Electronic Supplementary Information

Single atom modification leads to enhanced nucleotide self-assembly: the role of cation bridging

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Experimental details

Solid-state NMR experiments were performed on Bruker Avance-500 and Avance-600 NMR spectrometers. Chemical shifts for ^{13}C, ^{23}Na, ^{31}P were referenced to the signals of TMS, $Na^+(aq)$, and 85% $H_3PO_4(aq)$, respectively. All FT-IR spectra were obtained from a Scimitar 1000 FT-IR (Varian) as KBr pellets with a resolution of 4 cm^{-1} from wavenumber 500 to 3000 cm^{-1}. A total of 10 scans were accumulated for each spectra with a sensitivity of 1 cm^{-1}. All XRD spectra were obtained on a Philips X'Pert Pro Multi Purpose Diffractometer (2002) using Ni-filtered Cu K_α 1,2 radiation (λ_1 = 1.5406 Å, λ_2 = 1.5444 Å), a fixed divergence slit width of 0.5°, 0.02 Radian soller slit, 15 mm mask, 2 s revolution and 40 s count time. Samples were prepared on flat borosilicate glass discs and the diffraction data were collected from 10° to 70° using an X'pert X'celerator high speed detector for a total scan time per sample of approximately 20 min. Data were processed on a Pentium PC using PanAlytical X'pert HighScore for Windows XP.

Quantum chemical calculations were performed using Gaussian 03 suite of programs on a SunFire 6800 symmetric multiprocessor system. Each of the four nodes is equipped with 24 × 1.05 GHz (8 MB E-Cache) UltraSPARC-III processor and 96 GB of RAM. Shielding calculations were performed using the GIAO method as implemented in Gaussian 03. Basis sets of cc-pVTZ and 6-31G(d) were used for Na and other atoms, respectively. The computed absolute shielding constant (σ) was converted to the chemical shift scale (δ) using $\delta = \sigma_{ref} - \sigma$, where σ_{ref} is the absolute shielding constant for the reference sample. In this study, we used $\sigma_{ref}(^{23}Na)$ = 574.6 ppm and $\sigma_{ref}(^{31}P)$ = 317.0 ppm.

Fig. S1. ^{31}P NMR titration experiment for Na_2(5′-GSMP). The value of pK_{a2} was determined to be 5.1 ± 0.2.

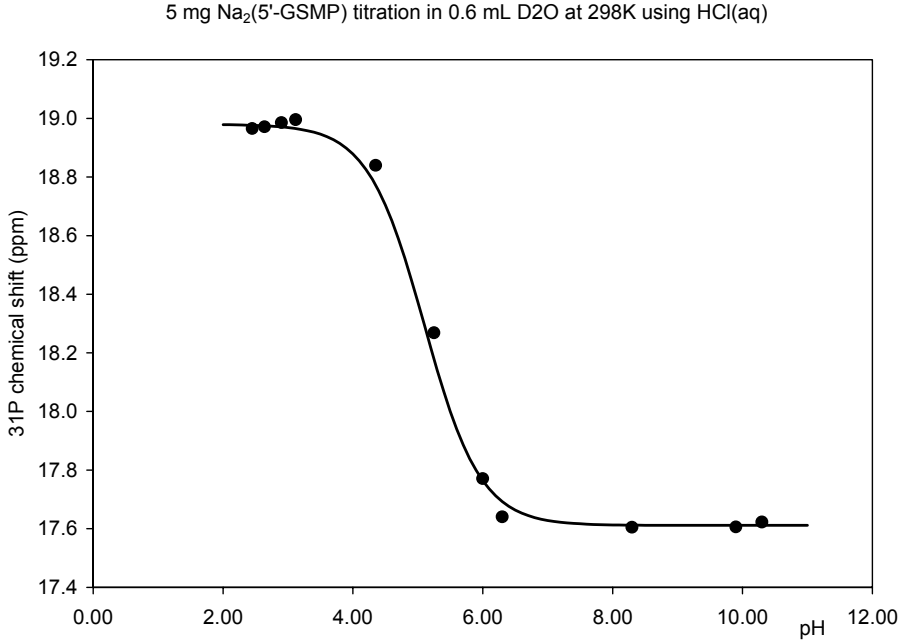


Fig. S2. FTIR spectra of solid samples.

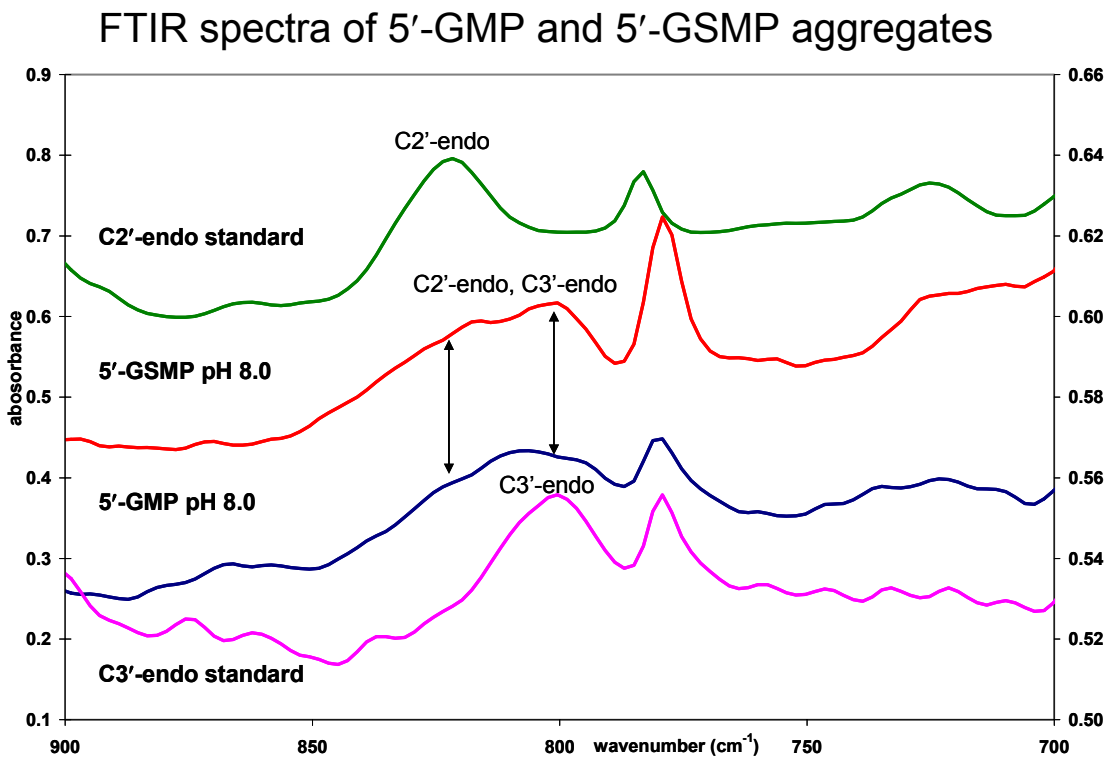
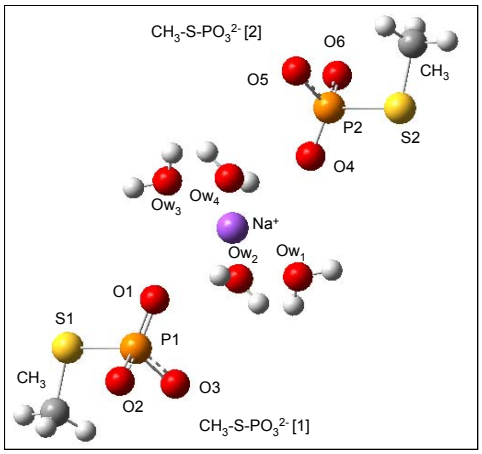


Table S1. Structural details of the cluster model used in ab initio calculations.



	Bond distances (Å)		Bond angles (°)
		Na-P1-S1	132
Na-O1	3.20	P1-S1-CH3	101
Na-O2	4.22	O1-P1-O2	119
Na-O3	4.08	O1-P1-O3	114
Na-Ow_{1-4}	2.48	O2-P1-O3	100
		O1-P1-S1	113
P1-O1	1.48	P1-Na-Ow_{1-4}	84-97
P1-O2	1.61		
P1-O3	1.63		
P1-S1	2.10		
S1-C	1.84		
Ow_1-Ow_2	3.45		
Ow_1-Ow_3	4.96		
Ow_1-Ow_4	3.51		

CH_3-S-PO_3^{2-} [1] and CH_3-S-PO_3^{2-} [2] are related by an inversion centre.
The plane of symmetry contains Na^+ and the four waters (square planar).
The two CH_3-S-PO_3^{2-} molecules and Na^+ are related by the following parameters:

Bond distances (Å)	Na-P2	same as Na-P1
	Na-O4	same as Na-O1
Bond angles (°)	P1-Na-P2	180
	P1-Na-S2	164
Dihedral angle (°)	P1-O1-O4-P2	180

Fig. S3. Powder XRD patterns for Na_2(5′-GMP), Na_2(5′-GSMP) and NaCl.

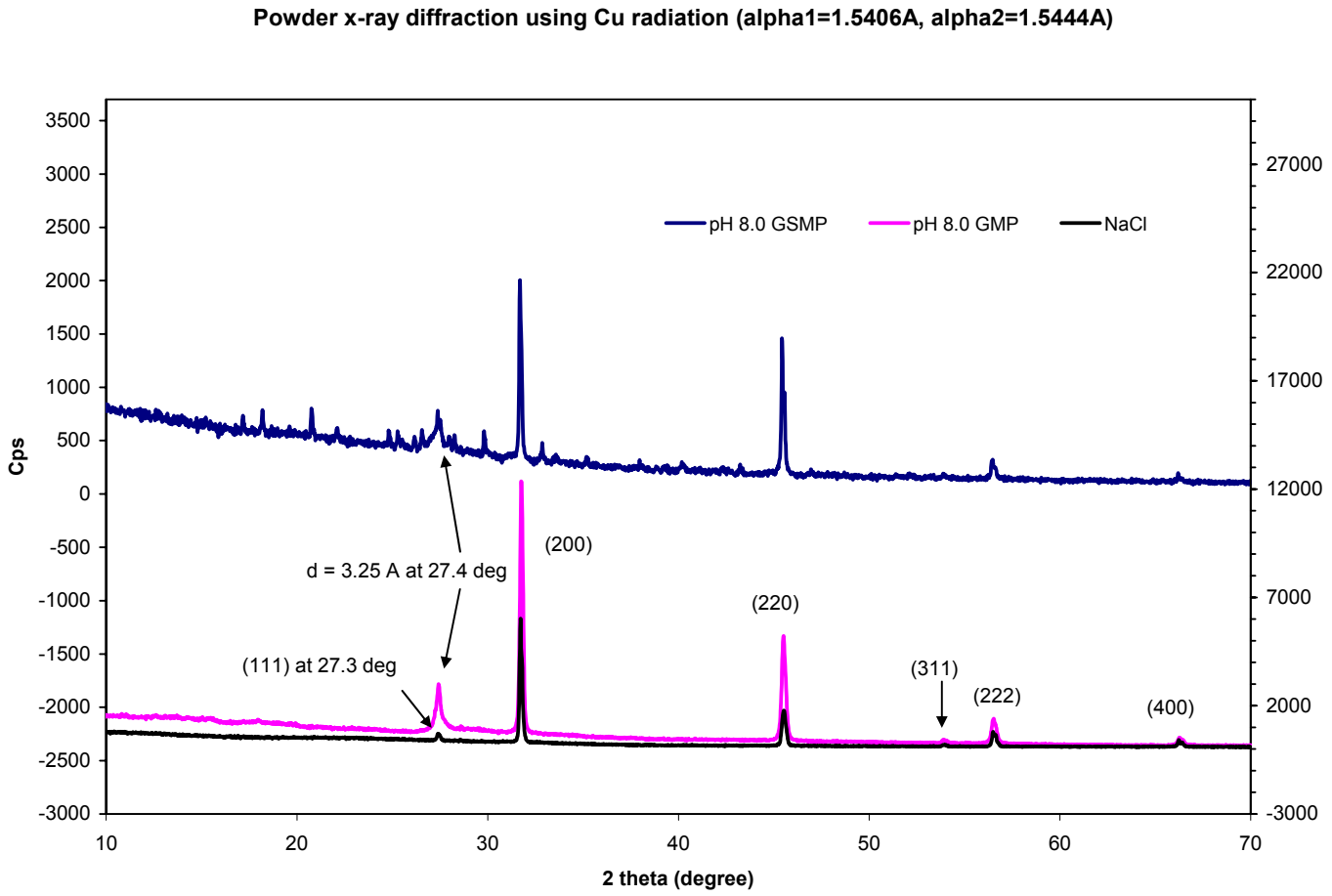


Fig. S4. ^{13}C CP/MAS spectra of Na_2(5′-GMP) and Na_2(5′-GSMP). All spinning sidebands are marked by "*".