Porous Solids by Design: [Zn(4,4'-bpy)$_2$(SiF$_6$)$_2$]$_n$ x DMF, A Single Framework Octahedral Coordination Polymer with Large Square Channels**

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The concept of crystal engineering has in recent years provided numerous examples of rationally designed one- (1D), two- (2D), and three-dimensional (3D) polymeric structures. Of particular potential interest to inclusion chemistry are 2D and 3D coordination polymers which, in principle at least, can be designed to have very specific pore size and type. In such a context, there already exist examples of 2D square and hexagonal/honeycomb grids generated from metal ions in square-planar or trigonal environments, respectively, coordinated to linear bifunctional ligands such as 4,4'-bipyridine or pyrazines. Furthermore, 3D diamondoid coordination polymers based upon tetrahedral or $S_8$ coordination environments have been generated by either coordinate covalent bonds or hydrogen bonding. However, given the ubiquity of octahedral metal environments, it is somewhat surprising that simple 3D octahedral polymers remain largely unexplored. Indeed, to our knowledge $\mu$-cyano polymers such as Fe$_{6n}$[Fe$^6$(CN)$_6$,$n$], Prussian Blue, and triply interpenetrated $[\text{Cd}(\text{4,4'-bpy})]_6[\text{Pd}(\text{CN})_4]$ represent the only examples of such structures. Recently a coordination polymer from silver ions and pyrazine was synthesized and structurally characterized. In this contribution we detail a potentially general strategy for generation of such polymers.

Scheme 1 illustrates how cross-linking of cationic square grids with suitable linear bifunctional anionic ligands could in principle afford neutral octahedral polymers with porosity controlled by the length, volume, and chemical type of the spacer ligands. Compound 1 polymerizes to afford square grids with sides of length 11.43 Å. Unfortunately, unlike [Cd(4,4'-bpy)$_2$][NO$_3$)$_2$, which eschews interpenetration, the large

$$[\text{Zn}(4,4\text{-bpy})_2\text{H}_2\text{O})_2\text{SiF}_6]_n$$

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cavity in 1 is self-included with hexafluorosilicate ions, which are bound through hydrogen bonds to water molecules, and a second independent [Zn(4,4'-bpy)$_2$] square grid. It occurred to us that the anhydrous form of 1 could be expected to fit the hypothetical network proposed in Scheme 1 since SiF$_6^{2-}$ ions are capable of acting as a linear bridge between transition metal moieties such as [Co(N-vinylimidazole)$_2$]$^{2+}$ and [Cu(5-phenylpyrazole)$_2$$^{2+}$. We therefore synthesized the anhydrous form of 1, namely 2, and herein report its remarkable crystal structure.

$$[\text{Zn}(4,4\text{-bpy})_2]\text{SiF}_6$$

2

The compound 2 x DMF crystallizes in the tetragonal space group $P4/mmm$ with $Z = 1$ and therefore sits around a crystallographic $4/mmm$ position. This alone is quite a remarkable feature since the space group symmetry manifests the maximum $D_4h$ point group symmetry that can be sustained by an MX$_2$ species. The space group symmetry and cell dimensions are therefore entirely rational or indeed predictable based upon the chemical composition of 2. However, an even more remarkable feature of 2 is that it eschews interpenetration and therefore, as Figure 1 reveals, large square channels are generated parallel
to the crystallographic c axis. As would be anticipated, these channels have essentially the same dimensions as those seen in the interpenetrated dihydrate, 11.3959(11) Å × 11.3959(11) Å, and the effective size of their pores (8 × 8 Å) compares well with the pore sizes of "large zeolites." The volume of the channels is about 50% of the total volume. The μ-SiF$_6^{2-}$ ions form perfectly linear bridges, and the Zn–F distances of 2.082(10) Å, are shorter than the M–F distances encountered in previous studies concerning μ-SiF$_6^{2-}$ units. The Zn–N distances (2.157(8) Å) are also within the expected range. That there is no interpenetration in 2 can possibly be attributed to the orientation of the 4,4'-bipyridine ligands (Fig. 2). These ligands are disposed such that the pyridine moieties are almost coplanar with each other and the crystallographic ac and bc planes, respectively. The former is quite unusual since such a conformation for 4,4'-bipyridine is sterically disfavored, and the latter is important since it precludes porosity and interpenetration along either the crystallographic a or b directions. We attribute this conformation and orientation to the existence of C-H···F hydrogen bonds between α-C-H hydrogen atoms and fluorine atoms of the SiF$_6^{2-}$ ions.

Although 2 does not compare to other zeolitic solids in terms of stability in aqueous environments or potential catalytic activity, we consider the following features of this study to be particularly salient: 1) Compound 2 represents, to our knowledge, the first example of a neutral octahedral coordination polymer and, therefore, there are no counterions occupying the microchannels. 2) Compound 2 is inherently modular and all three components are in principle interchangeable. 3) The dimensions of the channels are precisely what one would expect based upon the geometric features of the three components. 4) The channels in 2 are hydrophobic. 5) The space group of 2 can be regarded as a direct manifestation of the point group symmetry (i.e. the structure of 2 can be regarded as having been "crystal engineered" even from the perspective of space group symmetry). We consider 2 to be the prototype of a potentially wide range of porous octahedral structures and are actively investigating the generality of this class of solid and its ability to incorporate medium-sized hydrophobic molecules of cross-sectional area consistent with the dimensions observed in 2.

**Experimental Procedure**

2: [Zn(OH)$_3$]$_{2n}$SiF$_6$ (0.31 g, 1.0 mmol) was suspended in 1,4-dioxane (25 mL) and benzene (25 mL), and the mixture was heated to reflux in a Dean– Stark apparatus at aerotropically remove the water. The powder of ZnSiF$_6$ thus formed was dissolved by adding DMF (25 mL) to the above mixture. Most of the benzene and 1,4-dioxane were removed by rotevaporation at this point. The mixture was cooled and a solution of 4,4'-bipyridine (0.31 g, 3.0 mmol) in 1,4-dioxiane (10 mL) was added. The solution was heated to reflux for 30 min. The resulting pale gold yellow solution was cooled and allowed to stand at room temperature for 12 h. This afforded colorless crystals of 2 (0.45 g). Crystals appear to lose solvent and crystallinity within minutes if left to stand exposed to a solvent-free atmosphere and dissolve readily in water. IR (nujol mull): 7 = 2985, 2872 (bpy·H); 1668 (DMF C≡O); 1609, 1457, 1379, 1268, 1086, 833, 770, 635 cm$^{-1}$.

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**References**


[5] For the purpose of this study, we define an octahedral polymer as an infinite 3D framework that is sustained by octahedral metal centers that are cross-linked by linear bifunctional ligands. We exclude infinite frameworks which consist of both octahedral metal centers and those with a different coordination geometry.


[12] X-ray structure of 2·DMF: C$_{27}$H$_{12}$F$_{6}$N$_{2}$SiZn·DMF, colorless cubes (0.30 × 0.30 × 0.40 mm), tetragonal, space group P4/mmm, with a = 11.3959(11) Å, c = 7.675(6) Å, V = 997.05(15) Å$^3$, Z = 1, μ = 0.87 Mgm$^{-1}$ (octahedral polymer only) or 1.27 Mgm$^{-1}$ (including disordered solvent). Data were collected on an Enraf-Nonius CAD-4 diffractometer with Mo K$_x$ radiation (λ = 0.71073 Å). Non-hydrogen atoms of the coordination polymer were refined with anisotropic thermal parameters. The solvent molecules were observed to be disordered in a manner that could not be readily resolved. Solvent atoms were therefore treated as carbon atoms and refined with fixed isotropic thermal parameters and variable site occupancy. Values of R = 0.063 and R$_{w}$ = 0.061 were obtained for 426 out of 569 reflections with I ≥ 2σ(I) and 48 parameters. Hydrogen atoms of the 4,4'-bipyridine moieties were placed in calculated positions with d$_{C-H}$ = 1.00 Å. Further details of the crystal structure investigation may be obtained from the Director of the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK on quoting the full journal citation.


Rational Design of Orthogonal Receptor–Ligand Combinations**
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Signal transduction in cells occurs primarily by two mechanisms, one involving allostery and the other involving proximity.[1] The role of ligand-induced allosteric change in proteins has been appreciated for many years, and has led to the synthesis of numerous molecules that either promote or inhibit the allosteric change required to transduce information in cells. More recently, cell biological studies have illuminated the role of regulated protein dimerization or oligomerization as a means of information transfer. Such an event can promote a proximal relationship between an enzyme and its substrate or a receptor and its ligand, thereby facilitating a molecular interaction leading to a signaling event. Examples include the dimerization of growth factor receptors,[2] oligomerization of antigen receptors,[3] and dimerization of transcription factors.[4] These insights have created new opportunities for chemists to synthesize molecules with two protein-binding surfaces and thereby to induce protein association. Such chemical inducers of dimerization (CIDs) have the potential to activate many cellular processes, including ones of biological and medical significance. We recently described a method to inducibly control the association of proteins in cells.[5, 6] This was accomplished through the expression of chimeric proteins in mammalian cells, consisting of a dimerization domain fused to a protein or protein domain of interest. By treating these cells with a synthetic, cell-permeable CID that binds to the dimerization domain, self-association of the protein occurs and a signal is transmitted (Fig. 1).

Although in theory many receptor–ligand systems can be used, the immunophilins FKBP12 and cyclophilin A (CyP) and their ligands FK506 and cyclosporin A (CsA) were selected for this purpose. The ligands are cell permeable and can be modified synthetically in a rational way to remove their intrinsic immunosuppressive and toxic properties. This requires modifying the calcineurin-binding (but not the immunophilin-binding) domain of these naturally occurring CIDs. FKBP12 and CyP bind their ligands with high affinity (K_D = 0.5 nM and 5 nM, respectively), are monomeric, have no discernible effect when expressed in cells, and their small size (12 kDa and 18 kDa, respectively) facilitates the incorporation of their cDNA into expression vectors. A shortcoming is that the natural immunophilins are expressed at high levels in many cells and can therefore diminish the potency of CID ligands toward immunophilin fusion proteins by forming nonproductive receptor–ligand complexes (Fig. 2a). The resulting loss in specificity is expected to be especially troublesome in whole organisms, where cells expressing the fusion proteins may be relatively few in number, thus magnifying the buffering effect of natural immunophilins.

To solve this problem we envisioned the creation of new receptor–ligand pairs with interacting surfaces that ensure a high degree of specificity. Immunophilin ligands were designed to contain substituents that clash sterically with amino acid sidechains in the immunophilin receptor, thereby abolishing their interaction with endogenous immunophilins. Compensatory mutations in the receptor were sought that would remove the offending interaction, thereby creating a unique receptor that would be used as a dimerization domain (Fig. 2b). Herein, we report the implementation of this strategy using CyP-CsA as a test system. In addition to providing an effective solution to the specific research problem outlined above, we propose that the creation of new receptor–ligand pairs in this manner will result in new experimental systems for testing our understanding of molecular recognition involving protein receptors.