

MS.59.2

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.

References

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

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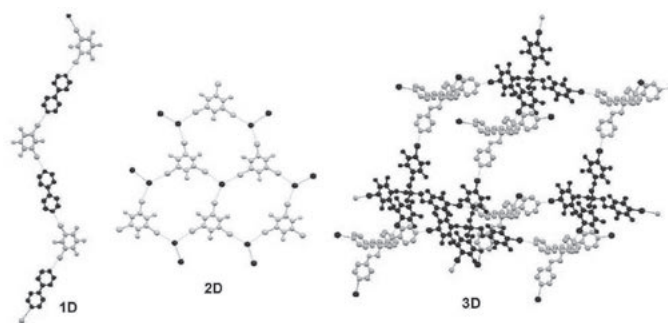
Acta Cryst. (2008). A64, C104**A molecular Legoland through halogen bonding**Giuseppe Resnati^{1,2}, Pierangelo Metrangolo¹, Tullio Pilati², Giancarlo Terraneo¹

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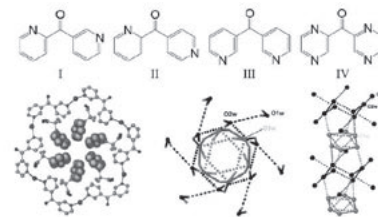
Acta Cryst. (2008). A64, C104-105**Coordination network assembly with carbonyl-bridged nitrogen heterocycles**

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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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