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Acta Cryst. (2008). A64, C104**Porous coordination polymers having guest accessible functional organic sites**

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Porous coordination polymers (PCPs) or Metal-Organic Frameworks (MOFs) have attracted much attention due to scientific interest in the creation of nanometer-sized spaces and for their potential application in molecular sieves, gas storage and heterogeneous catalysis. Besides porosity, stability and pore shape and size, pore surface functionalization and framework flexibility are currently considered to be one of the key factors for the next generation of PCPs. Some porous coordination polymers have dynamic nature and they can be developed as a unique class of materials such as highly selective gas sensors or gas separation compounds, which could not be obtained in a rigid porous material. To functionalize the channel surface two types of strategies are used; introduction of organic groups to provide guest-accessible functional organic sites (FOSs) and immobilization of coordinatively unsaturated (open) metal sites (OMSs). The use of OMS for Lewis acid catalysis and specific gas adsorption has been explored significantly in PCP but less attention has been devoted to the study of FOS, despite their importance. This is because of the difficulty of producing guest-accessible FOS on the pore surface, as organic groups tend to coordinate metal ions via a self-assembly process, resulting in frameworks in which FOSs are completely blocked. In most cases the framework flexibility results from coordination bonds, H-bonds, π -electron stacking and van der Waals interactions. In this context, we have succeeded in obtaining several PCPs having FOSs and reported important properties characteristic of their organic functionality and flexibility.

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Keywords: porous coordination polymers, functional organic sites, porous properties

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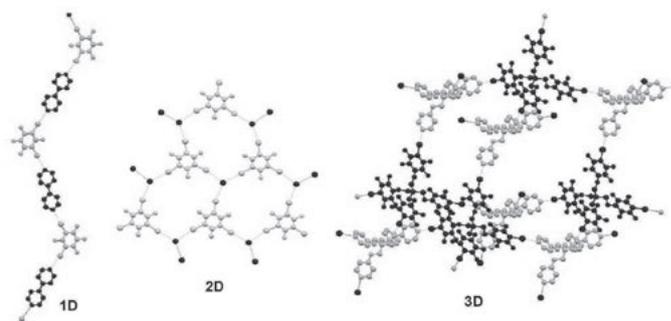
Acta Cryst. (2008). A64, C104**A molecular Legoland through halogen bonding**Giuseppe Resnati^{1,2}, Pierangelo Metrangolo¹, Tullio Pilati², Giancarlo Terraneo¹

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The halogen bonding (XB) is defined as any noncovalent interaction involving halogens as electrophilic species [1]. It will be shown how the XB is a strong, reliable, and powerful interaction that can be successfully employed as a general protocol to design and synthesize numerous tectons and to construct several supramolecular synthons. Heuristic principles will be presented to engineer complex and functional architectures topologies proving how the topology of a supramolecular architecture can be anticipated from the structure

and geometry of the starting tectons. A variety of 1D, 2D, and 3D nets will be presented. A zig-zag chain, an honeycomb net and an adamantanoid net are reported below as prototype examples of 1D, 2D, and 3D architectures, respectively.

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Keywords: halogen bonding, anion coordination, supramolecular chemistry

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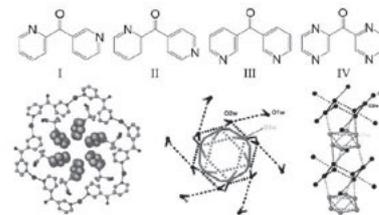
Acta Cryst. (2008). A64, C104-105**Coordination network assembly with carbonyl-bridged nitrogen heterocycles**

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Metal complexes of 2-pyridinyl-3-pyridinylmethanone **I** exhibit single-strand helical chain structures with adjustable pitch length,¹ including a pair of silver(I) conformational polymorphs in which the 2₁ screw helices are stacked alternately to form a racemate while the 4₁ screw helices are assembled to generate a conglomerate.² With 2-pyridinyl-4-pyridinylmethanone **II**, an ordered sequence of coordinating ability of a series of polyatomic monoanions is established on the basis of structural parameters of its disilver(I) metallacycles: NO₂ \approx HCO₂ > CF₃CO₂ > ClO₃ > NO₃ > CF₃SO₂ > ClO₄ > BF₄ > PF₆.³ Di-3-pyridinylmethanone **III** yields a series of iso-structural porous MOFs with size-controllable nano-scaled channels, and selective guest accommodation is realized through synthetic control of the channel size. Di-2-pyrazinylmethanone **IV** affords a nano-scaled metal-organic coordination tube generated by rolling up a (4,4) net, and another host MOF in which cyclohexane-like and twisted triangular prismatic water clusters are linked alternately to form a column that binds to the channel wall via additional guest water molecules.

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Keywords: coordination crystal chemistry, carbonyl-bridged nitrogen heterocycle, supramolecular assemblies

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Molecular recognition and self-organization of three-way DNA junctions and supramolecular helicates

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Helicates are mixed metallic-organic structures with three-fold symmetry that exhibit high affinity for DNA. We have crystallized several helicates in complex with palindromic DNA oligomers and solved their structures. The analysis reveals a DNA three-way junction (3WJ), where the helicate occupies the central cavity of the junction. The shape complementarity between both is extraordinary. We describe the recognition of the three-way junction by the helicate in detail. The interactions in the complex consist of pi-pi interactions between the DNA bases and the central aromatic region of the helicate and electrostatic interactions between the Fe(II) centres and the phosphate backbone. In addition, we describe the macroscopic features of the crystal structures that we have determined. The crystals are porous materials that are formed as a result of the incorporation of additional helicate molecules at the extremes of the DNA arms. A three-dimensional, chicken wire-like network is formed through alternation of 3WJ's of different topologies. The chirality of some of the helicate centres modulates the overall topology of the crystal network. We suggest that helicate-bound 3WJ's may constitute a valuable addition to the existing tools and structural modules for the design and assembly of DNA-based nanomaterials.

Keywords: self-organization, nanomaterials, single crystal

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Analysis of residual stresses induced by surface processing: Angle vs. energy dispersive diffraction

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Mechanical, thermal and/or chemical surface processing as well as coating introduce residual stresses in the near-surface zone of technical parts, which may influence the material properties significantly. Among the methods for residual stress analysis diffraction techniques take up a unique position, because they allow for non-destructive and phase-selective evaluation of stress distributions from the surface down to the volume of the material. Compared to X-ray stress analysis (XSA) performed in the angle-dispersive (AD) mode of diffraction which has a very long tradition, energy-dispersive (ED) stress analysis is a comparatively young

method. The advantages of ED synchrotron diffraction are the short measuring times allowing for fast in-situ studies and the multitude of diffraction lines recorded in each spectrum, which contain additional information for depth-resolved XSA. The absolute resolution of ED experiments being mainly controlled by the detector system, however, is lower than that attainable by AD methods. Assets and drawbacks of AD and ED XSA techniques are discussed with respect to their ability to detect non-uniform residual stress fields in the near surface region of polycrystalline materials. It will be shown that there is no universal method which solves all problems related to X-ray stress analysis at once. The decisive parameter which adjudicates on the applicability of a method to a special problem is the ratio of the sampled volume to the steepness of the expected stress gradient. This general rule applies for all methods independently of the diffraction mode (AD or ED) and the way used for depth resolution (Real- or Laplace space approach). To succeed in case of complex systems the use of complementary methods is recommended.

Keywords: residual stress analysis, synchrotron radiation, X-ray diffraction techniques

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X-ray line profile analysis for the characterization of nanostructured materials

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For the characterisation of micro- and nanostructures in bulk as well as in loose powder materials the X-ray Line Profile Analysis (XPA) has proven to be an excellent method. According to the kinematical theory of scattering, diffraction profiles are the convolution of the size and distortion profiles [1]. Size broadened profiles can be described by assuming (i) a size distribution function and (ii) the shape of crystallites or of coherently scattering domains. From a log-normal size distribution function $f(x)$, which is given by the median m and the variance σ , weighted average crystallite sizes can be evaluated [2]. In the case of strain broadening the major task is the description of the mean square strain. Phenomenological and also dislocation models have been designed to describe the diffraction vector dependence of the mean square strain [3, 4]. This way the density and distribution of dislocations can be determined even for very high densities. Further improvements enable the verification of planar faults such as stacking and twin faults in parallel to the hitherto parameters. A whole profile fitting procedure, previously worked out for determining the dislocation structure and crystallite size distributions, is extended for planar fault by including these parameter into the evaluation algorithm [5]. The universal character of the method are documented by several examples.

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Keywords: X-ray diffraction, line profile analysis, microstructure