Supramolecular hydrogels derived from silver ion-mediated self-assembly of 5[']-guanosine monophosphate[†]

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Scheme 1 Addition of Ag+ ions to GMP (1) produces an enolate tautomer (2) and release of a proton from N1, and subsequent formation of a Ag-GMP dimer (3) by binding at N7 and O6.



Scheme 2 Molecular structures for the cationic dyes, methylene blue (4) or Hoechst-33258 (5).



Figure S1 (b) Oscillation frequency sweep at a fixed stress 100 Pa for 1:1 (G', G'') and 1:1.25 (G', G'') hydrogels



Figure S2 (a,b) Histogram of nanofilaments widths for Ag-GMP hydrogels prepared at GMP : Ag molar ratios of (a) 1:1 and (b) 1:2. (c) Particle size distribution of Ag nanoparticles produced in association with Ag-GMP nanofilaments. (d) UV-Vis spectra of Ag-GMP wet (1:1 red, 1:2 green) and lyophilized (1:1 black, 1:2 blue) hydrogels after photoreduction showing surface plasmon resonance band at 438 nm.



Figure S3 AFM tapping mode images of supramolecular 1:2 hydrogel nanofilaments dried onto a mica substrate



Figure S4. DSC curves for 1:1 (black) and 1:2 (red) Ag-GMP hydrogels showing broad gelsol transitions at 52 or 75 °C, respectively (arrows). Additional endothermic peaks at ~ 5° C and 105/110°C correspond to the melting and boiling of water strongly associated with the Ag-GMP nanofilaments.



Figure S5 Electrospray mass spectrum of Ag-GMP hydrogel,



Figure S6 (a) PXRD patterns of wet hydrogels prepared at (i) 1:1 or (ii) 1:2, or (iii) lyophilized 1:2 gel powder showing strong 0.34 nm reflection at $2\theta = 26^{\circ}$. The broad band at $2\theta = 34^{\circ}$ possibly corresponds to reflections originating from Na₂GMP as reflections at $2\theta = 33^{\circ}$ and 34.7° were observed in the control samples. (b) SAXS profile of lyophilized 1:2 hydrogel showing reflections at 2.9 and 1.45 nm.



Figure S7 (a) UV-visible and (b) CD spectra for the titration of a 1:1 Ag-GMP hydrogel dispersion into aqueous methylene blue. Arrows indicate direction of change in peak intensities/ellipticity associated with increasing hydrogel concentration.



Figure S8 TEM images of supramolecular Ag-GMP filaments produced in the presence of (a) methylene blue and (b) Hoechst-33258. Scale bars = 200 nm and 500 nm respectively.



Figure S9 UV-Vis spectrum of Ag-GMP/cyt c hydrogel (red profile) showing nucleotide bands at 252 and 276 nm, and blue-shifted Soret peak at 402 nm. Black trace shows corresponding spectrum for native cyt c in aqueous solution.