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Heat and light dual switching of a single-walled carbon nanotube/thermo-responsive helical polysaccharide complex: a new responsive system applicable to photodynamic therapy†

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A thermo- and light-responsive system consisting of single-walled carbon nanotube and helical polysaccharide modified with poly(*N*-isopropylacrylamide) side-chains has been developed through supramolecular polymer wrapping. Coagulation of the complex can be induced by the external stimuli, which leads to a catch-and-release action of a porphyrin derivative.

Carbon nanotubes (CNTs) are expected as promising functional nanomaterials in various fields including medical, opto-electronic and mechanical applications due to their unique one-dimensional (1D) nanostructures and π-conjugated characters.[1] Supramolecular polymer wrapping of CNTs is one of potential techniques to improve their solvent solubilities and to change surface characters through the noncovalent modification, which is a more beneficial approach than the covalent modification that disrupts the inherent sp^2 structure and π-conjugation of CNTs.[2]

We have revealed that schizophyllan (SPG) and curdlan (Cur) that are helix-forming natural polysaccharides can wrap various functional materials such as CNTs and conjugated polymers, resulting in unique water-soluble helical complexes.[3] In case of CNTs, we have found that SPG wrapping imparts the good water solubility to single-walled CNT (SWNT).[4] In addition, a versatile modification of Cur through click chemistry has allowed us to create a polyelectrolyte type and a PEGylated type of modified Curs with sufficient water solubility.[5,6] The resultant modified Curs were able to work as aqueous dispersants for SWNT and the SWNTs wrapped with the modified Cur were assembled into highly ordered sheet-like structures through electrostatic interactions[5b] or into a CNT capsule made of SWNT and double-walled CNT by a layer-by-layer technique.[5c] These research examples reveal that CNTs can acquire new functions (particularly, in molecular assemblies) through the polysaccharide wrapping.

More recently, development of stimuli-responsive smart systems have been attracting a great deal of attention.[7] This new trend has been combined with our system: that is, we have succeeded in fabricating a thermo-responsive polymer complex consisting of PEGylated Cur and a polythiophene derivative.[6] It clearly shows that the modified Cur wrapping will be used more fruitfully to develop novel stimuli-responsive nanomaterials.

Here, to introduce a new heat and light dual responsive function into SWNT, poly(*N*-isopropylacrylamide) (pNIPAM) was grafted to Cur (Cur-pNIPAM, Scheme S1†) and SWNT wrapped with this thermo-responsive Cur-pNIPAM was newly developed (SWNT/Cur-pNIPAM complex).

Cur-pNIPAM was synthesized through click chemistry between 6-azido-6-deoxy Cur (Cur-N_3) and alkyne-terminated poly(*N*-isopropylacrylamide)[8] (for the detail see supplementary information†). SWNT was dispersed into water by using Cur-pNIPAM under ultrasonication followed by centrifugation (20 000 g).

The resultant black solution was homogeneous and the well-dispersed state of SWNTs was confirmed by a TEM observation (Fig. 1a and b). An absorption spectrum of SWNT/Cur-pNIPAM complex showed several clear peaks from the visible to near infrared (NIR) region which are ascribable to metallic and semiconductor SWNTs called M_{11}, S_{22} and S_{11} bands (Fig. 1c).[9] Upon heating at 40 °C, on the other hand, a black precipitate was formed and the solution became colourless (Fig. 1a). From a TEM image of the heated sample, generation of SWNT aggregates was confirmed (Fig. 1b). This finding indicates that SWNT/Cur-pNIPAM complex coagulates owing to heat-induced dehydration of pNIPAM side-chains. Upon cooling at 25 °C, the precipitate was dispersed into water again. Thus, SWNT/Cur-pNIPAM complex showed the reversible dispersion-coagulation action in response to temperature. It was reported

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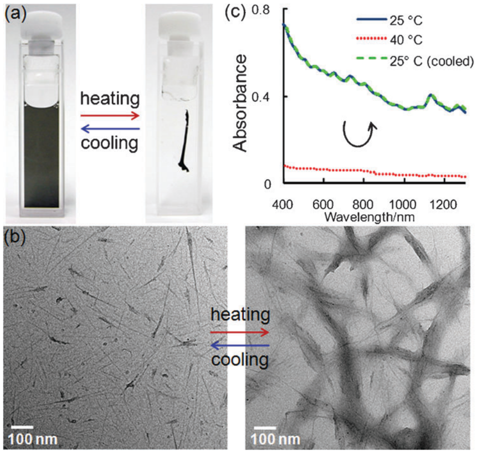

Fig. 1 (a) Photos, (b) TEM images and (c) Vis/NIR spectra of aqueous SWNT/Cur-pNIPAM complex at 25 °C and 40 °C.

that pNIPAM itself is useful as a dispersant for a CNT but the complex is easily dissociated,[10] probably because it is only physically adsorbed onto the CNT. On the other hand, SWNT/Cur-pNIPAM complex gave no precipitate even after three months or against high speed centrifugation. We consider that this high stability stems from the wrapping ability inherent to the main-chain of Cur.[11]

To evaluate thermo-responsiveness of SWNT/Cur-pNIPAM complex, a temperature sweep experiment was performed. As shown in Fig. S1, the absorbance at 500 nm increased from 33 °C due to coagulation.† The temperature was almost the same as a cloud point of Cur-pNIPAM itself (Fig. S1†) or that of pNIPAM itself.[12] This result supports a view that the thermal dehydration of pNIPAM side-chains acts as the origin of coagulation in SWNT/Cur-pNIPAM complex.

It is known that SWNT can act as a 'local heater' through thermal conversion of NIR light.[2a,13] Judging from the absorption spectrum of SWNT/Cur-pNIPAM complex in Fig. 1a, a useful absorption band exists in NIR region at 1130 nm. Then, a Nd–YAG laser (1064 nm, 240 mW) was employed to irradiate SWNT/Cur-pNIPAM complex in water. As expected, coagulation of the complex was induced within 1 min and continuous 15 min irradiation made a large aggregate only at the irradiation spot (Fig. 2). When aqueous Cur-pNIPAM itself was irradiated with the same light intensity over 1 h, no aggregate was formed (Fig. S2†). From this difference, one can confirm that coagulation of SWNT/Cur-pNIPAM complex occurs by local heating induced by energy conversion of the excited SWNT, but not by direct heating of water with the laser light.

Interestingly, heat-induced coagulation of SWNT/Cur-pNIPAM complex was successfully utilized for thermo-reversible retention and release of a porphyrin. In particular, porphyrins are well-known as phototherapeutic agents in photodynamic therapy (PDT).[14] Here, partially water-soluble 5,10,15,20-tetrakis(3,5-dehyderoxphenyl)porphyrin (DHP) was employed for the experimental convenience (Scheme S1†). By a naked eye observation, the presence of DHP in the DHP and SWNT/Cur-pNIPAM complex mixture was identified from its fluorescence emission at 25 °C (Fig. 3). On the other hand, heating up to 40 °C induced coagulation of SWNT/Cur-pNIPAM complex and the observed fluorescence intensity drastically decreased. Upon cooling to 25 °C again, the fluorescence intensity was recovered.

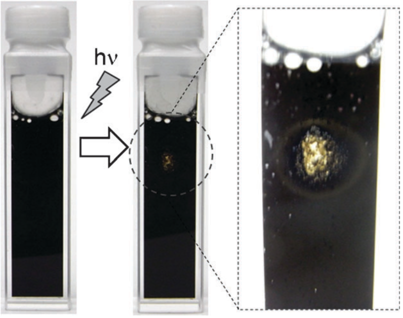

Fig. 2 Photos of SWNT/Cur-pNIPAM complex in water before or after NIR laser irradiation: Nd : YAG laser 1064 nm, 240 mW, 15 min, room temperature.

Fig. S3 compares the UV/Vis/NIR absorption and fluorescence spectra of the DHP and SWNT/Cur-pNIPAM complex mixture before heating and after a heating–cooling process. In the UV/Vis/NIR absorption spectrum of the mixture, one can recognize a sharp peak at 422 nm ascribable to a Soret band of DHP[15] and several peaks arising from SWNT exemplified by 808 nm and 1130 nm. After the heating and cooling treatment (25 °C → 40 °C → 25 °C), the absorption spectrum of the mixture gave the same peaks and intensities as those of the untreated mixture. As shown in Fig. S3a,† the fluorescence spectrum of the mixture having the emission peaks at 649 nm and 707 nm for DHP[15] showed that this system is enjoying a clear reversibility in the thermal treatment processes. To evaluate the DHP incorporation at 40 °C, the coagulated portion was separated from the mixture by the centrifuge. Fig. S3b shows the UV/Vis/NIR absorption and fluorescence spectra of the supernatant obtained through centrifugation.† In UV/Vis/NIR spectroscopy, the absorbance of DHP was negligibly weak in the supernatant. In addition,

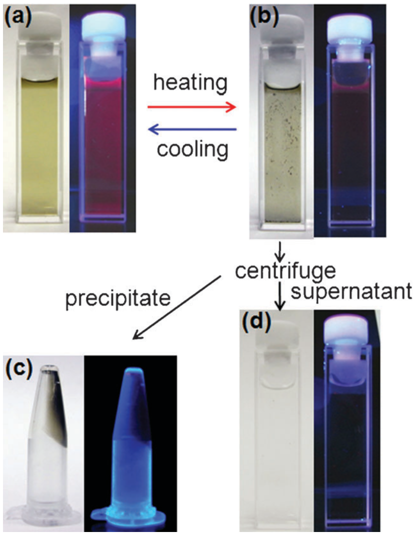

Fig. 3 Photos of the DHP and SWNT/Cur-pNIPAM complex mixture in water containing 2.5 vol% DMSO (a) at 25 °C, (b) at 40 °C, (c) solid portion collected by centrifugation at 40 °C and (d) supernatant after centrifugation at 40 °C. Left: bright image, right: fluorescence image (λ_{ex} = 365 nm), [DHP] = 25×10^{-6} M.

the DHP emission intensity drastically decreased. These results indicate that most DHP molecules were incorporated from the solution into the coagulated SWNT/Cur-pNIPAM complex. The fluorescence intensity of the collected solid was extremely weak, wherein energy transfer from DHP to SWNT could occur.

The incorporation phenomenon was further examined by using pNIPAM itself. As shown in Fig. S4 and S5,† the UV/Vis/NIR absorption and the fluorescence spectra changed reversibly and DHP was totally separated from the solution through centrifugation at 40 °C because of incorporation into the coagulated pNIPAM. However, the fluorescence intensity of DHP became quite strong at 40 °C owing to the hydrophobic environment of the coagulated pNIPAM.[16] This fact supports a view that energy transfer from DHP to SWNT occurs in the coagulated mixture of DHP and SWNT/Cur-pNIPAM complex, where DHP exists in the energy transfer range from the central SWNT.

As DHP itself has no absorption band at the NIR region, NIR laser irradiation induced similar coagulation in the DHP and SWNT/Cur-pNIPAM mixture (Fig. S6†). At the irradiated spot, the fluorescence of DHP was quenched according to the same mechanism occurring in the thermo-induced coagulation phase of the SWNT/Cur-pNIPAM complex and DHP mixture. Toshima *et al.* reported that porphyrins bearing hydroxyphenyl groups (including DHP) decompose proteins upon UV or visible light irradiation, where reactive oxygen species (ROS) are generated by photo-excitation of porphyrin and O_2.[17] In addition, porphyrins including Foscan (*meta*-tetra(hydroxyphenyl) chlorine) and Photofrin (hematoporphyrin derivatives) are practically employed for PDT.[14] In our system, the photo-excited DHP can emit the fluorescence light but it can be quenched by temperature control or by NIR laser irradiation in the presence of SWNT/Cur-pNIPAM complex. This method, therefore, is expected to develop a novel site selective PDT technique[18] by dual light irradiation using visible and NIR light sources; for example, a non-disease site close to a disease site can be protected by irradiating with NIR laser through SWNT quenching and only the disease site was selectively decomposed by visible light irradiation.

In conclusion, we have succeeded in fabricating a thermo-responsive SWNT wrapped with Cur-pNIPAM that showed the reversible heat-induced coagulation in water by temperature or by NIR laser irradiation. The references reporting the combination of SWNT and pNIPAM are still limited because of their weak interaction.[10] On the other hand, SWNT/Cur-pNIPAM complex was stable and could be applied to a catch-and-release system of a porphyrin, which is expected to be applicable to novel PDT control techniques. Therefore, we believe that modified Curs that possess broad wrapping abilities and designable side chains would become universal compounds to develop novel smart materials such as sensors, opto-electronic devices and drug delivery systems.

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