Structural manipulation of hydrogen-bonded networks – inclusion of metal centres and chromophores and response to loss of symmetry,

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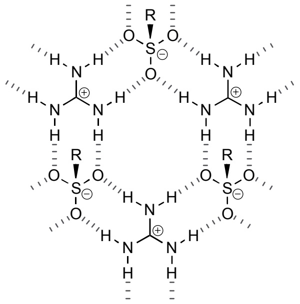
Crystal engineering can be defined as the synthesis of solid-state structures with predictable structures and properties. The two most commonly employed strategies for this make use of coordination bonds and hydrogen bonds. One of the most reliable hydrogen bond networks is the hexagonal sheet structure shown below which is adopted by guanidinium sulfonates, $[C(NH_2)_3][O_3SR]$ [1].



The guanidinium sulfonate (GS) structure is tolerant to wide changes in the steric demands of the substituent R, and GS layers can be bridged between using disulfonates. In this presentation the inclusion of both metal centres and chromophores into GS networks is discussed. Metal centres can be included through use of sulfonated phosphine ligands such as $PPh_2(C_6H_4SO_3$-*m*) [2, 3], though in such cases the strong N–H···O hydrogen bonds of the GS array can be compromised by weaker interactions involving the phenyl rings. Chromophores can be included into GS networks through use of sulfonated indicators such as methyl orange, $Na[O_3SC_6H_4N{=}NC_6H_4NMe_2]$. The guanidinium derivative of methyl orange has been shown by powder X-ray diffraction and diffuse reflectance UV-visible spectroscopy to react sequentially with HCl and NH_3. In addition, the tolerance of the GS network to substitution on the guanidinium cation has been examined. The structural impact of substituting one or two hydrogen atoms for methyl or ethyl groups has been assessed for a range of sulfonates.

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