# Binary Guanosine Gels for Single Walled Carbon Nanotube Dispersion, Separation and Manipulation

by

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# ABSTRACT

Guanine derivatives and guanine-rich oligonucleotides have been long studied due to their unique self-assembly capability. It is well known that aqueous solutions of individual guanosine compounds can form gels (G-gels) through Hoogsten hydrogen bonding, assisted by cation-dipole forces and π-π stacking. Typically, gelation is favored at low temperature and acidic pH. This dissertation presents the discovery that binary mixtures of 5′-guanosine monophosphate (GMP) and guanosine (Guo) can form stable G-gels at neutral pH over a temperature range that can be tuned by varying the relative proportions of the hydrophobic Guo and the hydrophilic GMP in the mixture. Gelation was studied over the temperature range of 5-40 °C or 5-60 °C at pH 7.2 using visual detection, circular dichroism spectroscopy (CD), and CD thermal melt experiments. Solutions with high GMP/Guo ratios behaved similarly to solutions of GMP alone while solutions with low GMP/Guo formed firm gels across the entire temperature range. CD results show the ability of hydrophobic Guo to preserve the gel structure at higher temperature. Most interesting were solutions between these two extremes, which were found to exhibit thermoassociative behavior; these solutions are liquid at refrigerator temperature (~4 °C) and undergo sharp transitions to a gel at higher temperatures. Increasing the GMP/Guo ratio and increasing the total concentration of guanosine compounds shifted the onset of gelation to higher temperatures (ranging from 20 to 40 °C), narrowed the temperature range of the gel phase, and sharpened the reversible phase transitions. Increasing the KCl concentration shifted the onset of gelation to higher temperature, sharpened the transition and significantly reinforced the gelation structure. The combination of reversible self-assembly and tunability over biologically relevant

temperature and pH offers exciting possibilities for these simple and inexpensive materials in medical, biological, analytical, and nanotechnological applications.

The binary G-gels were then applied to dispersion, separation and manipulation of single walled carbon nanotubes (SWNTs), which are typically synthesized as heterogeneous mixtures of metallic and semiconducting tubes with varying chirality and diameters. Uniform, highly stable SWNT suspensions were achieved. UV-Vis absorption spectroscopy, near infrared fluorescence spectroscopy and atomic force microscope revealed a surprisingly high proportion of individually solubilized SWNTs in these preparations, which is in contrast to other dispersion methods that solubilize SWNTs as bundles and require lengthy treatment to achieve individually dispersed tubes. The presence of increasing Guo in the gels with constant GMP strongly enhanced the selectivity toward large diameter tubes and narrowed the diameter distribution of the dispersed SWNTs. Increasing GMP in the gels with constant Guo also shifted selectivity toward larger diameter nanotubes and additionally, showed a preference towards semiconducting tubes over metallic tubes. Adding KCl decreased selectivity of the gels to large diameter tubes. Fractions enriched in metallic and in semiconducting tubes were achieved by selective dispersion in particular G-gels. Transparent thin films fabricated from the metallic-enriched fraction showed over twice the sheet conductivity compared to films fabricated from the semiconductor-enriched fraction. A simple, scalable and economical method to fabricate aligned SWNT arrays was achieved based on the thermoassoative properties of some G-gels. These results show that binary G-gels offer a low-cost, tunable, sensitive and biocompatible medium for nondestructive dispersion of high concentrations of individual SWNTs that can also be used for selective enrichment

and separation of SWNTs based on diameter, chirality and metallic properties, and for parallel alignment of SWNTs. This work opens a new door in SWNT processing and offers novel applications for SWNTs in medical, biological and materials industries.