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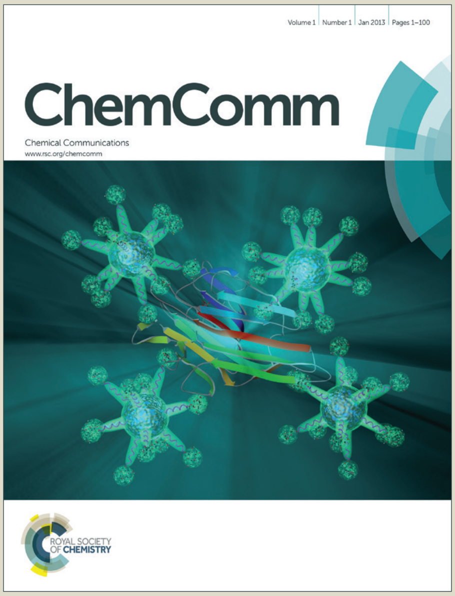

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Supramolecular Hydrogen-bonding Assembly of Silanediols with Bifunctional Heterocycles

Cite this: DOI: 10.1039/x0xx00000x

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Received 00th January 2012,
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

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X-ray crystallography showcases the distinct self-association and hydrogen-bonding patterns of organic silanediols, $R_2Si(OH)_2$, with bifunctional heterocycles for supramolecular assembly. Diffusion-ordered spectroscopy (DOSY) studies identify the dominant hydrogen-bonding patterns and structures in solution, which correlate with solid-state patterns at high concentrations.

The ability to predict and control hydrogen-bonding structures is important for supramolecular architecture, molecular recognition and catalysis.[1,2] Functional groups such as carboxylic acids and ureas assemble higher order structures upon H-bonding, providing predictable patterns to control molecular architecture.[3-5] Silanediols, $R_2Si(OH)_2$, are a double H-bonding group similar to a urea group with unique H-bonding properties for self-association,[6] yet there is no example using silanediol H-bonding to control supramolecular assembly.[7] Here we report the first example of the silanediol group as a supramolecular synthon to design molecular architecture with bifunctional heterocycles.

Silanediols exhibit two distinct modes of H-bonding depending on the Lewis basic acceptor. Kondo and Unno have reported chloride anion recognition with di(1-naphthyl)silanediol as a dual H-bond donor (Figure 1A)[8] in a manner that is similar to models proposed for anion recognition and catalysis using thioureas.[9] In the course of investigating silanediols as H-bonding catalysts,[10,11] we have observed that silanediols exhibit a distinct alternative pattern of H-bonding with a neutral Lewis base (e.g. carbonyls, ether, Figure 1B). Self-association of silanediols forms a cyclic donor-acceptor dimer and, as a result of cooperative H-bonding, the two remaining external protons are acidified and behave as a single H-bond donor to the Lewis base.

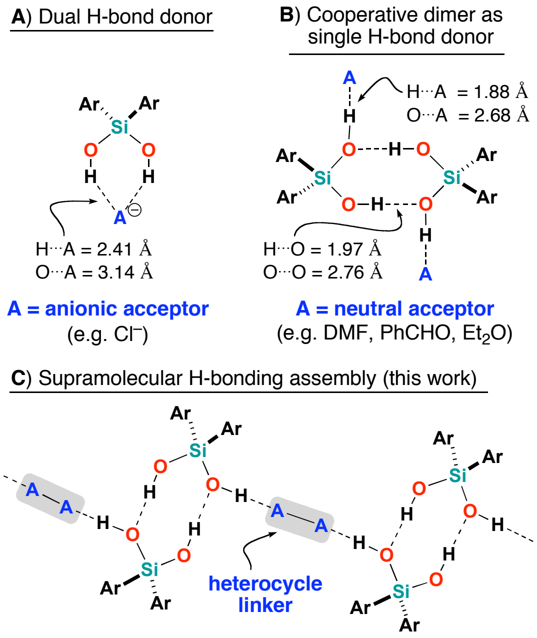


Figure 1: A) Schematic of two primary modes of H-bonding co-crystals known for silanediols (e.g. Ar = 1-Np, 9-anthryl or Mes) based on X-ray structures from refs 8, 10 and 11. Bond lengths for part B represent average values. B) Supramolecular assembly with bifunctional heterocyclic linkers. C) Supramolecular assembly of silanediols with heterocycle linkers described in this work.

Here we utilize X-ray crystallography and pulse gradient spin echo (PGSE) diffusion spectroscopy (DOSY) NMR studies to characterize self-association and H-bonding patterns of silanediols with bifunctional heterocycles relevant for supramolecular assembly. Dimesitylsilanediol (**1**) was chosen because it is stable towards condensation, has excellent solubility properties, and has crystallization ability both as a single crystal and for co-crystallization experiments.[10]

Heterocycles such as 4,4'-bipyridine and phenazine were selected as rigid molecules with the ability to form strong hydrogen bonds and function as spacers in the construction of supramolecular assemblies.[12,13,14] These molecules also provide the opportunity to study the affect of multiple H-bonding sites on silanediol self association. For all heterocycles, we have observed a consistent trend where silanediols self-associate to form a dimeric structure, which has both acceptor and donor sites available for H-bonding to form higher order structures.

Co-crystals of silanediol **1** with 4,4'-bipyridine construct an infinite chain with the 4,4'-bipyridine as a rigid spacer connecting cyclic silanediol dimers in a 2:1 ratio (Figure 2A). We observe the same H-bonding pattern for other bifunctional Lewis bases that can function as linkers, such as phenazine and 1,4-dimethoxybenzene (Figure 2B,C). The linear architecture and the spacing between cyclic dimers, which varies from 8.16-12.55 Å for the structures studied here, can be controlled based on the distance between the two Lewis basic sites of the heterocycle.

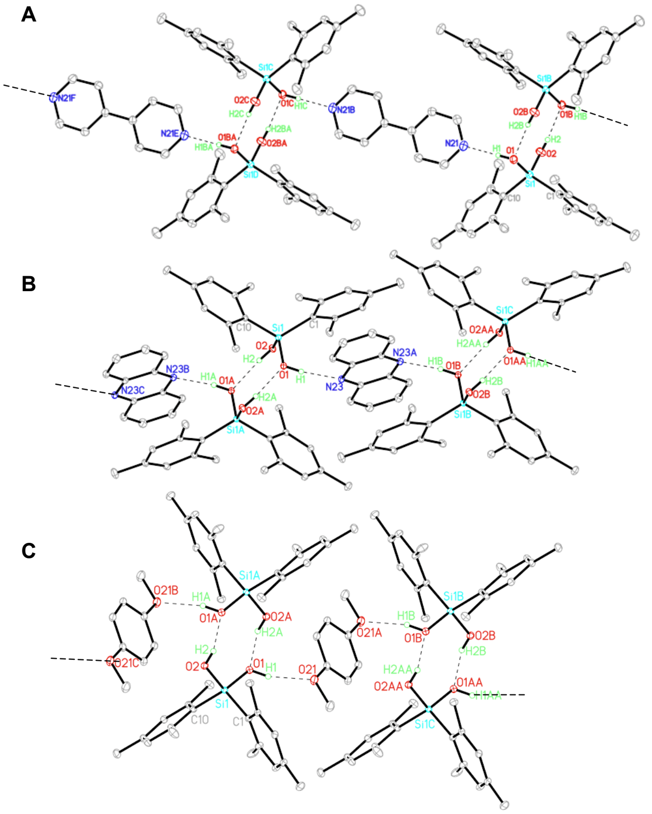


Figure 2. Cyclic dimers of dimesitylsilanediol are linked to form chains with 4,4'-bipyridine (A), phenazine (B), and 1,4-dimethoxybenzene (C). Thermal displacement plots show 50%, 30% and 30% probability displacement ellipsoids for non-hydrogens, respectively (CCDC 958825, 958790, 958824). Selected hydrogens and non-interacting CH_2Cl_2 solvent molecules are omitted for clarity. Selected bond lengths [Å] for (A) $Mes_2Si(OH)_2$•4,4'-bipy: H1⋯N21 1.88(2), O1⋯N21 2.7138(18); H2⋯O1B 2.00(2), O2⋯O1B 2.7476(16); (B) $Mes_2Si(OH)_2$•phenazine: H1⋯N23 1.946(19), O1⋯N23 2.7932(12); H2⋯O1A 1.920(19), O2⋯O1A 2.7446(11); (C) $Mes_2Si(OH)_2$•OMeAr: H1⋯O21 2.004(17), O1⋯O21 2.8399(9); H2⋯O1A 1.961(18), O2⋯O1A 2.8087(9). Distances between dimers (Å) = (A) 12.55, (B) 8.16, and (C) 9.14.

In comparison to linkers such as 4,4'-bipyridine, bifunctional heterocycles such as 7-azaindole co-crystallize with silanediol **1** as a 2:2 adduct in a H-bonding cluster where all donor and acceptor sites are fully exploited (Figure 3). While steric and other crystal packing effects can also alter the H-bond parameters, we observe that donor-acceptor H-bonding with the Lewis base generally increases the strength of all H-bonding interactions of the silanediol dimer as evidenced by the shorter O⋯A and O⋯O distances for the azaindole adduct compared to other adducts.

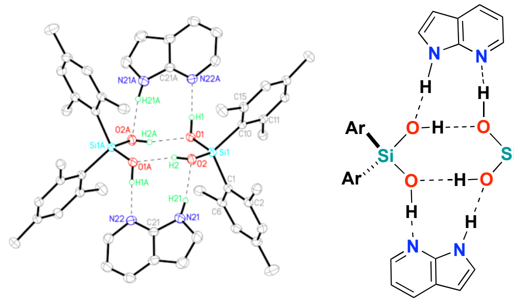
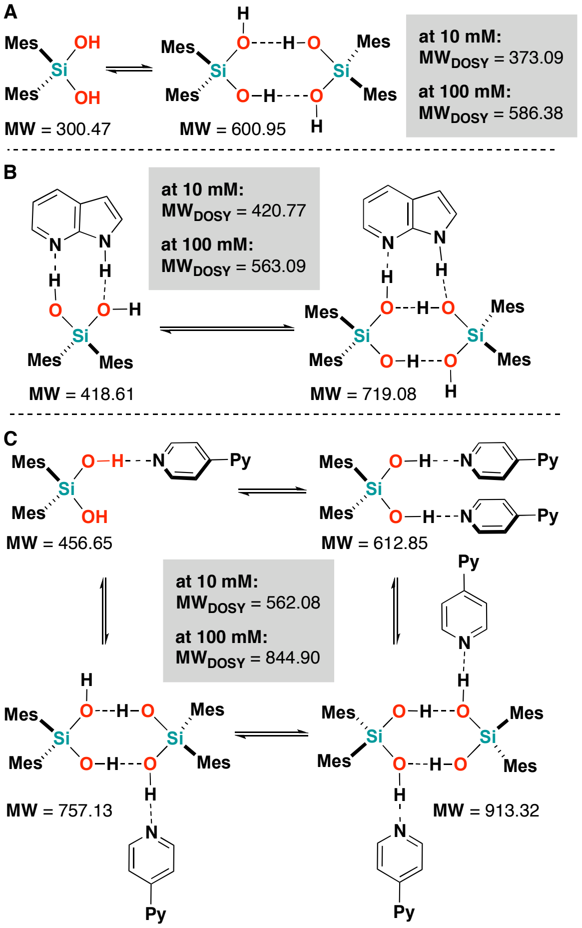


Figure 3. Dimesitylsilanediol (Ar = Mes) adduct with 7-azaindole (CCDC 958784). Thermal displacement plot shows 50% probability displacement ellipsoids for non-hydrogens. Selected hydrogens are omitted for clarity. Selected bond parameters [Å] for $Mes_2Si(OH)_2$•7–azaindole: H1⋯N22 1.79(3), O1⋯N22 2.6769(15), H2⋯O1A 1.91(2), O2⋯O1A 2.7049(14).

To investigate the self-association and H-bonding of silanediols in solution, we used PGSE diffusion-ordered NMR spectroscopy (DOSY).[15,16] The ability to correlate H-bonding structures in solution and solid state remains a significant challenge. Due to the self-association of silanediols at high concentration, we expect that the H-bonding patterns in crystals may correlate with solution equilibria. Diffusion constants can be used to calculate the average MW of the individual and assembled species in equilibrium and compare assemblies observed with different heterocycles. Although DOSY has been used previously to study organometallic complexes, the study of small molecule H-bonding interactions remains a challenge due to lower binding affinity and solubility issues at higher concentrations.[17] At low concentration of silanediol (10 mM in C_6D_6), we observe a MW of 373.09 g/mol that correlates with the monomeric silanediol while indicating that some H-bonding association is occurring even at this concentration. At higher concentration (100 mM), we observe a MW of 586.38 g/mol, which correlates with the silanediol dimer and confirms the favorable self-association of silanediols in solution.

When using DOSY to compare solution structures with different heterocycles, we observe distinct H-bonding patterns of silanediols with heterocycles such as 7-azaindole and 4,4'-bipyridine that are concentration dependent (Scheme 1).[18] Because H-bonding assemblies often have low binding affinities relative to metal complexes, we addressed this challenge by introducing excess Lewis base (500mM) to shift the equilibrium towards the hydrogen-bound species. Upon mixing 7-azaindole with silanediol at 10 mM, the measured MW (420.77 g/mol) correlates with the structure of a well-defined 1:1 complex (MW_{calcd}: 418.61 g/mol). Under the same experimental conditions with 4,4'-bipyridine, the MW of the NMR-observed species (562.08 g/mol) correlates with the structure of a 1:2 silanediol/bipyridine complex (MW_{calcd}: 612.85 g/mol). NMR binding studies of silanediol (10 mM in C_6D_6) with azaindole and 4,4'-bipyridine also demonstrate H-bonding interactions based on SiOH shifts with $\Delta\delta$ = 3.21 and 2.70 ppm, respectively (see ESI).



Scheme 1. Major complexes observed in solution using DOSY NMR.

At higher concentrations of silanediol (e.g. 100 mM), DOSY indicates self-association and the formation of higher order H-bonded assemblies. With 7-azaindole, the MW measured for the observed species is 563.09 g/mol, which is attributed to an equilibrium with a 2:1 adduct as a major species. For 4,4'-bipyridine, the MW measured is 844.90 g/mol, which correlates with an equilibrium between a 2:1 and a 2:2 adduct species, and matches the pattern observed in the crystal structure. This concentration-dependent shift in MW confirms that the dimeric structure is favored in solution even with binding to Lewis bases. Overall, DOSY NMR correlates H-bonding patterns of silanediols in solution at high concentration with those observed in the solid state, while suggesting that alternative binding patterns can exist at lower concentrations.

In conclusion, we have presented silanediols as a promising new supramolecular structural motif based on predictable H-bonding properties. For all heterocycles investigated, we observe that self-association of silanediols is a predictable trend both in the solid state and in solution at high concentration. Through the selection of different bifunctional heterocycles, we can modulate the supramolecular H-bonding assemblies of silanediols. The ability to predict and control silanediol H-bonding patterns has implications for molecular recognition, sensor design, and supramolecular assembly.

Notes and references

The authors would like to acknowledge the National Science Foundation (CHE-0847358) for support of this research. A.K.F. acknowledges 3M Corporation for a Nontenured Faculty Award, N.T.T. and S.O.W. acknowledge the Department of Education for GAANN Fellowships and UC Davis for Bradford Borge Chemistry Fellowships. We acknowledge M. Olmstead (UC Davis) for helpful advice.

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† Electronic Supplementary Information (ESI) available: Experimental Procedures and DOSY NMR.

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