SUPPORTING INFORMATION

Metal-mediated Fabrication of New Functional G-quartet-based Supramolecular Nanostructure and Potential Application as Controlled Drug Release System

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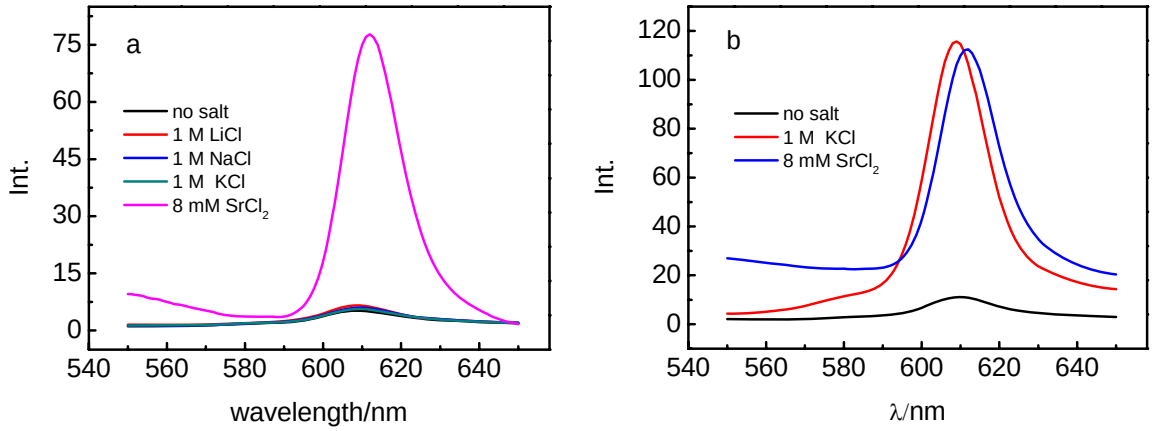


Figure S1. Fluorescence spectra of NMM mixed with 5'-GMP in deionized water upon addition of different salts. (a) Control (black), 1 M LiCl (red), 1 M NaCl (blue), 1 M KCl (cyan) and 8 mM $SrCl_2$ (blue). [NMM] = 2×10^{-6} M, [GMP] = 2×10^{-2} M. (b) Control (black), 1 M KCl (red), 8 mM $SrCl_2$ (blue). [NMM] = 2×10^{-6} M, [GMP] = 1×10^{-1} M.

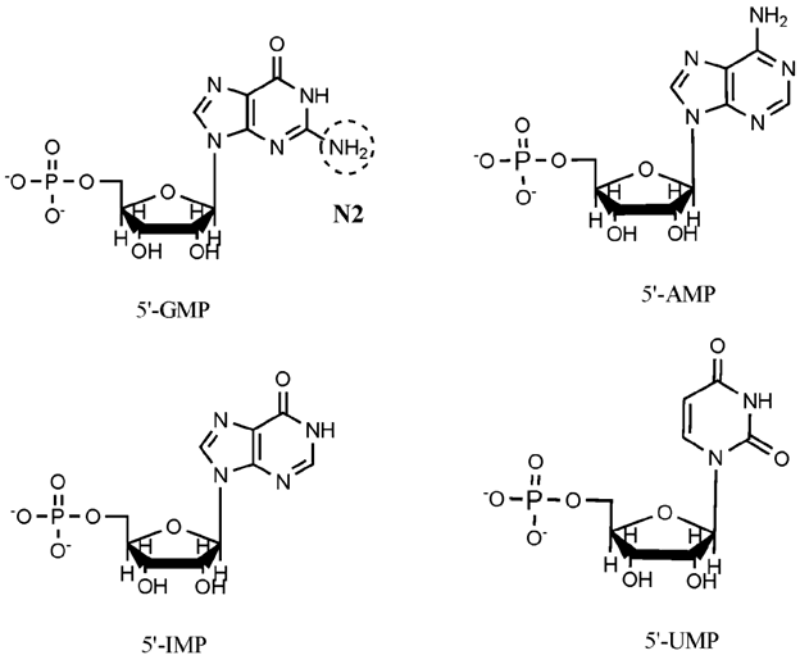


Figure S2. Structures of the nucleotides used for these studies.

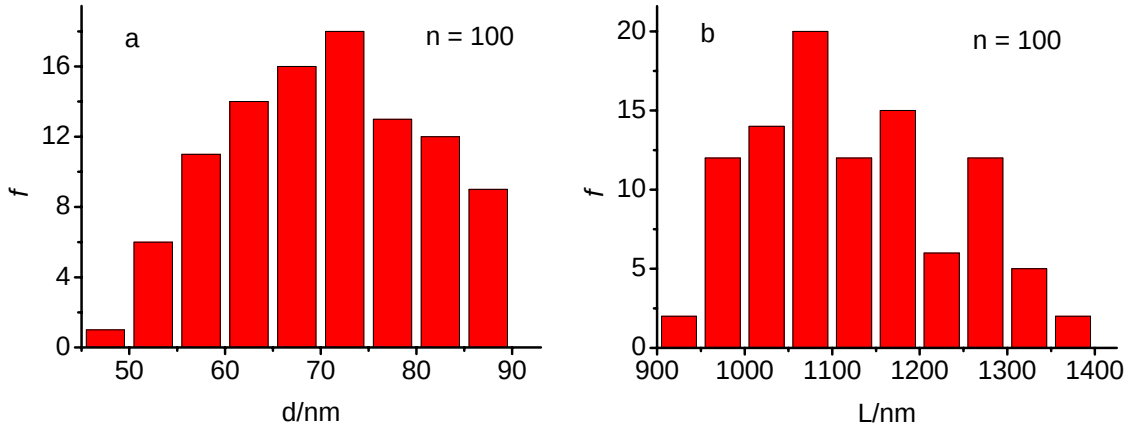


Figure S3. Histograms showing the width (a) and length (b) of a sample with 100 distinct wires

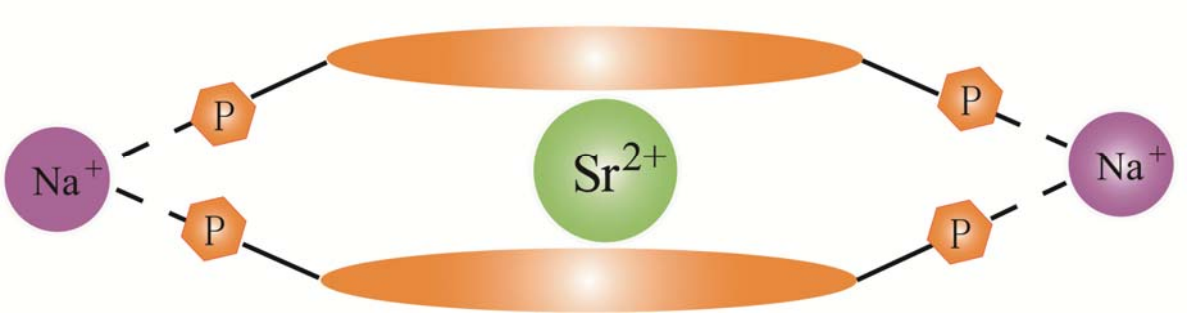


Figure S4. Proposed binding site for Sr^{2+} in ordered 5'-GMP octamers. The binding site defined by the eight O6 atoms of neighboring guanine bases are believed to be highly Sr^{2+}-specific structure-directing sites.

Table S1. Chemical shift of excessive NaCl (free NaCl), Na^+ bound to the phosphate groups (surface Na^+ ions) and Na^+ ions residing inside the G-quartet channel（channel Na^+ ions）in solid-state ^{23}Na NMR spectra.

Ion type / Sample type	Free Na^+ ions	Surface Na^+ ions	Channel Na^+ ions
Na-gel [1]	7 ppm	-1 ppm	-19 ppm
Lipophilic G-quadruplex [2]	—	—	-18ppm
Na-gel [3]	7 ppm	-4 ppm	-19 ppm
Na-gel [4]	7 ppm	-5 ppm	-20 ppm
Na-gel(in our manuscript）	No signal	-7.5 ppm	-21.5 ppm
Na-Sr gel(in our manuscript)	6.8 ppm	-8.2 ppm	No signal

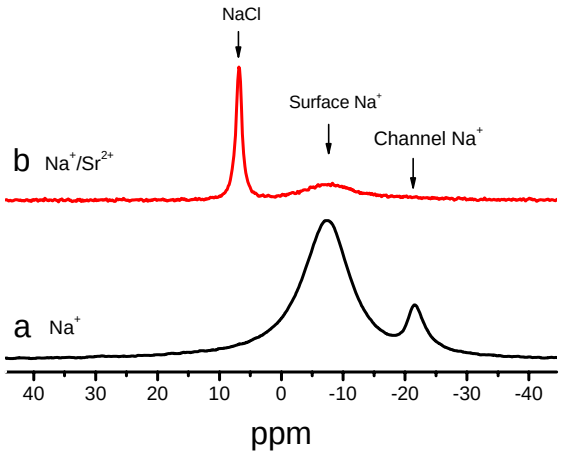


Figure S5. Solid-state ^{23}Na NMR MAS spectra of (a) Na_2 (5'-GMP) gel. (b) Na_2 (5'-GMP)/Sr^{2+} nanowires.

Solid-state ^{23}Na NMR approach is a useful technique for detecting other metal-directed self-assembly systems as well as in nucleic acids. In this study, we apply ^{23}Na magic-angle spinning (MAS) to Na_2 (5'-GMP)/Sr^{2+} nanowires. *Figure S5* shows portions of the solid state ^{23}Na NMR spectra for Na_2 (5'-GMP) in the absence or presence of 8 mM Sr^{2+}. As can be seen in *Figure S5*a, the ^{23}Na NMR signal at approximately -7.5 ppm is attributed to the Na^+ ions bound to the phosphate groups (denoted as the surface Na^+ ions in this study), and the small peak at -21.5 ppm is due to the Na^+ ions residing inside the G-quartet channel (denoted as the channel Na^+ ions).This ^{23}Na chemical shift value is in excellent agreement with the NMR signature obtained for channel Na^+ cations by solid-state ^{23}Na NMR.[1-4] In the case of Na_2 (5'-GMP)/Sr^{2+} nanowires, as shown in *Figure S5*b, the sharp peak centered at δ = 6.8 ppm is assigned to the presence of excessive NaCl in the nanowires (denoted as free Na^+ ions in this study). The small peak at δ = -8.2 ppm is attributed to surface Na^+ ions. It is worth noting that the signal at -21.5 ppm which is characteristic of the channel Na^+ ions disappeared completely. This implies that the presence of Sr^{2+} inhibits the entering of Na^+ into the G-quadruplex channel. Thus, the ^{23}Na NMR signal associated with the free Na^+ ions appeared. Moreover, the fluorescence enhancement of NMM indicates the existence of G-quartet structures in Na_2 (5'-GMP)/Sr^{2+} nanowires. These results unambiguously demonstrate that the G-quartet structures are promoted by Sr^{2+} ions, which is consist with recent crystallographic and NMR studies that Sr^{2+} ions are observed in every other guanine tetrad plane, sitting on the fourfold axis and associated to the eight O6 atoms of neighboring guanine bases. [5-7]

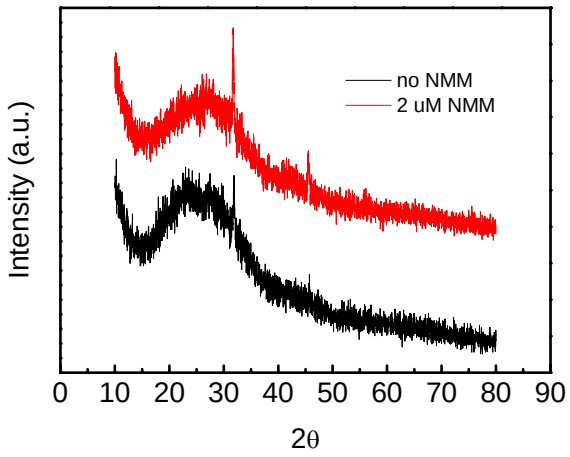


Figure S6. XRD patterns of 5'-GMP /Sr^{2+} nanowires prepared in the absence (bottom) and presence (top) of 2 μM NMM.

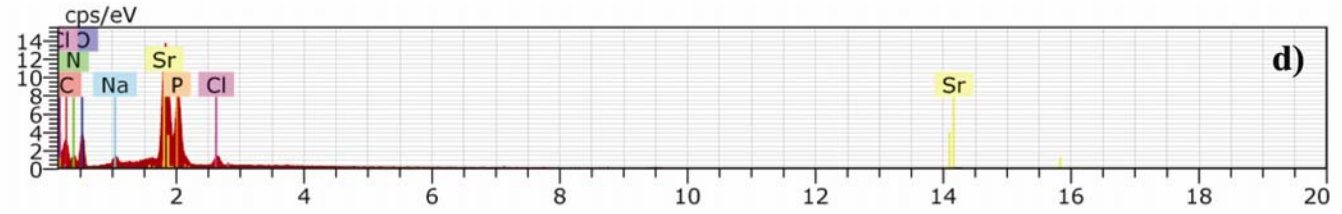


Figure S7. EDX data of synthesized functional nanowires, [NMM] = 2×10^{-6} M, [GMP] = 2×10^{-2}M.

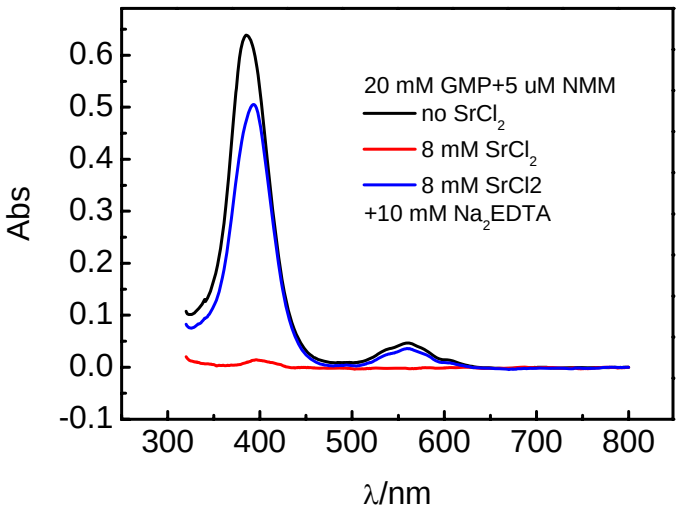


Figure S8. Absorbance spectra of the supernatant of the mixture of NMM and 5'-GMP in deionized water, and the following: no extra agent (black), 8 mM $SrCl_2$ (red), or 8 mM $SrCl_2$ plus 10 mM Na_2EDTA (blue) at ambient temperature.

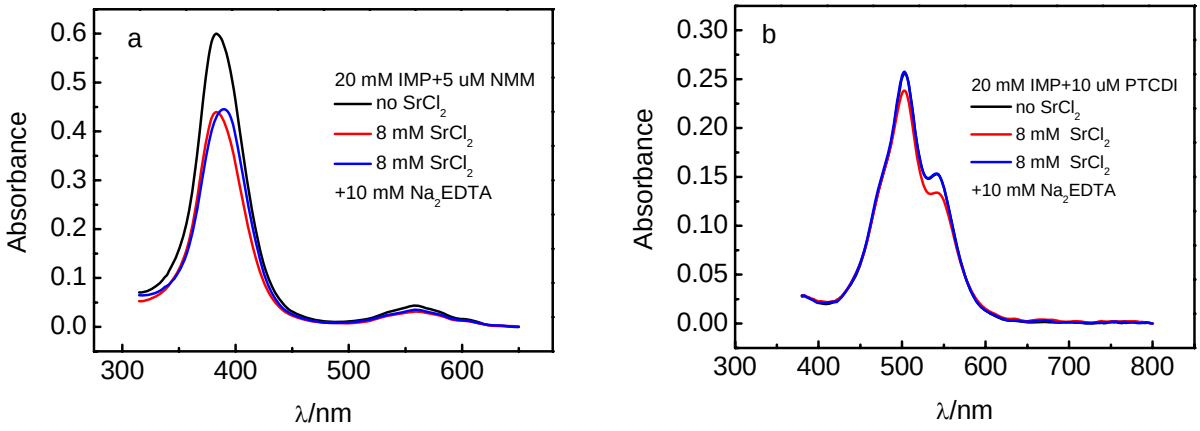


Figure S9. Absorbance spectra of the supernatant of the mixture of (a) 5 μM NMM and (b) 10 μM cationic PTCDI derivative and 5'-IMP in deionized water, and the following: no extra agent (black), 8 mM SrCl2 (red), or 8 mM SrCl2 plus 10 mM Na_2EDTA (blue) at ambient temperature. [IMP] = 2×10^{-2} M.

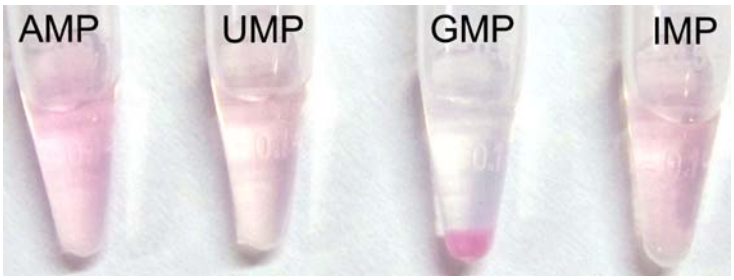
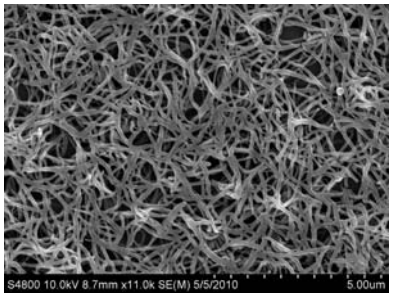
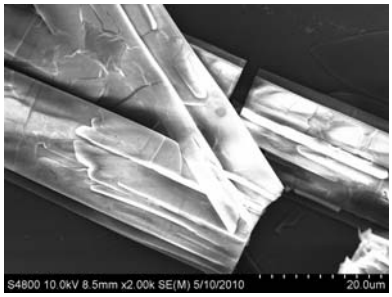


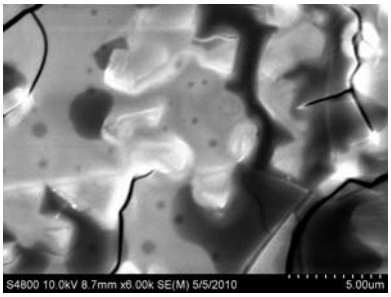
Figure S10. Encapsulation of cationic PTCDI derivative into four nucleotides mediated by 8 mM Sr^{2+}. [PTCDI derivative] = 10 μM. [AMP] = [UMP] = [GMP] = [IMP] = 2×10^{-2} M.

(a) **(b)**





(c) **(d)**



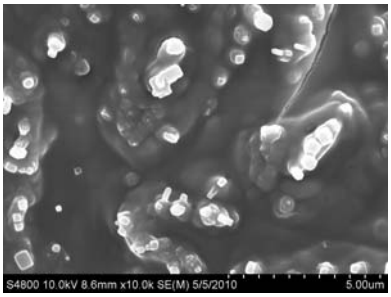


Figure S11. SEM images of NMM mixed with (a) 5'-GMP, (b) 5'-IMP, (c) 5'-AMP, (d) 5'-UMP upon the addition of 8 mM $SrCl_2$ in deionized water. [NMM] = 2×10^{-6} M, [GMP] = [IMP] = [AMP] = [UMP] = 2×10^{-2} M.

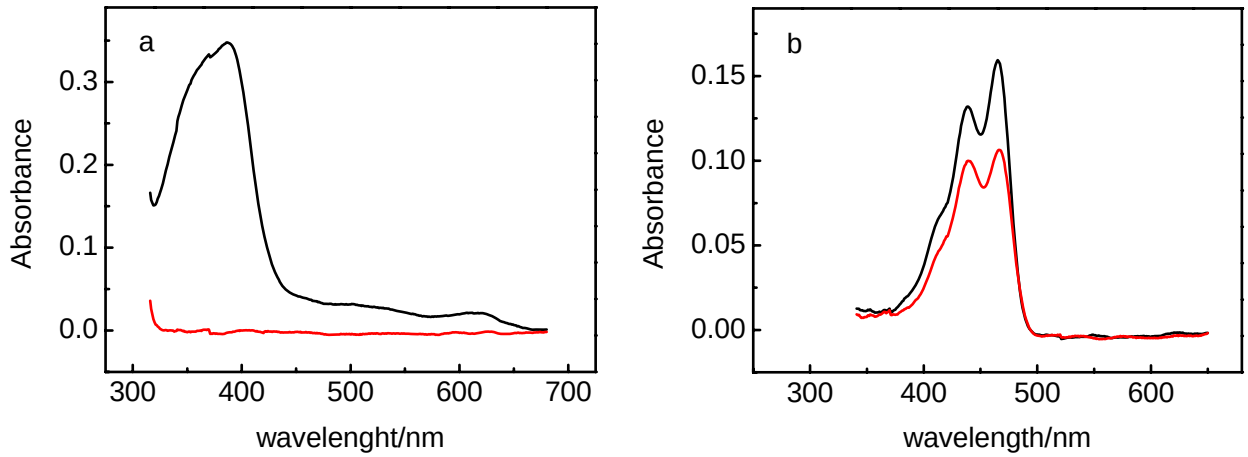
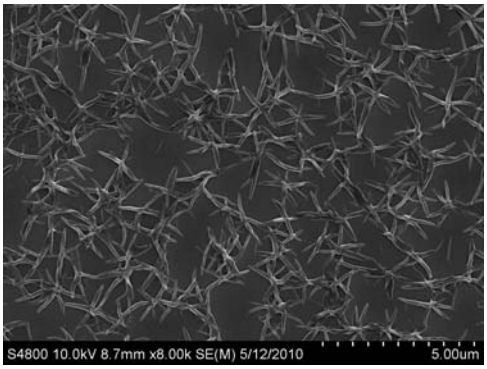
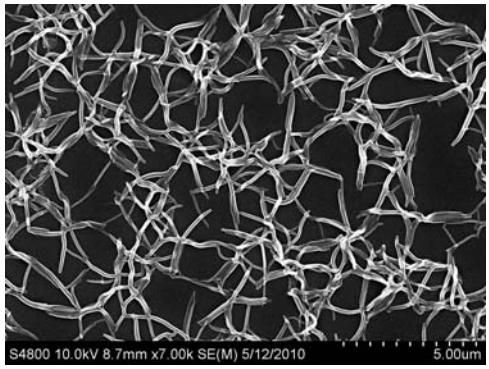


Figure S12. Encapsulation of (a) hemin and (b) perylene tetracarboxylic acid into the Sr^{2+}/GMP nanowires. Absorbance spectra of the supernatant of the mixture of 10 μM hemin or perylene tetracarboxylic acid and 5'-GMP in deionized water, and the following: no extra agent (black), 8 mM $SrCl_2$ (red), [GMP] = 2×10^{-2} M.

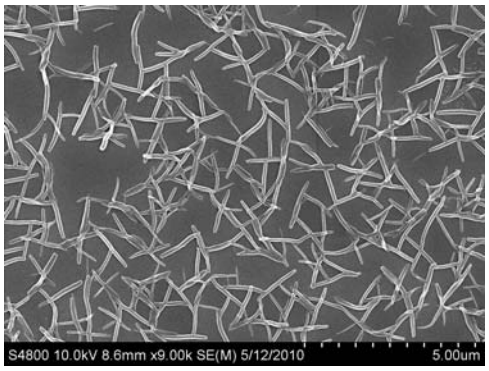
(a)



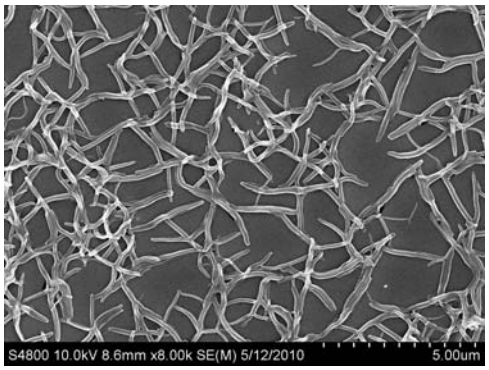
(b)



(c)



(d)



(e)

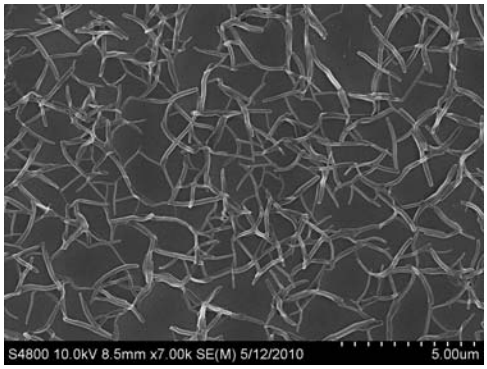


Figure S13. SEM images of various amounts of NMM (a) 0 μM, (b) 2 μM, (c) 5 μM, (d) 10 μM, (e) 20 μM, mixed with 5'-GMP and $SrCl_2$ in deionized water. [GMP] = 2×10^{-2} M, [$SrCl_2$] = 8 mM.

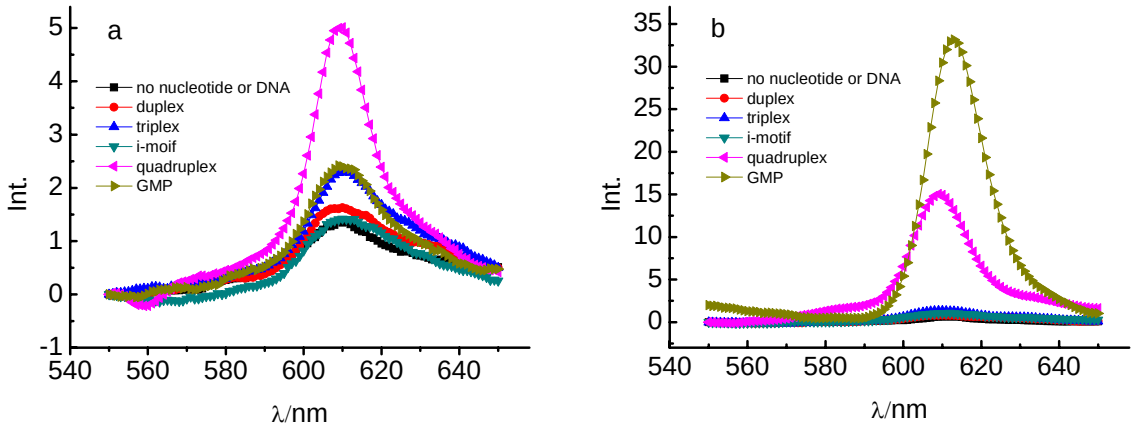


Figure S14. Fluorescence spectra of NMM with various DNA forms and GMP (a) before and (b) after addition of 8 mM $SrCl_2$. [NMM] = 2×10^{-6} M, [duplex] = [triplex] = [*i*-motif] = [quadruplex] = 1×10^{-6} M, [GMP] = 2×10^{-2} M.

Reference

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