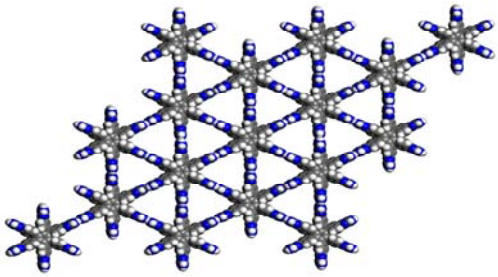
MS19 O1

Guidelines for Engineering Molecular Crystals James D. Wuest, *Département de Chimie, Université de Montréal, Montréal, Québec H3C 3J7, Canada.* E-mail: james.d.wuest@umontreal.ca

Keywords: supramolecular chemistry, crystal engineering, materials science

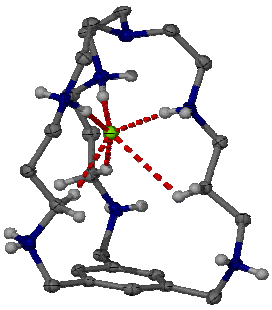
No reliable method exists for predicting the structure of molecular crystals in detail, and the relationship between the structure and properties of crystals remains poorly understood. Our limited knowledge of these subjects is an obstacle to progress in many areas of science and technology, and attempts to engineer crystals for specific applications have remained largely empirical activities. A promising strategy in crystal engineering uses molecules with arrays of well-oriented sticky sites that direct association according to reliable motifs, linked to cores that orient the sticky sites and introduce other desirable molecular properties. In favorable cases, the oriented sticky sites play a dominant role in association and place each molecule in a predetermined position relative to its neighbors, leading to the programmed construction of particular networks. The concepts that underlie this strategy are simple and qualitative, but they are powerful enough to lead consistently to the discovery of molecular crystals with properties not previously observed. The approach can also be used to direct 2D crystallization and to thereby nanopattern surfaces. Guidelines for engineering 2D and 3D molecular crystals will be illustrated by referring to recent published and unpublished work of the Wuest group.



MS19 O2

Anion Binding as a Trigger in Sensing and in Supramolecular Gels Jonathan W. Steed Chemistry Department, Durham University, Durham DH1 3LE, UK. E-mail: Jon.steed@durham.ac.uk

We have designed a number of anion-binding containers exhibiting dynamic conformational behaviour. These systems range from macrobicyclic cryptands (**1**) exhibiting conformational twisting to tripodal (**2**) and tetrapodal hosts (**3**) exhibiting significant flexibility of the pendant arms. The containers' dynamic properties are modulated by anion binding. Anion binding may also be used to modulate self-assembly and hence rheological properties in supramolecular gel phase systems. This lecture explores the scope and uses of this kind of fundamental process in preparing new supramolecular sensors and materials.



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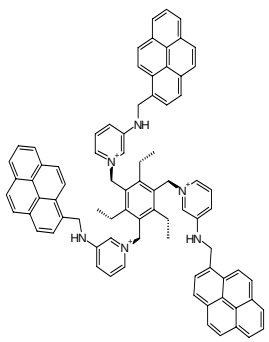

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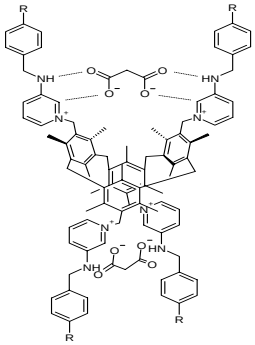

3

Gels: Stanley, C. E.; Clarke, N.; Anderson, K. M.; Lenthall, J. P.; Steed, J. W., *Chem. Commun.* 2006, 3199-3201.
Confomational Effects: Turner, D. R.; Paterson, M. J.; Steed, J. W., *J. Org. Chem.* 2006, *71*, 1598-1608.

MS19 O3

Structural characterization of α-cyclodextrin/lipid complexes. Delphine Gallois-Montbrun[a], Sylviane Lesieur[a], Sax Mason[b], François Bonhomme[a], Bernard Fraisse[c], Nouredine Ghermani[a,c], Thierry Prangé[d], , Geneviève Le Bas[a], [a]*UMR CNRS 8612, Université Paris Sud, Châtenay-Malabry, France.* [b]*ILL, Grenoble, France.* [c]*UMR CNRS 8580, ECP, Châtenay-Malabry, France.* [d]*UMR CNRS 8015, Université Paris V, France.*
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Keywords: cyclodextrins, supramolecular assemblies, X-ray neutron single-crystal diffraction

A systematic study of complexes formed from α-cyclodextrin and monoalkyl amphiphiles was performed as a model of intermolecular interactions between lipids and carbohydrates which are so important in biological structures and processes. We observed that depending on the crystallization conditions (temperature, hydration level) and the characteristics of the lipid (chain-length, nature of its polar head group) these complexes crystallize in different crystalline forms. Three different forms were identified : a triclinic P1 (pseudo-hexagonal) lattice (this packing mode was already observed for polyiodide complexes[1]), a hexagonal lattice with R3 symmetry and a monoclinic C2 lattice[2,3]. The last two structures had not been described before for α-cyclodextrin inclusion complexes. In all cases, the complexes crystallize in channel-type structures, where head to head dimers of α-cyclodextrin molecules are stacked like coins in a roll and the alkyl chain of the guest compound is embedded in the tubular cavity of the cyclodextrins.

Here we report the detailed crystal structure of the C2 form obtained for the complexes of α-cyclodextrin with decanol, undecanol and lauric acid. This crystal form is fully hydrated, with 25 water molecules at least for one dimer of α-cyclodextrin in the asymmetric unit. Water channels lie between the columns. The lipid molecule has an all-trans elongated conformation in the tubular cavity formed by the α-cyclodextrin dimer. The columnar structure is stabilized by hydrogen bonds but the interactions between the columns are different from those previously observed. Investigation of the hydrogen bonds is essential to understand how the water molecules influence the crystal packing and how the same complexes can crystallize in the C2 form as well as in the triclinic or hexagonal forms. X-ray diffraction measurements were made on the W32 beamline at LURE and on a Bruker SMART CCD area detector diffractometer at low temperature (100 K) in the "Ecole Centrale Paris". As these complexes yield suitable single crystals, neutron diffraction data were collected at 15 K on the new D19 instrument at ILL.

[1] Noltemeyer M., Saenger W., *J. Am. Chem. Soc*., 1980, 102(8), 2710-2722.
[2] Gallois-Montbrun D., Lesieur S., Ollivon M., Prangé T., Durand D., Le Bas G., *Proceeding of the 12th International Cyclodextrin Symposium*, Montpellier, France, May 16-19, 2004.
[3] Gallois-Montbrun D., Lesieur S., Prangé T., Durand D., Ollivon M., Le Bas G., *Acta Cryst*., 2005, A61, C288.

MS19 O4

Cooperation of Tandem Hotdog Domains in Acyl-CoA Thioesterase 7 Bostjan Kobe, Jade K. Forwood, Anil S. Thakur, Gregor Guncar, Mary Marfori, Dmitri Mouradov, Stuart Kellie, David A. Hume, Thomas Huber, Jennifer L. Martin, *School of Molecular and Microbial Sciences and Institute for Molecular Bioscience, University of Queensland, Brisbane, Australia*
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Keywords: enzyme, thioesterase, hotdog domain

We present a comprehensive structural and functional characterization of the enzyme acyl-CoA thioesterase 7 (Acot7). Acots catalyze the hydrolysis of fatty acyl-CoA to free fatty acid and coenzyme A, and thereby regulate lipid metabolism and cellular signalling. While prokaryotic homologues possess a single thioesterase domain, mammalian Acot7 contains a pair of domains in tandem. We determined the crystal structures of both the N- and C-terminal domains (1.8 and 2.5 Å resolution, respectively) of the mouse enzyme, and inferred the structure of the full-length enzyme using a combination of chemical crosslinking, mass spectrometry, and molecular modelling. The novel quaternary arrangement features a trimer of hotdog fold dimers. We show that both domains of Acot7 are required for activity, that only one of two possible active sites in the dimer is functional, and identify the catalytic residues through site-directed mutagenesis. We also designed an enzyme with higher activity than wild-type Acot7 by mutating the residues in the non-functional active site. We demonstrate the highest enzyme activity against arachidonoyl-CoA (a precursor of eicosanoids), suggesting a role in inflammatory processes. Together, our results provide a foundation to relate the molecular and cellular functions of Acot7 in mammalian tissues.

MS19 O5

Crystal Engineering of Propargylic Alcohols-New Developments and Applications Marilise A. Hyacinth,[a] Ashley R. Borges,[b] Michelle Lum,[b] Maksymilian Chruszcz,[c] Kevin L. Caran,[b] Lin Pu,[a] Michal Sabat[a]
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Keywords: supramolecular chemistry, crystal engineering, cooperative phenomena

Propargylic alcohols, especially their diaryl-substituted chiral derivatives, possess functional groups that make these alcohols well-suited for the formation of supramolecular assemblies. Of special interest are cyclic hexameric systems occurring as a result of the cooperation between three major intermolecular forces: O-H…O hydrogen bonding, C-H…F-C hydrogen bonding involving organic fluorine atoms, and π–π
stacking interactions between the pentafluorophenyl and phenyl rings [1]. These hexagonal assemblies feature channels and cavities that can be used in several applications. Structural chemistry and possible applications of propargylic alcohols in gelation and as gas storage containers will be discussed.

[1]Hyacinth M., Chruszcz M., Lee K.S., Sabat M., Gao G., Pu, L. *Angew.Chem. Int .Ed.* 2006, ***45***. 5538.