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Acta Cryst. (2011) A67, C65**Phasing of an unpredicted palindromic coiled-coil motif**

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Coiled-coil (CC) motifs are simple folds consisting of two to five amphipathic helices that wind around each other to form a supercoil. The sequences of the integrating helices contain repeats of seven- or eleven-residues, often biased in composition [1]. CC motifs are amongst the most ubiquitous folds found in proteins, where they have roles in mediating self- and hetero-association, folding and molecular recognition. The importance of CC folds is further enhanced by the fact that, through the design of synthetic sequences, their properties are exploited in the development of self-assembled and bioactive polymeric materials.

Despite the apparent simplicity of CC architectures, their crystallographic analysis remains a challenge. Factors contributing to this are: *i*) their filamentous nature and individualized helical twist that confers them a varying degree of long-range order and complicates molecular replacement approaches through cumulative deviations along the molecular axis of the superhelix; *ii*) the formation of idiosyncratic crystal lattices resulting from their acutely anisometric molecular shape; *iii*) the repetitive nature of their sequences that are often deficient in methionine and cysteine residues that could assist MAD phasing; and, most importantly, *iv*) the acute mutability of their self-association properties that are highly dependent on medium conditions and exact sequence content causing drastic and unpredictable changes of their overall conformation and troubling the interpretation of electron density maps. These factors often act in combination to trouble the structural elucidation of this important class of proteins.

Recently, we have elucidated the crystal structure of a core CC fragment, CC₇, from a muscle-specific E3 ubiquitin ligase involved in the response of the muscle tissue to mechanical stimulation [2]. The structure reveals a novel, tetrameric, off-registry, palindromic arrangement not previously observed in this fold class. In this, two parallel dimeric CC (each resembling a pair of open scissors) intertwine into each other through their C-terminal ends to form an inverted tetramer, where the shared tetrameric fraction contains an aromatic hydrophobic core, rarely found in CC motifs. Such inverted arrangement is possible because the parallel chains that compose each of the CC dimers are offset by exactly one heptad repeat at the sequence level.

Crystals of CC₇ were obtained in three distinct crystal habits, all arising from closely related mother liquor condition: needles (P2₁2₁2₁), plates (P2₁) and bipyramides (apparent symmetry P4₁22/P4₃22 arising from merohedral twinning with twinning fraction >0.4). Diffraction data were obtained from all symmetries, with the maximal resolution collected being 2.1 Å for P2₁ plate crystals. Attempts at phasing using MR, MIRAS or MAD on cluster derivatives proved unproductive. Finally, the fragment-based MR approach implemented in Arcimboldo [3] was successful in overcoming phasing problems and providing an initial, workable model. In this contribution, we will offer an analysis of the factors that troubled the elucidation of this CC motif and will place this in the context of persistent difficulties with this protein fold.

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Keywords: coiled-coil motif, fragment-based phasing

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Acta Cryst. (2011) A67, C65**S-SAD phasing of protein o-fucosyltransferase-1at a resolution of 2.6 Å in the monoclinic space group C2**

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Protein O-fucosylation is an essential post-translational modification, involved in embryonic development, adult tissue homeostasis and folding of proteins. Two different enzymes are responsible for this modification, Protein O-fucosyltransferase 1 and 2 (POFUT1 and POFUT2, respectively). Both enzymes have been characterized biologically and enzymatically but nothing is known at molecular level. A catalytically functional POFUT1 (356 residues) in an apo-form has been crystallized in the monoclinic space group C2. The crystals have been notoriously difficult to derivatise and up to 30 different heavy atoms were tried without any significant anomalous signal. Two data sets were taken in order to solve the structure: a highly redundant data set collected in-house on a Bruker microsource (with a Kappa goniometer and an Axiom detector) to 2.6 Å resolution; and a high resolution data set collected at a synchrotron source (collected at BM16 in the ESRF at wavelength of 0.99 Å) to 1.55 Å resolution. The determination of the structure by Sulphur – Single Anomalous Diffraction (S-SAD) phasing has proven to be challenging at two stages: the determination of the substructure and the phase extension to high resolution. The successful procedure for structure determination by S-SAD will be presented as well the application of this procedure to a few additional novel and test proteins.

Keywords: s-sad, pofut1, phasing

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Acta Cryst. (2011) A67, C65-C66**Molecular tectonics: Design of enantiomerically pure tubular crystals**

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The preparation of chiral porous solids is of interest for chiral transformation. However, the design of crystalline materials displaying enantiomerically pure cavities or channels still remains a challenge. A possible strategy for the generation of such materials may be based on crystals composed of helical strands provided that the dimension of the helical space can be controlled and its handedness imposed. Several examples of helical metal-organic frameworks have been reported. Although the majority of infinite helical architectures described is composed of 1-D networks, examples of 2-D and 3-D helical networks have been also published.

Using the molecular tectonics approach [1] coordination networks [2] may be obtained by combining metallatectons, i.e. metal centres or metal complexes offering at least two free coordination sites oriented in a divergent manner with organic coordinating tectons possessing at least two divergently oriented ligating sites. For the design of helical coordination networks, one may combine ZnSiF₆, forming in the presence of organic tectons an infinite pillar by bridging consecutive zinc cations by SiF₆²⁻, anions through Zn-F bonds [3].

The formation of enantiomerically pure 2-D helical coordination networks based on combinations of rigid enantiomerically pure bisonodentate tectons with ZnSiF₆ will be presented and discussed.

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Keywords: crystallochemistry, helical, supramolecular

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Fluorocarbon control of crystal structures: NLO materials and supramolecular LCs

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Perfluorocarbon moieties are endowed with unique and useful aggregation features [1]. Perfluoroalkyl residues have a very poor affinity for both polar and non-polar moieties and this accounts for their tendency to form a separate phase in the liquid and to segregate into lamellar domains in the solid. Perfluoroaryl residues have a quadrupolar moment opposite to that of their hydrocarbon analogues and this accounts for the strong $\pi\cdots\pi$ staking interactions exemplified in the columns formed by hexafluorobenzene when interacting with benzene.

Electron distribution around covalent bonded halogens is highly asymmetric resulting in an electron rich belt perpendicular to the covalent bond and an electron poor cap (σ -hole) on its elongation. Both electron-poor and electron-rich sites can thus interact attractively with halogen derivatives and this occurs perpendicular to and on the elongation of the covalent bond, respectively. The interaction involving halogens and electron-rich sites is known as halogen bonding [2]. Due to the strong electron withdrawing properties of perfluorocarbon residues, the σ -hole on the heavier halogen in haloperfluorocarbons is particularly positive and the halogen bonding given by haloperfluorocarbons is a robust supramolecular synthon.

In this communication it will be described how the hierarchical organization of molecular components into heteromeric solid architectures can be designed and realized through a cooperative interplay of the strong halogen bonding given by heavier halogen of iodo- and bromoperfluorocarbons and the unique aggregation features of their perfluorocarbon skeleton. The correlation between the crystal structure of the supramolecular materials thus obtained and their functional properties will be discussed. For instance, it will be shown how the halogen bonding drives the formation of dimers and trimers when alkoxystilbazoles interact with mono- and diiodoperfluoroalkanes and -arenes. These oligomers further organize into 2D and 3D architectures under control of the segregation of perfluoroalkyl chains or the $\pi\cdots\pi$ staking interactions of the perfluoroaromatic residues [3]. While the single pure molecular components do not show any mesomorphic property, the obtained heteromeric architectures described above do show liquid crystalline properties which disappear on architecture disruption. Similar phenomena will be described for non-linear optical materials.

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Unprecedented chemical and thermal stability of MOFs with exposed metal Sites

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Natural and synthetic zeolites find worldwide applications in strategic industrial fields as adsorbents, desiccants and heterogeneous catalysts, due to their remarkable robustness and moderate surface area. Yet, their performances are somehow hampered by their framework stiffness, whose features cannot be easily tuned by self-assembly approaches. Metal-Organic Frameworks (MOFs) represent an authentic breakthrough in this context: a sagacious selection of metal nodes and organic spacers potentially allows the modulation of their key chemico-physical properties- surface area, pore size and decoration, guest affinity and catalytic activity. Nevertheless, MOFs current thermal and chemical stability cannot compete with that of zeolites, especially if *O*-donor spacers are adopted.

Following our long term tradition, this contribution describes how the *N*-donor ligand *sym*-tris(pyrazol-4-yl)benzene (H_3BTP) can be successfully coupled to transition metal ions to isolate MOFs of $M_3(BTP)_2$ formula (1_M , $M = Ni, Cu$; 2_M , $M = Zn, Co$).

As disclosed by XRPD, 1_M exhibit a sodalite-like framework with accessible metal sites, while 2_M possess a 3D architecture with hydrophobic surfaces and narrower channels. Desolvation of 1_M and 2_M reveals their permanent (micro)porosity, confirmed by BET surface areas in the range 930-1860 m²/g. Thermo-gravimetric and thermo-diffractometric analyses demonstrate the exceptional thermal stability of these materials, peaking to 510 °C in the case of 2_{Zn} . While 1_{Cu} and $2_{Co,Zn}$ undergo phase transitions to non porous 3D frameworks upon heating in boiling water, 1_{Ni} possesses an unprecedented robustness. Not only it is stable to heating in air up to 430 °C; more strikingly, it faces a number of harsh conditions mimicking those of industrial processes: as shown by juxtaposing XRPD and N_2 adsorption measurements, 1_{Ni} stands boiling water and boiling acidic or basic solutions for prolonged periods of time, preserving its structural features, crystallinity and surface area.

This stability definitely parallels that of zeolites. Combined with the presence of exposed metal sites- the preferred binding sites for adsorbates- it increases the potential of 1_{Ni} in key applications currently exploiting conventional porous inorganics.

Keywords: MOFs, XRPD, chemical inertness

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From molecules, via supramolecular assembly, to tunable physical properties

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