Electrostimuli-responsive supramolecular hydrogel cross-linked by guanine quadruplex

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Keywords: Guanine quadruplex; Supramolecular gel; Electrochemistry; Polyethylene glycol

Guanine-terminated PEG (G_2-PEG) is known to form supramolecular hydrogels in the presence of alkali metal cations (K^+).[1] This gelation is caused by the formation of a network structure with guanine quadruplexes as crosslinking points, which are cation-templated assembly of four guanines. Recently, we discovered that PEG chain forms the helical structure by incorporating K^+ into the helices in aqueous triiodide (I_3^-) solution. The oxygen atoms of PEG coordinate to K^+ while iodine molecule (I_2) and I_3^- are located outside the PEG helices.

In this presentation, we aimed to switch the mechanical properties of G_2-PEG hydrogels by electrochemical redox reaction of KI; when iodide (I^-) is oxidized to I_3^- in G_2-PEG hydrogel matrix containing KI, the PEG moiety of G_2-PEG is expected to form the helical structure and coordinate to K^+. In other words, the oxidation of I^- allows G_2-PEG to coordinate to K^+ at two different sites—the guanine residue and the PEG chain. This conformational change in the PEG chain may result in two possible changes in the physical state of hydrogel: a) if K^+ is lost from the G-quadruplex and bound by the PEG chain, the G_2-PEG hydrogel would collapse, and the hydrogel turns into sol phase (Figure 1 (a)). b) if K^+ remains in the G-quadruplex and PEG forms the helix at the same time, the hydrogel remains as gel phase, while its physical properties such as viscosity and elasticity may change (Figure 1 (b)). Our preliminary result showed that aqueous solution of G_2-PEG forms a viscous gel after addition KI, which is consistent with the report by Lehn et al.[1] Further, addition of I_3^- in the gel transformed the gel into dark viscous precipitate. This dark precipitate is more viscous than the precipitate formed by unmodified PEG, possibly because of the coordination of K^+ by the G_2 terminal. More detailed studies such as the influence of molecular weight of PEG on this phase transformation upon the addition of I_3^- are ongoing, and the result will be presented to elucidate the structural change of G_2-PEG.

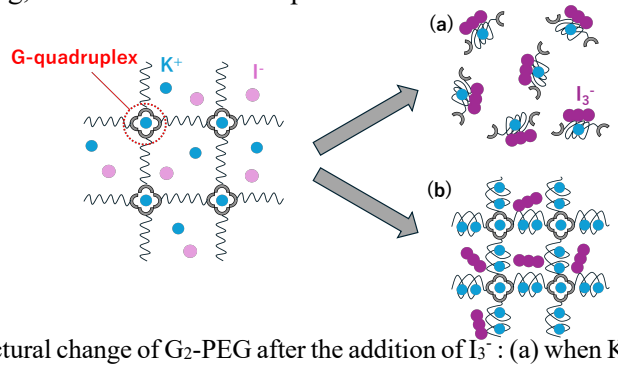

Figure 1. Structural change of G_2-PEG after the addition of I_3^- : (a) when K^+ is lost from the G-quadruplex (b) when K^+ remains in the G-quadruplex.

1) A. Ghoussoub, J. M. Lehn, *Chem. Com.* **2005**, *46*, 5763-5765.