecular capsules were found to host different organic guests as well as different unconventional solvent clusters.

Here we report on the formation of a well-defined, preorganized dimeric capsules of *meso*-hexamethyl-*meso*-hexaphenyl calix[6]pyrrole, **1**,[4] in the solid state. These preorganized dimeric capsule are found to host different organic guests.

In dilute solutions, *meso*-hexamethyl-*meso*-hexaphenyl calix[6]pyrrole, **1**, is found to form 1 : 1 complexes with a large variety of motopic and ditopic guests.[5] In the crystalline state, calix[6]pyrrole, **1**, is found to form two types of complexes with different guests. Most solid state complexes isolated so far represent the first type of complexes in which calix[6]pyrrole, **1**, dimerizes into a well defined bimolecular capsule, hosting the guest inside the cavity. Interestingly, the structure of the calix[6]pyrrole capsule, once formed, is independent of the nature of guest that it encapsulates. Furthermore, in some cases the two calix[6]pyrrole molecules are not interconnected by the guest, an evidence of its guest-independent character. Fig. 1 depicts an overlay of nine capsules originating from nine different crystalline complexes with different host–guest stoichiometries. As can be seen from the figure, the calix[6]pyrrole capsule is clearly preorganized and adopts a well defined structure regardless of the nature of the guest.† The capsules seem to be held together through six H–π interactions between the two sets of axial phenyl rings of the two calix[6]pyrroles, $\mathbf{d}_{\text{C}\pi\text{–H}\cdots\text{C}\pi} \approx 2.9$ Å.

Fig. 2 presents the structure of the complex between 4-chloronitrobenzene and the calix[6]pyrrole capsule.‡ The long axis of the guest molecule lies on a three-fold crystallographic axis and the centre of its aromatic ring is coinciding with the crystallographic centre of symmetry. Consequently, the guest molecule is disordered and the same site in the cavity is occupied both by the chlorine atom and the nitro group, each with 50% probability. In each position, one oxygen atom of the nitro group is bound to one acidic hydrogen atom of a pyrrole ring while the other oxygen atom of the nitro group is found to be within close distance from the π cloud of another pyrrole ring: $\mathbf{d}_{\text{N1-H1}\cdots\text{O32}} = 2.147$ Å, $\alpha_{\text{N1-H1}\cdots\text{O32}} = 156.58°$; $\mathbf{d}_{\pi\text{Pyrrole(N7C8-C11)}\cdots\text{O31}} = 2.912$ Å, $\alpha_{\text{N7-Ct-O31}} = 98.57°$. The chlorine atom is also situated in close vicinity to the same three pyrrole rings: $\mathbf{d}_{\pi\text{Pyrrole(N7C8-C11)}\cdots\text{Cl1}} = 3.821$ Å.

In the second type of crystalline calix[6]pyrrole complexes, a single calix[6]pyrrole molecule binds a single substrate in its cavity, usually through a combination of hydrogen bonds and π-



1

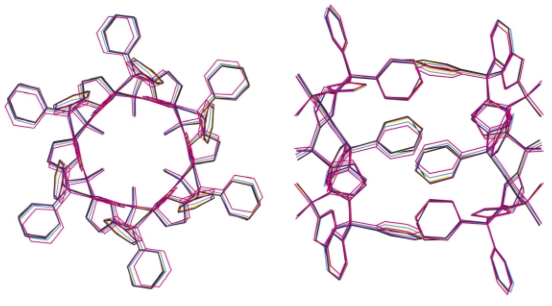


Fig. 1 Best fit superposition of nine different solid-state calix[6]pyrrole, **1**, capsules extracted from nine different crystalline host–guest complexes. For more details on the different structures, see supplementary information.†

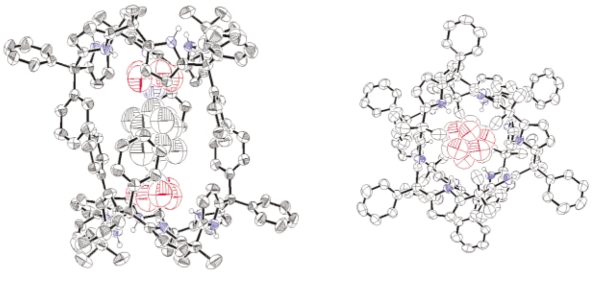


Fig. 2 Side and top views of the complex between 4-chloronitrobenzene and a dimeric capsule of calix[6]pyrrole, **1**. Solvent molecules located at extra cavity positions were removed for clarity.

DOI: 10.1039/b111281n

interactions with the guest.†[4,6] For example, in the complex between calix[6]pyrrole, **1**, and acetonitrile (Fig. 3) the guest is held within the cavity of the host by two hydrogen bonds between the acidic hydrogen atoms of two pyrrole rings and the nitrogen atom of the acetonitrile and π-interactions between the nitrile triple bond and the π cloud of two opposite pyrrole rings: $\mathbf{d}_{\text{N7-H7}\cdots\text{N87}} = 2.333$ Å, $\alpha_{\text{N7-H7}\cdots\text{N87}} = 176.30°$; $\mathbf{d}_{\text{N1-H1}\cdots\text{N87}} = 2.192$ Å, $\alpha_{\text{N1-H1}\cdots\text{N87}} = 171.99°$ $\mathbf{d}_{\pi\text{Pyrrole(N13C13-C17)}\cdots\pi\text{CN}} = 3.658$ Å, $\alpha_{\text{N13-Ct-}\pi\text{CN}} = 101.07°$; $\mathbf{d}_{\pi\text{Pyrrole(N31C32-C35)}\cdots\pi\text{CN}} = 3.630$ Å, $\alpha_{\text{N31-Ct-}\pi\text{CN}} = 106.64°$.§ [7]

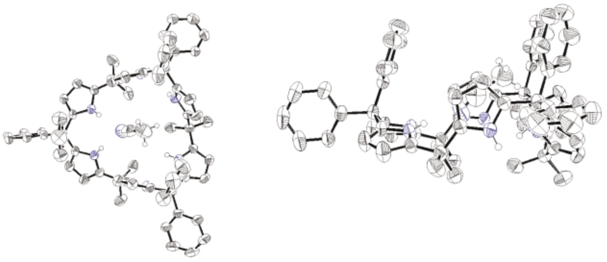


Fig. 3 Side and top views of the complex between acetonitrile and calix[6]pyrrole, **1**. Solvent molecules located at extra cavity positions were removed for clarity.

Replacement of the axial phenyl groups by self-complementary recognition units, such as pyridone groups, should provide systems that will be stable in the capsular form in solutions too. This approach is currently under investigation. We will report on these developments in due course.

This research was supported by the Israeli Ministry of Science, Culture and Sports and the Fund for the Promotion of Research at Technion.

Notes and references

† Details on the different crystal structures are provided in the electronic supplementary information. CCDC 101785, 175891–175898. See http://www.rsc.org/suppdata/cc/b1/b111281n/ for electronic files in .cif or other electronic format.

‡ *Crystal data* for 2 calix[6]pyrrole : 4-chloronitrobenzene : chloroform : H_2O: hexagonal, $R\bar{3}$, $a = 23.517(1)$ Å, $b = 23.517(1)$ Å, $c = 24.148(1)$ Å, $V = 11565.8(8)$ Å^3, $Z = 6$, $R_{int} = 0.099$, $GOF = 1.079$.

§ *Crystal data* for calix[6]pyrrole : acetonitrile : 2 acetone: triclinic, $P\bar{1}$, $a = 11.838(1)$ Å, $b = 17.574(1)$ Å, $c = 19.236(1)$ Å, $\alpha = 114.034(3)$, $\beta = 101.639(3)$, $\gamma = 100.934(3)$, $V = 3410.5(4)$ Å^3, $Z = 2$, $R_{int} = 0.053$, $GOF = 1.051$.

1 (*a*) B. M. O'Leary, T. S. Szabo, N. Svenstrup, C. A. Schalley, A. Luetzen, M. Schaefer and J. Rebek, *J. Am. Chem. Soc.*, 2001, **124**, 11519; (*b*) Y. K. Cho, D. M. Rudkevich, M. Dmitry, A. Shivanyuk, R. Alexander, K. Rissanen and J. Rebek, *Chem. Eur. J.*, 2000, **6**, 3788; (*c*) J. Rebek, *Chem. Commun.*, 2000, 637; (*d*) M. M. Conn and J. Rebek, *Chem. Rev.*, 1997, **97**, 1647; (*e*) J. M. Rivera, T. Martin and J. Rebek, *Science*, 1998, **279**, 1021.

2 (*a*) J. L. Atwood, L. J. Barbour and A. Jerga, *Chem. Commun.*, 2001, 2376; (*b*) J. L Atwood, L. J. Barbour, M. Hardie and C. L. Raston, *Coord. Chem. Rev.*, 2001, **3**, 222; (*c*) L. R. MacGillivray and J. L Atwood, *Angew. Chem., Int. Ed.*, 1999, **38**, 1018; (*d*) L. R. MacGillivray and J. L. Atwood, *Nature*, 1997, **389**, 469.

3 (*a*) H. R. Webb, M. J. Hardie and C. L. Raston, *Chem. Eur. J. 7*, 2001, 3616; (*b*) M. J. Hardie, M. Makha and C. L Raston, *Chem. Commun.*, 1999, 2409.

4 B. Turner, M. Botoshansky and Y. Eichen, *Angew. Chem., Int. Ed.*, 1998, **37**, 2475.

5 (*a*) B. Turner, A. Shterenberg, M. Kapon, K. Suwinska and Y. Eichen, *Chem. Commun.*, 2001, 13; (*b*) B. Turner, A. Shterenberg, M. Kapon, K. Suwinska and Y. Eichen, *Chem. Commun.*, 2002, 404; B. Turner, A. Shterenberg, M. Kapon, K. Suwinska and Y. Eichen, unpublished.

6 G. Cafeo, F. H. Kohnke, G. L. Torre, A. J. P. White, D. J. Williams and J. David, *Chem. Commun.*, 2000, 1207.

7 See also : B. Turner, A. Shterenberg, M. Kapon, K. Suwinska and Y. Eichen, *Chem. Commun.*, 2001, **13** and structures in the supplementary material.