JACS
JOURNAL OF THE AMERICAN CHEMICAL SOCIETY
Communication
pubs.acs.org/JACS

Introducing Defects into Metal-Seamed Nanocapsules Using Mixed Macrocycles

Drew A. Fowler,[†] Asanka S. Rathnayake,[†] Stuart Kennedy,[†] Harshita Kumari,[†] Christine M. Beavers,[‡] Simon J. Teat,[‡] and Jerry L. Atwood*,[†]

[†]Department of Chemistry, University of Missouri, 601 South College Avenue, Columbia, Missouri 65211, United States
[‡]Advanced Light Source, Berkeley Lab, 1 Cyclotron Road, MS6R2100, Berkeley, California 94720, United States

Supporting Information

ABSTRACT: The synthesis and single-crystal X-ray diffraction structure of a dimeric zinc-seamed nanocapsule using a mixed pyrogallol/resorcinol[4]arene are presented. The use of "mixed" macrocycles results in an incomplete seam of coordination bonds around the nanocapsule's typically octa-metalated belt. The self-assembly of the nanocapsule occurs such that the single resorcinol moiety of each macrocycle aligns transversely. This yields a hepta-metalated capsule where the defect occurs in such a way as to provide minimal disruption to the overall structure of the nanocapsule.

Introducing defects into pre-synthesized nanoassemblies is a challenging task for many researchers. Tailoring the structural framework, by virtue of introducing defects, often leads to interesting properties. For example, introducing defects into P(VDF-TrFE) copolymers causes a transition from a normal ferroelectric to a relaxor ferroelectric.[1] Similarly, the chemical sensitivity of graphene can be modulated by etching the edges or introducing defects on the basal plane.[1] Inspired by this phenomenon that allows one to modify chemical and physical properties of materials, we employed strategies to tailor our existing calix[4]arene-based nanocapsules.

The pyrogallol-based siblings of calix[4]arenes have been established as an interesting building block in supramolecular chemistry over the past decade. In 1999, Gerkensmeier et al. synthesized what has become more commonly referred to as pyrogallol[4]arenes.[2] Recrystallization in acetonitrile revealed that the macrocycles self-assemble into a "supermolecule" that consists of six pyrogallol[4]arene (PgC_x) molecules which seam together through 72 intermolecular hydrogen bonds, yielding a stable capsule with an internal volume of over 1500 Å^3.[2,3] The report of this large self-assembled nanocapsule incited interest in this member of the calixarene family, which has since been shown to be a diverse building block in supramolecular chemistry. PgC_x's are capable of forming hydrogen-bonded and metal-seamed nanocapsules, nanotubes, and various host−guest systems.[2−4] Of particular interest here are the metal-seamed nanocapsules formed by coordination of the upper-rim phenolic oxygens to metal ions.[5] Atwood and co-workers showed that the addition of a methanolic solution of $Cu(NO_3)_2$ to a methanolic solution of pyrogallol[4]arene results in the replacement of 48 hydrogen bonds with 24 Cu^{2+} ions to form a metal-seamed hexamer with 96 Cu−O bonds and with metrics similar to those of the hydrogen-bonded analogues.[5a] It was later determined that the addition of a zinc salt precursor, $[Zn^{II}(NO_3)_2\text{-pyridine}_4\cdot 6H_2O]$, to a methanolic solution of C-propyl pyrogallol[4]arene (PgC_3, **1**, Figure 1a) results in the formation of an octa-metalated dimeric nanocapsule (**2**, Figure 1b).[5b] The pyrogallol[4]arenes, and particularly the hexameric and dimeric nanocapsules, have since been studied as possible host molecules for a variety of guests.[4a,b,d,e,6] In 1997, MacGillivray et al. first demonstrated that resorcin[4]arenes ($ResC_x$'s) could self-assemble into hexameric capsules via hydrogen bonding.[7] Reports of coordination to metal ions by non-functionalized resorcinarenes, i.e., at the upper-rim

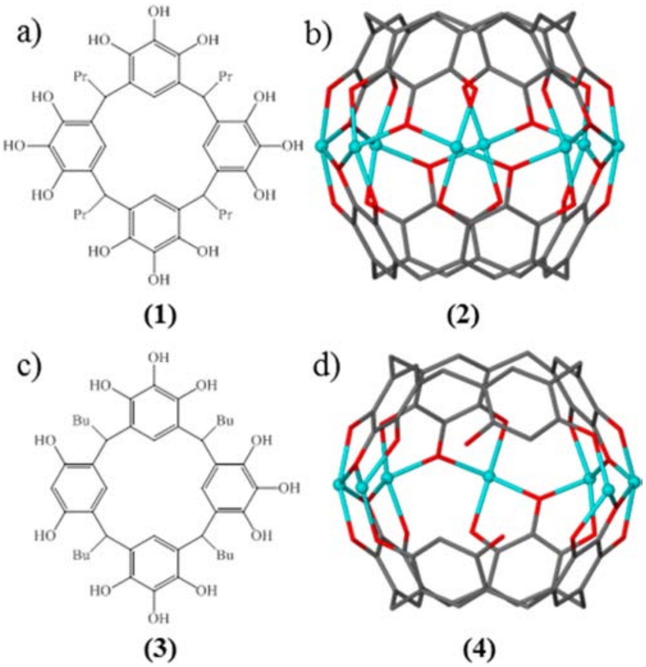

Figure 1. (a) Chemical structure of **1**. (b) Stick representation of **2**. Tail groups, axial ligands, and hydrogen atoms have been removed for clarity. (c) Chemical structure of **3**. (d) Stick representation of **4**. Tail groups, axial ligands, and hydrogen atoms have been removed for clarity.

Received: May 2, 2013
Published: August 2, 2013

phenolic or aromatic positions, are rare, and no nanocapsules have been formed in this way.[8] Continuing to determine new syntheses of nanocapsules through metal coordination and expanded control over known nanostructures is of significant interest.

Both cyclized PgC_x's and ResC_x's are synthesized via an acid-catalyzed reaction of the phenol and, typically, an aldehyde. The products formed when a mixture of resorcinol (Res) and pyrogallol (Pg) is used in the acid-catalyzed reaction with an aldehyde are referred to as "mixed macrocycles". Note that the mixed macrocyles are cyclized [4]arene products of pyrogallol and resorcinol in ratios of 2:2, 1:3, and 3:1. These mixed macrocycles have received little attention despite having also been shown to form interesting self-assembled structures, i.e., nanocapsules.[9] One of the major difficulties is separation of the mixed macrocyles (Pg:Res = 2:2, 1:3, and 3:1) and separation from the PgC_x's and ResC_x's. Herein, we report the use of a mixed macrocyle in the formation of a zinc-seamed dimeric nanocapsule. The so-formed dimer is synthesized following previously reported methods for the synthesis of octa-metalated dimeric pyrogallol[4]arene nanocapsules (Figure 1b).[5b] Here, however, the use of a solution containing mixed macrocycle (Pg:Res = 3:1) results in a hepta-metalated dimer seamed by coordination to seven Zn^{2+} ions.

The mixed macrocycle **3** (Figure 1c) was synthesized using a modification of the previously reported literature procedure.[9] Zinc(II) nitrate and pyridine were then added to a solution containing **3** in a 4:12:1 ratio, respectively (see Supporting Information for more details). The resulting solution was allowed to evaporate under ambient conditions, resulting in single,crystal X-ray diffraction quality crystals that provided the structure of a mixed macrocycle Zn-seamed dimeric nanocapsule (**4**, Figure 1d).

In all previously reported pyrogallol[4]arene-based octa-metalated dimeric capsules, the Pg moieties are off-center by 45°. Each M^{2+} ion is doubly coordinated by both PgC_x macrocycles and, typically, a single exterior ligand, leading to a distorted square planar geometry for each metal center. Each equatorial coordination site consists of Zn−O coordination bonds with the upper-rim phenolic oxygen atoms. The overall structure here is very similar to that of the previously reported octa-metalated PgC_x dimers; however, in this case the Res moieties of the two opposing mixed macrocycles align transversely in the same manner, yielding a hepta-metalated dimer. The absence of two oxygen atoms in the equatorial belt of the Pg:Res dimer results in the concomitant loss of one square planar binding site for the Zn^{2+} ions and hence a hepta-metalated dimeric nanocapsule. The loss of these two oxygen atoms in the coordination belt has also affected the two Zn^{2+} ions adjacent to the newly open position. For a typical PgC_x-based dimer the central hydroxyl of each pyrogallol moiety is deprotonated and coordinates to two adjacent Zn^{2+} ions. The absence of the oxygen atoms in **4** is accompanied by the loss of one phenolic O−Zn coordination bond to the two Zn^{2+} ions adjacent to the empty site. In place of this, each Zn^{2+} ion is η^2-coordinated by nitrate ions, yielding six-coordinate distorted octahedral metal centers (see Figure 2b). As mentioned earlier, the coordination geometry around the zinc centers in the previously reported Zn-seamed dimeric capsules are five-coordinate with a distorted square pyramidal geometry where there is a single exterior axial ligand. This is the first reported example of six-coordinate geometry around the Zn centers in a dimeric nanocapsule. Previously we have reported the dimers of Ni- and Co-seamed PgC_x-based nanocapsules with six-coordinate sites; however, in both cases the sixth coordination bond was formed through the coordination of an extra exterior pyridine ligand, not ionic counterions.[10] The addition of nitrate ions also reveals a disruption in the charge balance of the capsule. The presence of the two nitrate ions reveals that two other hydroxyl groups, likely adjacent to the Res units, are atypically protonated. In a PgC_x-based zinc dimer, we expect these hydroxyls to be deprotonated, as formation of the dimer typically leads to deprotonation of two hydroxyl groups on each pyrogallol moiety, balancing the charge with the eight Zn^{2+} cations.

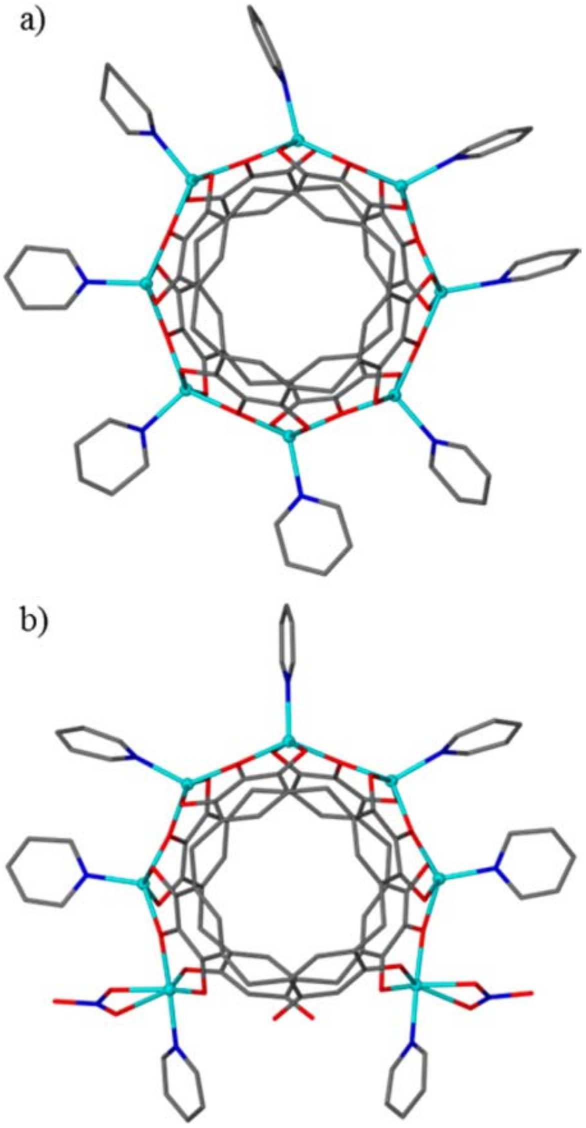

Figure 2. Top views of (a) **2** and (b) **4**. Tail groups and hydrogen atoms have been removed for clarity.

The aforementioned changes in the capsule framework have produced slight differences in the size and shape of the interior void of the capsule from the original octa-metalated PgC_3 dimer. The calculated volume for the void space of the interior of **2** and **4** is ca. 145 and 135 Å^3, respectively. The volume of each capsule was calculated using MSroll11 with a sphere radius of 1.5 Å. For **2** crystallographic data were obtained from the Cambridge Crystallographic Data Center (CCDC no. 628358). Figure 3 shows top and side views of **2** and **4** with the

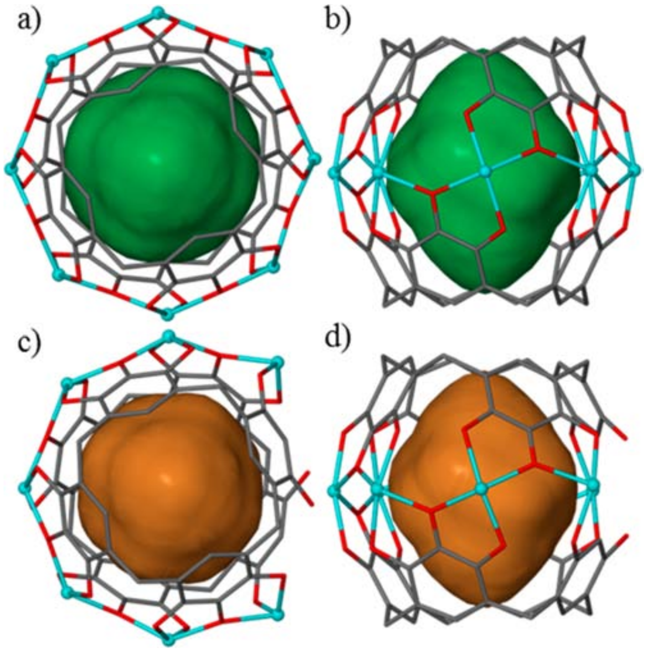

Figure 3. (a,b) Alternate views of **2** with the calculated void volume displayed in green. (c,d) Alternate views of **4** with the calculated void volume displayed in orange.

calculated void space shown in green and orange, respectively. It is interesting that the capsule assembled so that the loss of a single binding site has done little to distort the entirety of the capsule. The Zn−O bond lengths of the capsule have been essentially unaffected. The O−Zn−O bond angles around the five coordination sites that are not adjacent to the missing site have also been unaffected. This indicates not only that the capsule is robust but also that the changes in the two coordination sites adjacent to the vacant site have compensated for this loss and have done so in such a manner as to leave the capsule framework largely undisturbed.

This result illustrates the ability of self-assembly processes such as the formation of this dimer to also act as a mechanism for self-sorting. Due to the difficulty in separating the various possible mixed macrocycles, the product used in the synthesis of the dimeric capsule undoubtedly contained a variety of mixed macrocycles. Despite this, the 3:1 Pg:Res mixed macrocycles selectively formed the product capsule and crystallized as a single component. It is also apparent that the propensity of the pyrogallol[4]arenes to assemble with Zn^{2+} ions drives the formation of the zinc-seamed mixed macrocycle dimeric nanocapsule despite the loss of a binding site. The binding of Zn^{2+} ions has also been shown to overcome the large thermodynamic barrier of flipping chair conformer C-phenylpyrogallol[4]arene into the cone conformer so that formation of the zinc-seamed dimeric nanocapsule is possible.[12] While the loss of one binding site—one-eighth of the coordination bonds holding the nanocapsule together—has minimally affected the capsule framework, it will be interesting to determine how many defects can be introduced before capsule formation is prevented. Experiments are currently underway to elucidate if other mixed macrocycles (e.g., the two 2:2 ratio isomers) could also form dimeric capsules with larger defects.

In summary, we have demonstrated the formation of the first hepta-metalated zinc-seamed pyrogallol/resorcin[4]arene (3:1) mixed macrocycle dimeric nanoassembly in the solid state. The structural elucidation reveals the presence of nitrate ions on two zinc sites adjacent to the resorcinol units in each dimer. These are the first examples of octahedral zinc centers on a mixed macrocylic Pg:Res-based dimeric nanocapsule. Future studies will focus on deducing the robustness of this framework in solution and determining synthesis protocols using other metal centers, i.e., Co^{2+} and Ni^{2+}.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis and analysis details and CIF file. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic information can also be obtained from the Cambridge Crystallographic Data Center, CCDC no. 932255.

■ AUTHOR INFORMATION

Corresponding Author

atwoodj@missouri.edu

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the NSF for financial support of this work. The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

■ REFERENCES

(1) (a) Bauer, F. *Appl. Phys. A: Mater. Sci. Process.* **2012**, *107*, 567−573. (b) Vedala, H.; Sorescu, D. C.; Kotchey, G. P.; Star, A. *Nano Lett.* **2011**, *11*, 2342−2347.

(2) Gerkensmeier, T.; Iwanek, W.; Agena, C.; Frohlich, R.; Kotila, S.; Nather, C.; Mattay, J. *Eur. J. Org. Chem.* **1999**, 2257−2262.

(3) (a) Atwood, J. L.; Barbour, L. J.; Jerga, A. *J. Supramol. Chem.* **2001**, *1*, 131−134. (b) Atwood, J. L.; Barbour, L. J.; Jerga, A. *Chem.Commun.* **2001**, 2376−2377.

(4) (a) Dalgarno, S. J.; Power, N. P.; Atwood, J. L. *Coord. Chem. Rev.* **2008**, *252*, 825−841. (b) Jin, P.; Dalgarno, S. J.; Atwood, J. L. *Coord. Chem. Rev.* **2010**, *254*, 1760−1768. (c) Kulikov, O. V.; Daschbach, M. M.; Yamnitz, C. R.; Ratha, N.; Gokel, G. W. *Chem. Commun.* **2009**, 7497−7499. (d) Fowler, D. A.; Teat, S. J.; Baker, G. A.; Atwood, J. L. *Chem. Commun.* **2012**, *48*, 5262−5264. (e) Fowler, D. A.; Tian, J.; Barnes, C.; Teat, S. J.; Atwood, J. L. *CrystEngComm* **2011**, *13*, 1446−1449.

(5) (a) McKinlay, R. M.; Cave, G. W. V.; Atwood, J. L. *Proc. Natl. Acad. Sci. U.S.A.* **2005**, *102*, 5944−5948. (b) Power, N. P.; Dalgarno, S. J.; Atwood, J. L. *New J. Chem.* **2007**, *31*, 17−20.

(6) (a) Dalgarno, S. J.; Tucker, S. A.; Bassil, D. B.; Atwood, J. L. *Science* **2005**, *309*, 2037−2039. (b) Power, N. P.; Dalgarno, S. J.; Atwood, J. L. *Angew. Chem., Int. Ed.* **2007**, *46*, 8601−8604. (c) Jin, P.; Dalgarno, S. J.; Barnes, C. L.; Teat, S. J.; Atwood, J. L. *J. Am. Chem. Soc.* **2008**, *130*, 17262−17263. (d) Kline, K. K.; Fowler, D. A.; Tucker, S. A.; Atwood, J. L. *Chem.—Eur. J.* **2011**, *17*, 10848−10851.

(7) MacGillivray, L. R.; Atwood, J. L. *Nature* **1997**, *389*, 469−472.

(8) (a) Solari, E.; Lesueur, W.; Klose, A.; Schenk, K.; Floriani, C.; Chiesi-Villac, A.; Rizzoli, C. *Chem. Commun.* **1996**, 807−808. (b) Munakata, M.; Wu, L. P.; Kuroda-Sowa, T.; Maekawa, M.; Suenaga, Y.; Sugimoto, K.; Ino, I. *J. Chem. Soc., Dalton Trans.* **1999**, 373−378.

(9) (a) Atwood, J. L.; Barbour, L. J.; Jerga, A. *Proc. Natl. Acad. Sci. U.S.A.* **2002**, *99*, 4837−4841. (b) Maerz, A. K.; Fowler, D. A.; Mossine, A. V.; Mistry, M.; Kumari, H.; Barnes, C. L.; Deakyne, C. A.; Atwood, J. L. *New J. Chem.* **2011**, *35*, 784−787.

(10) Atwood, J. L.; Brechin, E. K.; Dalgarno, S. J.; Inglis, R.; Jones, L. F.; Mossine, A.; Paterson, M. J.; Power, N. P.; Teat, S. J. *Chem. Commun.* **2010**, *46*, 3484−3486.
(11) Connolly, M. L. *J. Mol. Graph.* **1993**, *11*, 139−141.
(12) Maerz, A. K.; Thomas, H. M.; Power, N. P.; Deakyne, C. A.; Atwood, J. L. *Chem. Commun.* **2010**, *46*, 1235−1237.