This article was downloaded by:
On: *29 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

**Supramolecular Chemistry**

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713649759

# Investigations into Chain Length Control over Solid-State Pyrogallol[4]arene Nanocapsule Packing

Gareth W. V. Cave[a]; Scott J. Dalgarno[b]; Jochen Antesberger[c]; Matthew C. Ferrarelli[c]; Robert M. McKinlay[c]; Jerry L. Atwood[c]

[a] School of Biomedical and Natural Sciences, Nottingham Trent University, Nottingham, UK [b] School of Engineering and Physical Sciences-Chemistry, Heriot-Watt University, Edinburgh, UK [c] Department of Chemistry, University of Missouri-Columbia, Columbia, MO, USA

**To cite this Article** Cave, Gareth W. V. , Dalgarno, Scott J. , Antesberger, Jochen , Ferrarelli, Matthew C. , McKinlay, Robert M. and Atwood, Jerry L.(2008) 'Investigations into Chain Length Control over Solid-State Pyrogallol[4]arene Nanocapsule Packing', Supramolecular Chemistry, 20: 1, 157 — 159

**To link to this Article: DOI:** 10.1080/10610270701762692

**URL:** http://dx.doi.org/10.1080/10610270701762692

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

*Supramolecular Chemistry*, January–March 2008 Vol. 20 (1–2), pp. 157–159

# Investigations into Chain Length Control over Solid-State Pyrogallol[4]arene Nanocapsule Packing

GARETH W. V. CAVE[a], SCOTT J. DALGARNO[b], JOCHEN ANTESBERGER, MATTHEW C. FERRARELLI,
ROBERT M. MCKINLAY and JERRY L. ATWOOD*

*Department of Chemistry, University of Missouri-Columbia, Columbia, MO, 65211, USA; [a]School of Biomedical and Natural Sciences, Nottingham Trent University, Clifton Lane, Nottingham, NG11 8NS, UK; [b]School of Engineering and Physical Sciences-Chemistry, Heriot-Watt University, Edinburgh, EH14 4AS, UK*

*(Received 16 August 2007; Accepted 11 October 2007)*

Dedicated to Prof. Dr Ir. David N. Reinhoudt on his retirement.

**Upon crystallising a series of pyrogallol[4]arenes from ethyl acetate as hydrogen bonded nanocapsules, structural study allows for the determination of the dependence of inter-capsule spacing on the chain length present at the lower rims of these 'bowl-shaped' molecules. Surprisingly, these nanocapsules pack closest together when a hexyl chain length is employed, and reasons for this phenomenon are suggested.**

*Keywords*: Calixarenes; Self-assembly; Hydrogen bonding; nanocapsules

## INTRODUCTION

Large supramolecular hydrogen bonded capsules continue to attract significant attention, given their potential in the fields of controlled chemical synthesis, phase transfer and separation science for example [1]. Commercially available *C*-methylcalix[4]resorcinarene (CMRC) has been shown to assemble as both dimeric and hexameric hydrogen bonded capsules in the solid state [2–*8*]. In the latter of these two motifs, it was initially shown that eight structural water molecules were essential for the formation of a 60-hydrogen bond regime at the seam of the assembly, one that is reminiscent of the Archimedean snub cube [2, 4]. More recently, however, the role of the structural water molecules has been further expanded by Holman and co-workers, with partial water substitution being demonstrated with 2-ethylhexenols [9].

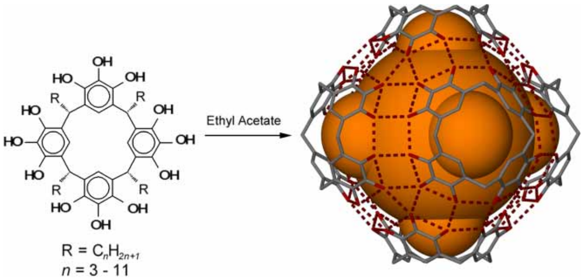
The related *C*-alkylpyrogallol[4]arenes (PgC$_n$, general structure displayed in Scheme 1) have been shown to form self-assembled hexameric nanocapsules that are of comparable size to those formed by CMRC (*10*–*18*). Although the enclosed volume in the PgC$_n$ nanocapsules is slightly less than the CMRC analogue ($\sim 1250\,\text{Å}^3$ for $[\text{PgC}_n]_6$ compared to $\sim 1500\,\text{Å}^3$ for $[\text{CMRC}]_6{\cdot}8\text{H}_2\text{O}$), the additional 'upper rim' hydroxyl groups present for the pyrogallol[4]-arenes affords a more stable nanocapsule relative to CMRC by precluding the need for structural water molecules; the pyrogallol[4]arene capsule possesses 72 hydrogen bonds in the capsule seam compared with 60 for the CMRC system. The solution phase stability of both the nanocapsule motifs has been demonstrated through detailed NMR and fluorescence spectroscopy for example [5–8, 15,16,19].

We recently reported that PgC$_n$ nanocapsules can (in one case) be seen to interact with one another in the solid state through hydrogen bonding interactions at the neighbouring capsule hydrogen bonded faces [13]. This occurs as a translation of both orientation and conformation through to the interior of the capsule *via* subtle structural anomalies. Herein, we report the synthesis and structural characterisation of four new pyrogallol[4]arene hexameric nanocapsules, which in combination with previous studies, have sequentially increasing chain lengths ($n = 4$–$11$). In addition, we show that chain length variation has a dramatic effect on the extended organisation of nanocapsules in the solid state.

---

*Corresponding author. Tel: + 1 573 882 8374; Fax: + 1573 882 2754. E-mail: AtwoodJ@missouri.edu

ISSN 1061-0278 print/ISSN 1029-0478 online © 2008 Taylor & Francis
DOI: 10.1080/10610270701762692



SCHEME 1 Crystallisation of $PgC_n$ nanocapsules from ethyl acetate solution.

## RESULTS AND DISCUSSION

As was the case in our previous report (where $n = 5$–7, Scheme 1) (*13*), ethyl acetate was found to be an excellent solvent for the quantitative formation of the present $PgC_n$ nanocapsules ($n = 4$, 8–11, Scheme 1) from the corresponding pyrogallol[4]arenes by slow evaporation of each solution in air. In each case, the nanocapsules were isolated as colourless crystals, the majority of which were suitable for X-ray diffraction studies.[1] Single crystal X-ray diffraction studies on each material afforded a nanocapsule structure similar to those found previously, but upon further examination, the extended structure of each showed that increasing the $PgC_n$ chain length resulted in changes in the nanocapsule packing, from ABA hexagonal close packing (HCP, for $n = 4$, 5) to displaced ABC cubic close packing (CCP, for $n = 7$–11), as shown in Fig. 1. Remarkably, and to our surprise, increasing $n$ from 4 to 5 caused the distance between centroids generated for the neighbouring nanocapsules in the solid state to shorten (Fig. 1 and 2). Examination of the structures found this phenomenon to be due to a capsule rotation, which results in the alignment of two hydrogen bonding faces from the two neighbouring assemblies. When these observations were combined with those found in our previous investigations, an interesting transition occurs in which the nanocapsules come together to form hexagonal arrays of hydrogen bonded nanorods, facilitated by capsule–capsule hydrogen bonding interactions when $n = 6$ [13].

This is indeed unique, as when $n = 6$, there are the closest inter-capsule spacings of 19.1 Å (Fig. 2). Upon increasing the chain length to $n = 7$, there appears to be a disruption to the inter-capsule hydrogen bonding observed when $n = 6$, with the insertion of an alkyl chain between the hydrogen bonded faces. This insertion also forces the nanocapsules into a CCP array in the extended structure (as shown in Fig. 1) and causes an increase in the inter-capsule separation (Fig. 2). Sequential lengthening of the chain length from $n = 7$ to 11 *does* in fact cause further increases in the inter-capsule separation (Fig. 2).

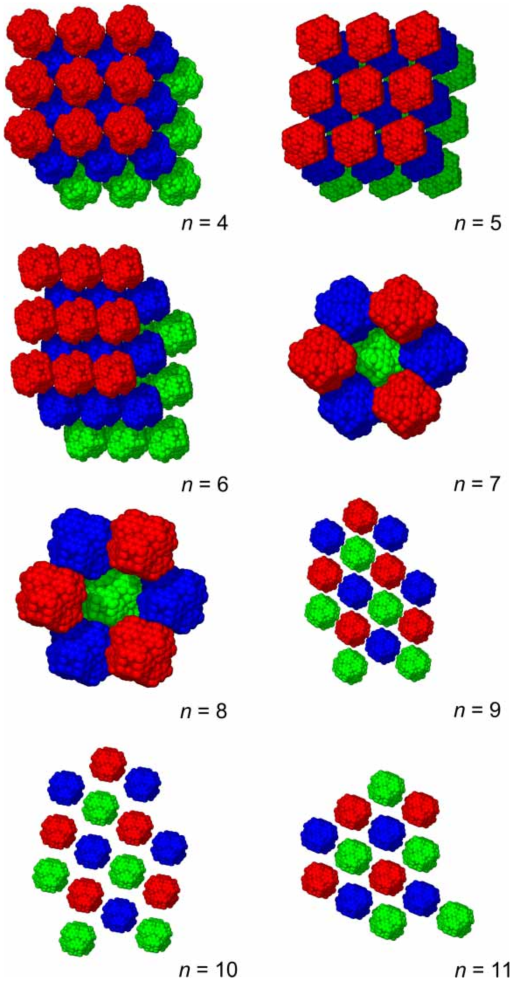


FIGURE 1 Extended packing diagrams of pyrogallol[4]arene nanocapsules ($n = 4$–11) as crystallised from ethyl acetate. Nanocapsules of identical colour originate from single planes within the extended structure. Hydrogen atoms and disordered alkyl chains have been omitted for clarity.

In both the HCP and CCP structural types, the alkyl chains aggregate in the interstitial sites between the nanocapsule frameworks, and any remaining space—typically that found at the central point between the $PgC_n$ chains at the lower rim is occupied by ethyl acetate molecules. When $n = 4$–8, the $PgC_n$ alkyl chains are found to radiate evenly from the nanocapsule framework (Fig. 3a). When $n \geq 9$ the alkyl chains splay out and form disk-like arrays, exposing two of the hydrogen bonded nanocapsule faces (Fig. 3b

---

[1] Single crystal X-ray data for the nanocapsules $[PgC_n]_6$ (where $n = 4$, 8–11) was collected on a Bruker SMART 1000 CCD diffractometer, CCDC 657476-657480. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: (international) + 44-1223/336-033;. E-mail: deposit@ccdc.cam.ac.uk]. The routine SQUEEZE was applied to the data for the nanocapsules based on $PgC_9$ and $PgC_{11}$ in order to remove diffuse electron density on the interior of the nanocapsules associated with disordered ethyl acetate molecules (*2, 21*). In all cases, the crystals were weakly diffracting and the structures displayed disorder either in the encapsulated ethyl acetate molecules or in the lower rim alkyl chains.

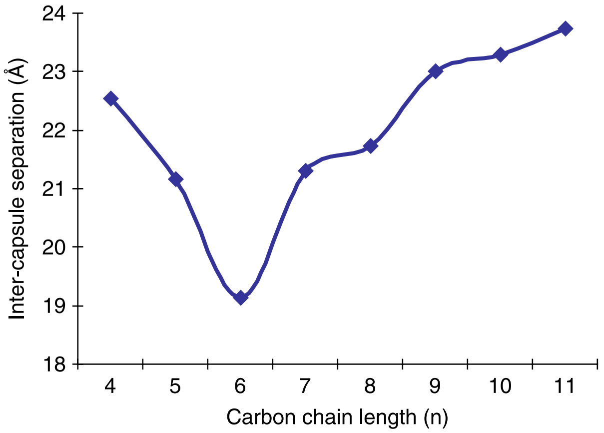


FIGURE 2 Graph showing chain length-dependent inter-capsule separations.

and 4b). An additional feature of this behaviour is that extensive inter-digitation of the longer alkyl chains causes displacement of all *exo*-capsule ethyl acetate molecules in the extended structure.

Despite the exposure of the two nanocapsule hydrogen bonded faces for $n \geq 9$, there are no inter-capsule hydrogen bonding interactions as observed for $n = 6$ [13]. The increase in chain length also appears to enlarge the interstitial space between the neighbouring nanocapsules, the result being the formation of more discrete hexagonal layers. For $n = 4$ (Fig. 4a), inter-layer separation is 39.5 Å, significantly larger than that observed when $n = 11$ (20.1 Å, Fig. 4b). The latter inter-layer proximity is due to the fact that the longer splayed alkyl chains of one layer (in Fig. 4b) interact with the exposed hydrogen bonding capsule faces from a crystallographically equivalent green layer.

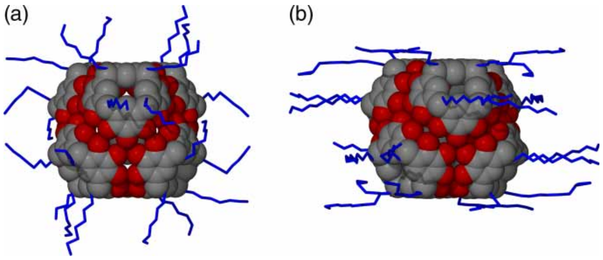


FIGURE 3 Single nanocapsules composed of (a) $PgC_8$ and (b) $PgC_{11}$. In (a), the $n = 8$ alkyl chains radiate in all directions from the nanocapsule framework. In (b), the $n = 11$ chains radiate in a disk-like arrangement exposing two of the hydrogen bonded faces of the nanocapsule.

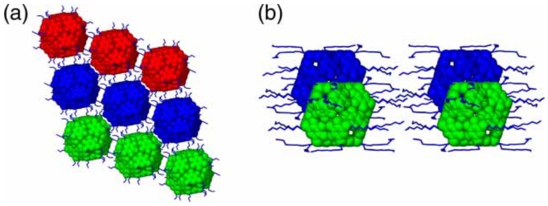


FIGURE 4 Extended packing structures for (a) $n = 4$ and (b) $n = 11$ with respective 39.5 and 20.1 Å HCP inter-layer separations (layer to layer). Hydrogen atoms and disordered alkyl chains omitted for clarity.

Recent speculation has hypothesised nanocapsule aggregation in the solution phase, thereby reducing the rate of guest diffusion to and from the interior of the hexamer (*8*). Both the nanocapsule packing and the behaviour of the lipophilic tails in the solid state (where $n > 8$) support this theory, given that they provide a pseudo-solvent environment for the globular assemblies. The favourable inter-capsule hydrogen bonding interactions observed in the solid state (when $n = 6$) also support the theory of nanocapsule aggregation (*13*).

We have shown that a sequential increase in pyrogallol[4]arene lipophilic tail length has dramatic effects on the extended packing of hexameric nanocapsules. These results provide insight into the dependence of nanocapsule aggregation on the 'lower rim' chain length in the solid state at least. Future studies will aim to correlate these findings with studies on metal-organic analogues to investigate the dominant forces involved in ordering these large nanoscale structures.

## *Acknowledgements*

We would like to thank the National Science Foundation for the financial support of this work.

## *References*

[1] Cram, D. J.; Cram, J. M. *Container Molecules and Their Guests*; Royal Society of Chemistry: Cambridge, For example see: (a)(b) Conn, M. M.; Rebek, J. Jr., *Chem. Rev.* **1997**, *97*, 1647. (c) Rudkevich, D.M. *Bull. Chem. Soc. Jpn.*, **2002**, *75*, 393. (d) Rebek, J. Jr. *Chem. Commun.* **2000**, 637-643. (e) Jasat, A.; Sherman, J.C. *Chem. Rev.* **1999**, *99*, 931, 1994.
[2] MacGillivray, L. R.; Atwood, J. L. *Nature* **1997**, *389*, 469.
[3] Shivanyuk, A.; Friese, J. C.; Döring, S.; Rebek, Jr., J. *J. Org. Chem.* **2003**, *68*, 6489.
[4] MacGillivray, L. R.; Atwood, J. L. *Angew. Chem. Int. Ed. Eng.* **1999**, *38*, 1018.
[5] Shivanyuk, A.; Rebek, Jr., J. *J. Am. Chem. Soc.* **2003**, *125*, 3432.
[6] Avram, L.; Cohen, Y. *J. Am. Chem. Soc.* **2002**, *124*, 15148.
[7] Avram, L.; Cohen, Y. *Org. Lett.* **2003**, *5*, 1099.
[8] Avram, L.; Cohen, Y. *Org. Lett.* **2003**, *5*, 3329.
[9] Ugono, O.; Holman, K. T. *Chem. Commun.* **2006**, 2144.
[10] Gerkensmeier, T.; Iwanek, W.; Agena, C.; Frölich, R.; Kotila, S.; Näther, C.; Mattay, J. *Eur. J. Org. Chem.* **1999**, 2257.
[11] Atwood, J. L.; Barbour, L. J.; Jerga, A. *Chem. Commun.* **2001**, 2376.
[12] Atwood, J. L.; Barbour, L. J.; Jerga, A. *J. Supramol. Chem.* **2001**, *1*, 131.
[13] Cave, G. W. V.; Antesberger, J.; Barbour, L. J.; McKinlay, R. M.; Atwood, J. L. *Angew Chem. Int. Ed. Eng.* **2004**, *43*, 5263.
[14] Yamanake, M.; Shivanyuk, A.; Rebek, Jr., J. *J. Am. Chem. Soc.* **2004**, *126*, 2939.
[15] Dalgarno, S. J.; Tucker, S. A.; Bassil, D. B.; Atwood, J. L. *Science* **2005**, *309*, 2037.
[16] Dalgarno, S. J.; Bassil, D. B.; Tucker, S. A.; Atwood, J. L. *Angew Chem. Int. Ed.* **2006**, *45*, 7019.
[17] Dalgarno, S. J.; Antesberger, J.; McKinlay, R. M.; Atwood, J. L. *Chem. Eur. J.* **2007**, *13*, 8248.
[18] Bassil, D. B.; Dalgarno, S. J.; Cave, G. W. V.; Atwood, J. L.; Tucker, S. A. *J. Phys. Chem. B* **2007**, *111*, 9088.
[19] Barrett, E. S.; Dale, T. J.; Rebek, Jr., J. *J. Am. Chem. Soc.* **2007**, *129*, 3818.
[20] Hibbs, D. E.; Hursthouse, M. B.; Abdul Malik, K. M.; Adams, H.; Stirling, C. J. M.; Davis, F. *Acta Cryst.* **1998**, C54.
[21] Spek, A. L. *Acta Cryst.* **1990**, *A46*, C34.