Electronic Supplementary Material (ESI) for Nanoscale.

Electronic Supplemental Information (ESI)

Title

Stacking of Nanorings to Generate Nanotubes for Acceleration of Protein Refolding

Authors

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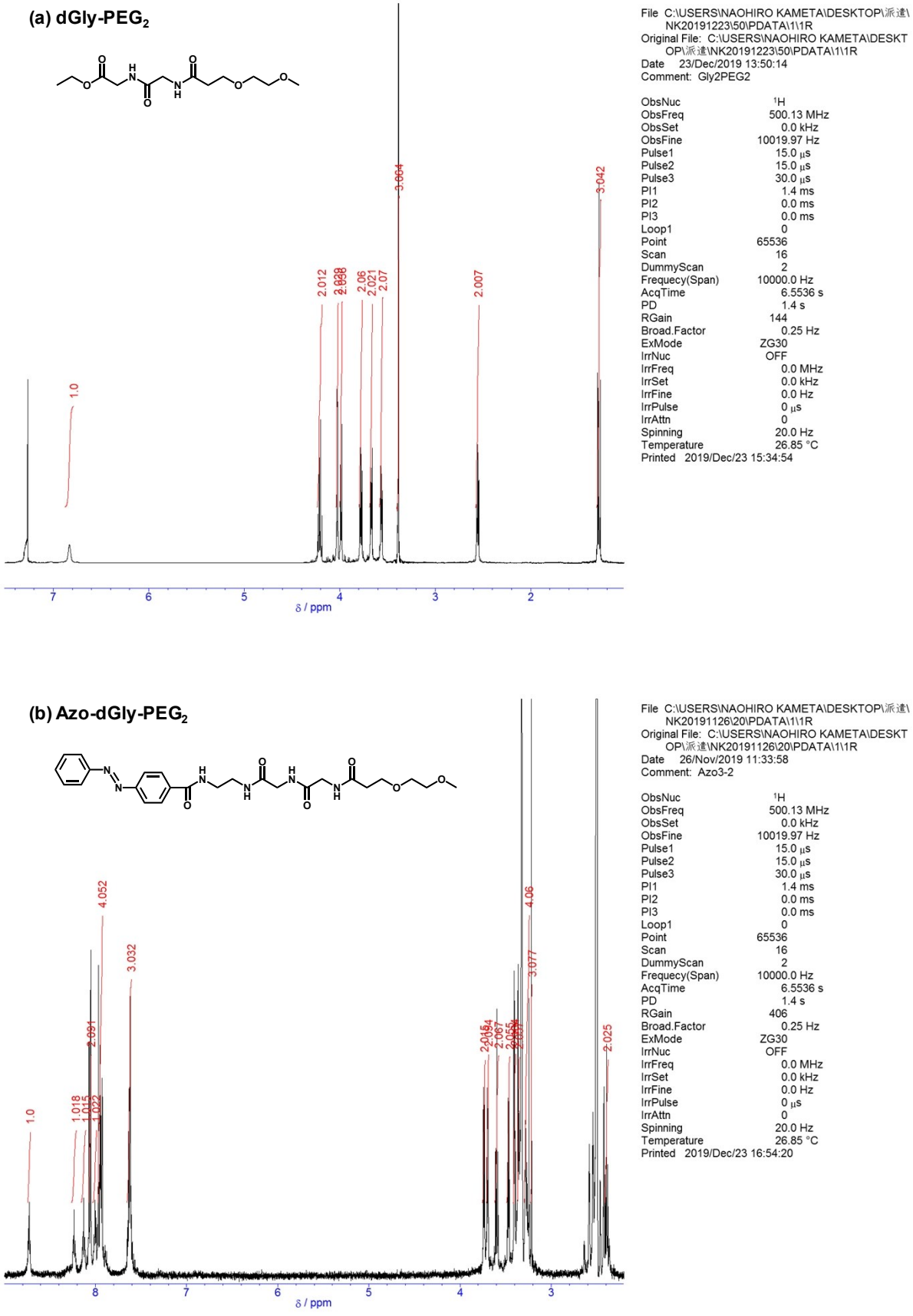

Fig. S1 ^{1}H NMR spectra of (a) dGly-PEG$_2$ in $CDCl_3$ and (b) Azo-dGly-PEG$_2$ in DMSO-d_6.

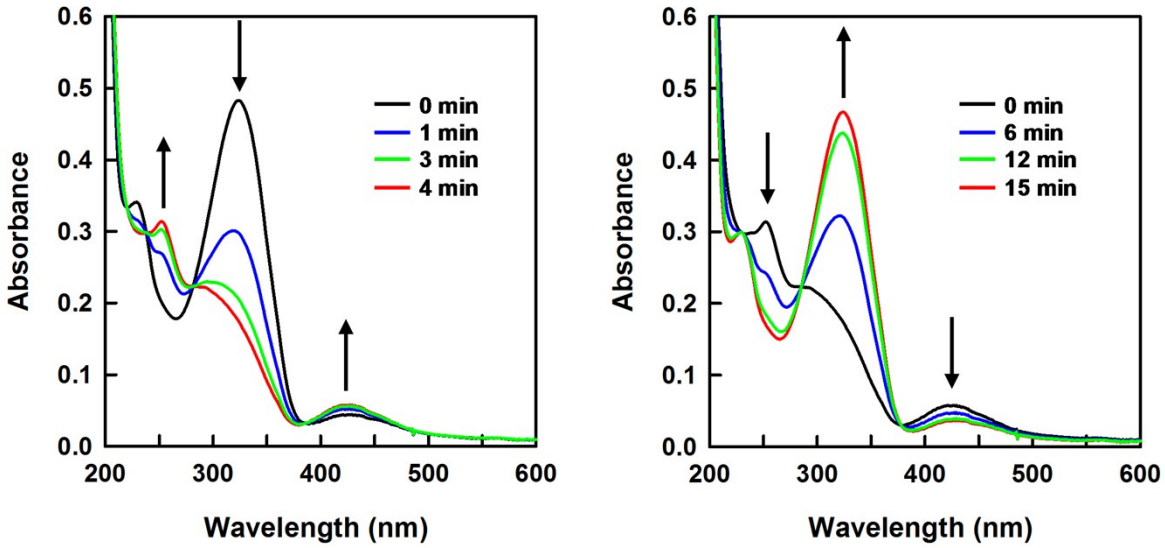

Fig. S2 (Left) Changes of absorption spectra upon UV-light irradiation of the nanotubes dispersed in water. The *trans*-to-*cis* photoisomerization of Azo-dGly within the bilayer membrane led to the morphological change of the nanotubes into the imperfect nanoring. (Right) Changes of absorption spectra upon VIS-light irradiation of the imperfect nanorings dispersed in water. The *cis*-to-*trans* photoisomerization of Azo-dGly within the bilayer membrane led to the morphological change of the imperfect nanorings into the stackable nanorings.

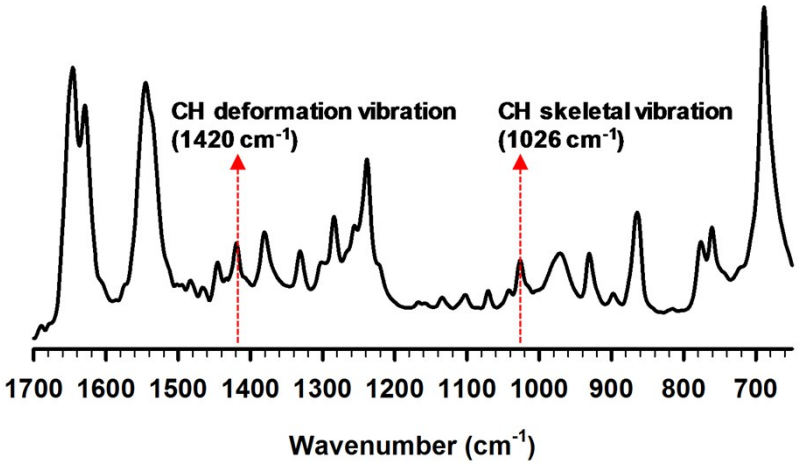

Fig. S3 IR spectra of the nanorings. The appearance of the CH deformation and CH skeletal vibration bands showed an existence of the polyglycine-II-type hydrogen bond network among Azo-dGly within the bilayer membrane of the nanorings.

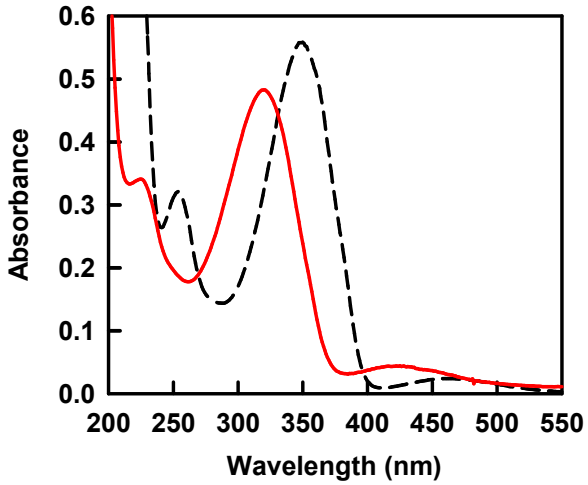

Fig. S4 Absorption spectra of the nanorings dispersed in water at 25 °C (a red solid line) and Azo-dGly molecularly dispersed in water at 90 °C (a black dot line). In the case of the nanorings, the spectrum was recorded just after VIS-light irradiation for 15 min for the morphological change of the imperfect nanorings to the nanorings accompanied with the *cis*-to-*trans* photoisomerization of Azo-dGly within the bilayer membrane. The blue-shifted absorption band of the nanorings comparing with the absorption band of Azo-dGly reveals that Azo-dGly within the bilayer membrane of the nanorings forms a *H*-type aggregate through the π-π interaction between the azobenzene moieties.

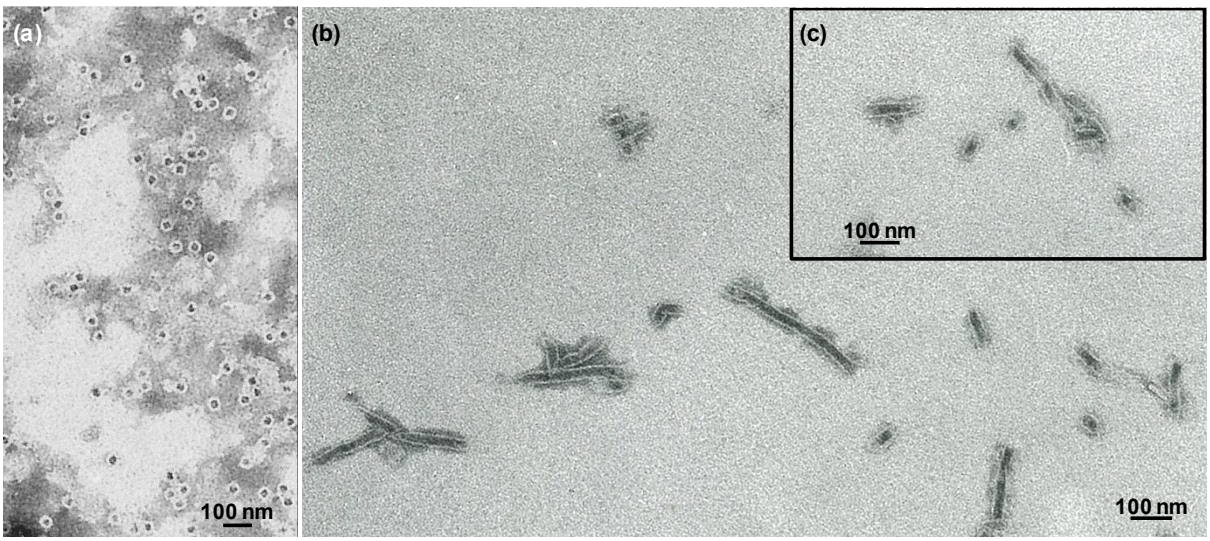

Fig. S5 TEM images of (a) the nanorings after incubation for one month at 25 °C (b) nanotubes formed by stacking of the nanorings under the lower concentration of dGly-PEG_2 (c) nanotubes without a heat-induced direct end-to-end jointing that was prohibited by dGly-PEG_2. The nanochannels were negatively stained with 2wt% phosphotungstate.

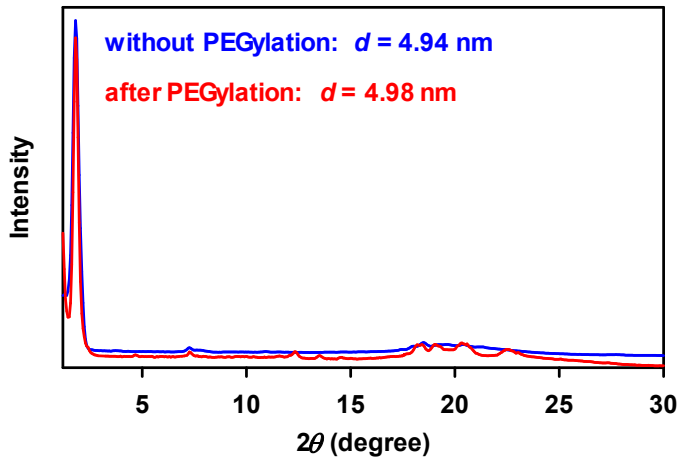

Fig. S6 X-ray diffraction patterns of the original nanorings (a blue line) and PEGylated nanorings (a red line).

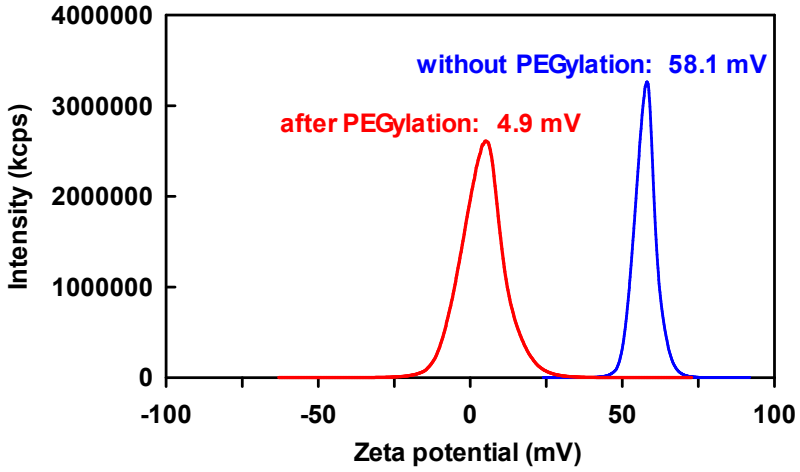

Fig. S7 Zeta potential distributions of the aqueous dispersions of the original nanorings (a blue line) and PEGylated nanorings (a red line) at pH 6.8.

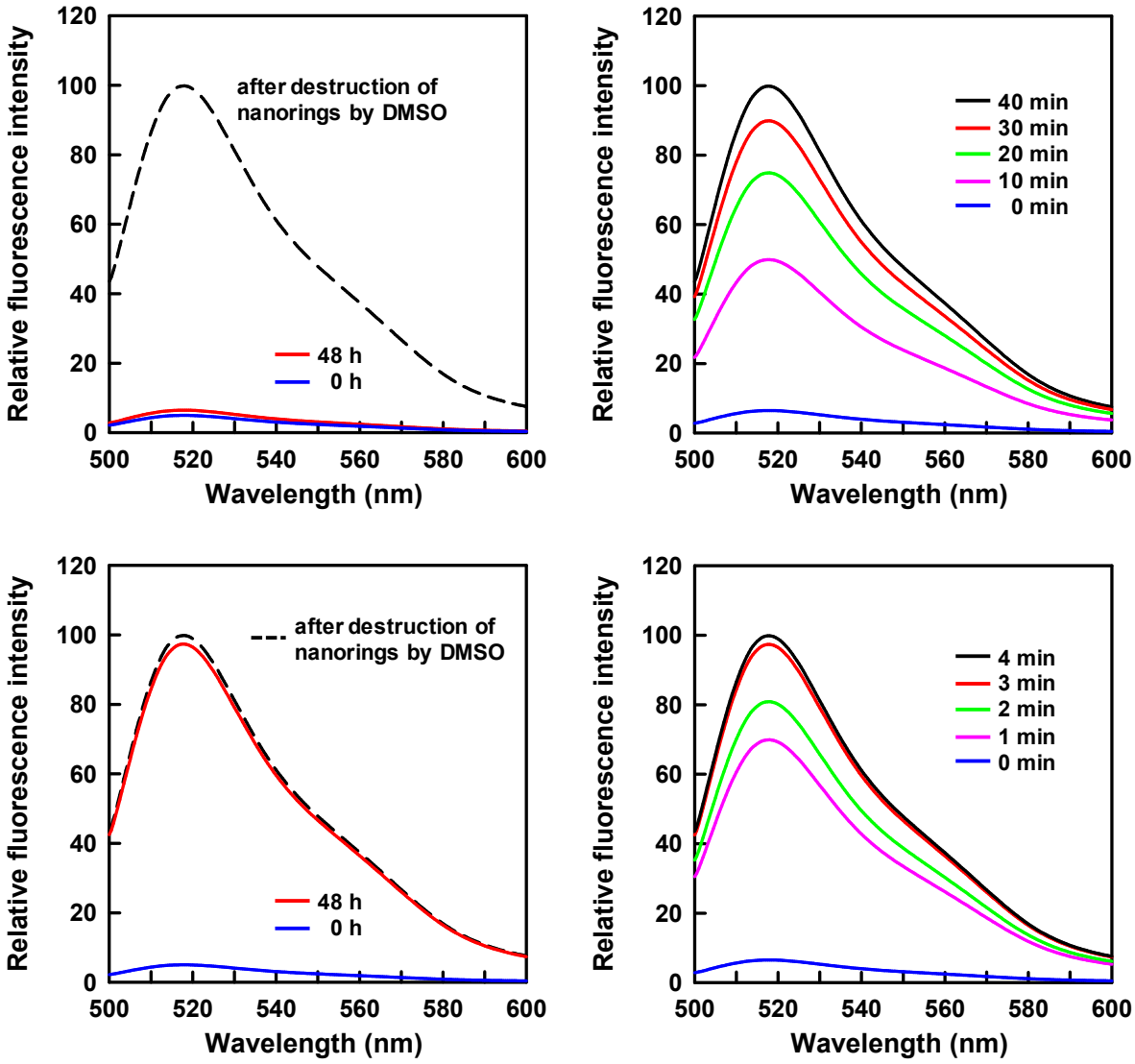

Fig. S8 Time dependence for the fluorescence spectra of 5(6)-carboxy fluorescein (CF) that was released from the PEG-NRs to the bulk solution at 25 °C under different pH conditions and different NaCl concentrations; pH 7.4 and [NaCl] = 0 mol L^{-1} (upper left), pH 8.2 and [NaCl] = 0 mol L^{-1} (upper right), pH 7.4 and [NaCl] = 1 mol L^{-1} (lower left) and pH 8.2 and [NaCl] = 1 mol L^{-1} (lower right). The encapsulated CF in the PEG-NRs has no fluorescence due to its self-dimerization, whereas free CF in the bulk solution strongly emits.

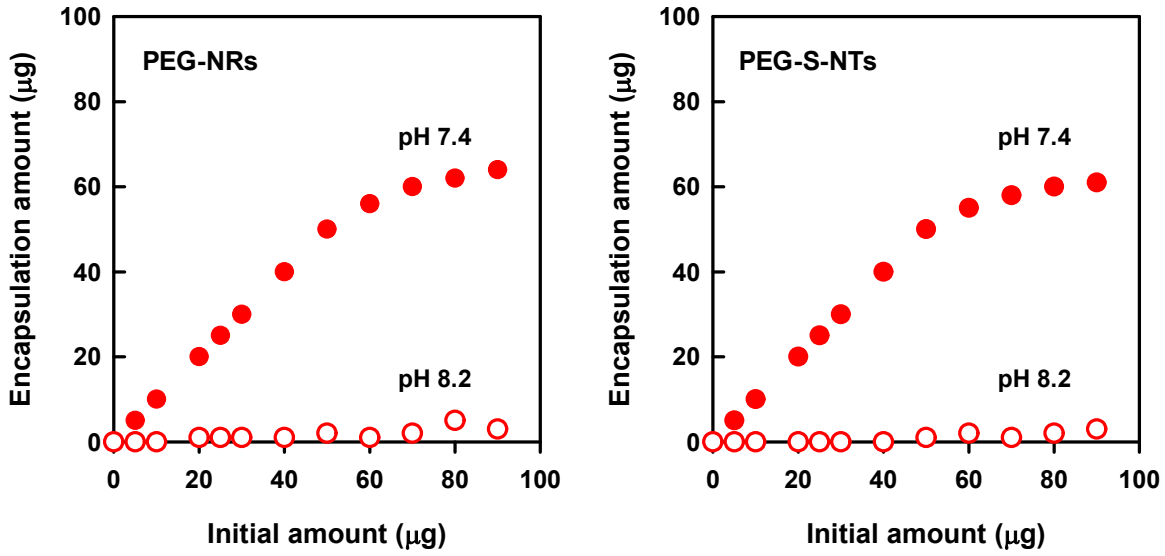

Fig. S9 Relationship between the initial amount of citrate synthase and the encapsulation amount of citrate synthase in the PEG-NRs (5 mg) and PEG-S-NTs (5 mg) at pH 7.4 and 8.2. The PEG-NRs and PEG-S-NTs were able to quantitively encapsulate 5–50 μg citrate synthase at pH 7.4.

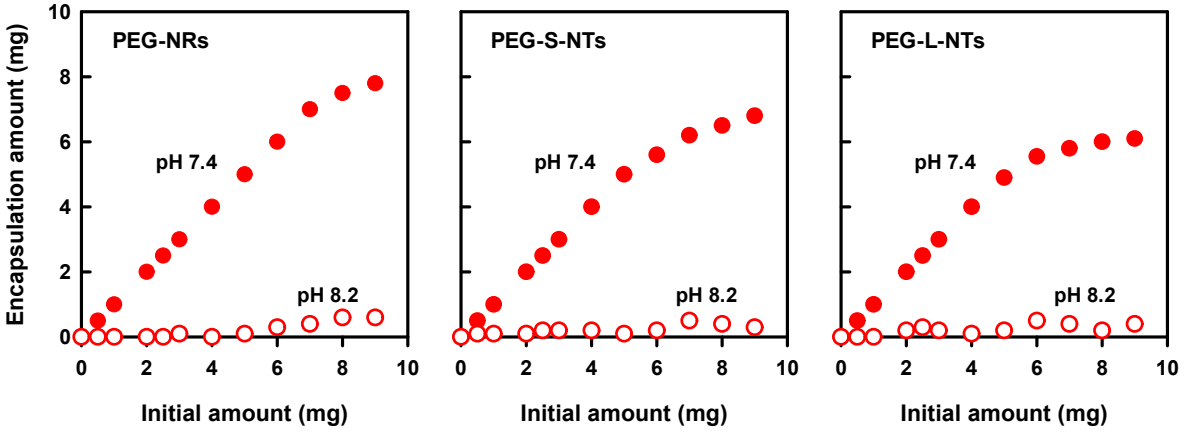

Fig. S10 Relationship between the initial amount of the denatured citrate synthase and the encapsulation amount of the denatured citrate synthase in the PEG-NRs (0.57 g), PEG-S-NTs (0.57 g) and PEG-L-NTs (0.57 g) at pH 7.4 and 8.2. The PEG-NRs was able to quantitively encapsulate 0.5–7.0 mg citrate synthase at pH 7.4. The PEG-S-NTs and PEG-L-NTs were able to quantitatively encapsulate 0.5–5.0 mg citrate synthase at pH 7.4.

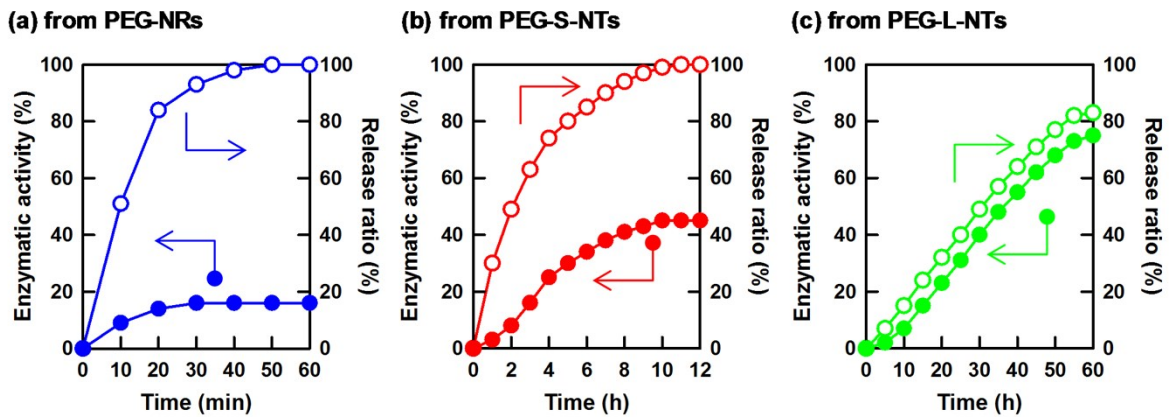

Fig. S11 (a) Left axis: Time dependence of the recovery ratio of the enzymatic activity of citrate synthase released from the PEG-NRs into the bulk solution. Right axis: Time dependence of the release ratio of the encapsulated citrate synthase from the PEG-NRs into the bulk solution. (b) Left axis: Time dependence of the recovery ratio of the enzymatic activity of citrate synthase released from the PEG-S-NTs into the bulk solution. Right axis: Time dependence of the release ratio of the encapsulated citrate synthase from the PEG-S-NTs into the bulk solution. (c) Left axis: Time dependence of the recovery ratio of the enzymatic activity of citrate synthase released from the PEG-L-NTs into the bulk solution. Right axis: Time dependence of the release ratio of the encapsulated citrate synthase from the PEG-L-NTs into the bulk solution.