Alignment of Polysaccharide–SWNT Composites by Metal–Ligand Interactions

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The composite of terpyridine-modified polysaccharide (TPySPG) and single-walled carbon nanotube (SWNT) afforded sheet-like morphologies in the presence of ferric ion. On the basis of TEM images, it was proposed that the sheet-like morphologies are created by the metal–ligand interaction cross-linking TPySPG/SWNT components.

It is known that schizophyllan (SPG), a β-1,3-glucan polysaccharide, adopts a triple-stranded helix (t-SPG) in nature, which can be dissociated into a single chain (s-SPG) by dissolving in dimethyl sulfoxide (DMSO). The s-SPG chain can recover its original triple-stranded helix by exchanging DMSO for water.[1] We reported that β-1,3-glucans and their derivatives can act as one-dimensional (1D) hosts for nanomaterials such as carbon nanotubes, conjugated polymers, and gold nanoparticles to dissolve them in water.[2] Furthermore, the 1D composites thus formed can be arranged into regular 2D sheets utilizing covalent or noncovalent bonding interactions operating between the SPG composites. For example, we have found that β-1,3-glucans can act as a sheath for guest nano materials such as SWNTs. Oriented sheet-like morphologies were obtained by mixing SWNTs solubilized with ammonium- or sulfonium-bearing β-1,3-glucan derivatives as a result of their mutual electrostatic interactions.[3] In another case, the covalent bonding interaction of a sugar–boronate interaction was utillized.[4] However, these interactions were difficult to discuss quantitatively. Therefore, we thought that the metal–ligand interaction should make quantitative discussions possible for the construction of SWNT-based functional materials. 2,2′:6′,2″-Terpyridine (tpy), bearing three nearly-coplanar nitrogen donor atoms to the metal center, has the stronger coordination ability compared to 2,2′-bipyridine (bpy) or 1,10-phenanthroline ligands which have two nearly coplanar nitrogen donors.[5] In this paper, we report the morphological study of SPG/SWNT composites bearing tpy ligands in the SPG side chains.

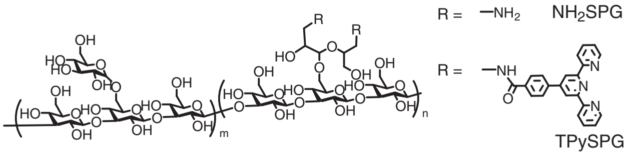

Figure 1. Molecular structures of NH$_2$SPG and TPySPG. The illustrated structure is one of two possible cleavage forms.

Aminated SPG (NH$_2$SPG, Figure 1) was synthesized by oxidation of SPG using sodium periodate followed by amination reaction: the fraction of aminated side chain glucose units was 10%.[2] The tpy moiety was synthesized by coupling methyl 4-formylbenzoate and 2-acetylpyridine in the presence of sodium hydroxide in a mixed solution of methanol and aqueous concd NH$_4$OH. After 2 days refluxing, 4′-(4-carboxyphenyl)-2,2′:6′,2″-terpyridine (TPyCOOH) was obtained from acidic solution (pH 4) adjusted with aqueous concd HCl.[6,7] Tpy-modified SPG (TPySPG) was synthesized by condensation between NH$_2$SPG and TPyCOOH using water soluble carbodiimide.[2] TPySPG was purified by dialysis. The incorporated fraction of TPy into the side chain glucose of SPG was estimated to be 1.6% by UV–vis absorption spectroscopy in DMSO (TPyCOOH in DMSO, $\varepsilon_{280} = 38000$). Water solubilization of SWNT by TPySPG was achieved through the method described previously,[2] where a mixture of SWNT ($0.5\,\mathrm{g\,L^{-1}}$, 2 mL) and TPySPG ($5\,\mathrm{g\,L^{-1}}$, 0.5 mL) in DMSO was poured into water under the sonication. The TPySPG/SWNT composite was purified three times by centrifugation (7000 G, 90 min). Finally, the TPySPG/SWNT composite was dispersed in 5 mL of water. The obtained aqueous dispersion had been clear at room temperature without precipitation of SWNTs for over 3 months (Figure S1).[12] The broad absorbance above 350 nm is attributable to the dissolved SWNTs. On the other hand, the absorption maximum for the TPy moiety appears at 280 nm (Figure S2).[12] In the TPySPG/SWNT composite, this band overlaps with that of SWNT and cannot be recognized clearly. The absorbance of the TPy moiety should be ca. 0.09 at 280 nm when it was estimated by theoretical calculation from its incorporated percentage.

The metal coordination ability of TPySPG was investigated by UV–vis absorption in aqueous media containing 10 vol % DMSO. Strangely, gradual addition of FeCl$_2$ caused a sigmoidal increase in the metal–ligand charge transfer (MLCT) band at 570 nm based on coordination of TPy and Fe^{2+} (Figure 2). The critical concentration of Fe^{2+} at this absorbance jump was about $0.2\,\mathrm{mmol\,dm^{-3}}$, suggesting that the significant interaction between Fe^{2+} and TPy moiety occurs for the first time at such a high Fe^{2+} concentration. Judging from the high stability binding constant of tpy for Fe^{2+} ($\log K_1 = 7.1\,\mathrm{dm^3\,mol^{-1}}$, $\log K_2 = 13.8\,\mathrm{dm^3\,mol^{-1}}$),[8] this Fe^{2+} concentration is unusually high. Presumably, it is relatively difficult for the TPy moieties pendent to the stiff t-SPG main chain to get together, so that the interchain 1:2 Fe^{2+}/TPy moiety complex can be formed only at such high Fe^{2+} concentration region. Thus, the jump may be related to the cooperative assembling of TPySPG: that is, once one TPySPG forms the interchain coordination complex, the subsequent complexation can occur acceleratively (Figure S3).[12]

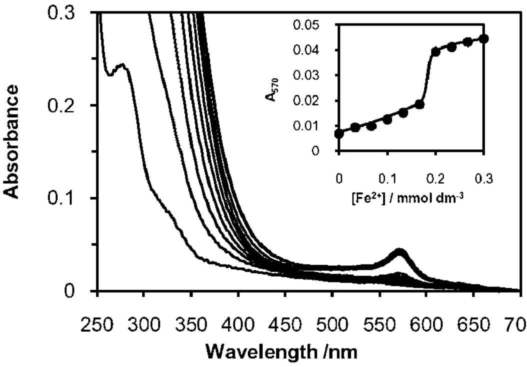

Figure 2. UV–vis spectra of TPySPG with various concentrations of $FeCl_2$ at 20 °C. Optical path length = 1 cm, [SPG unit] = 0.5 mmol dm^{-3}. Inset shows absorbance changes at 570 nm by gradual addition of $FeCl_2$.

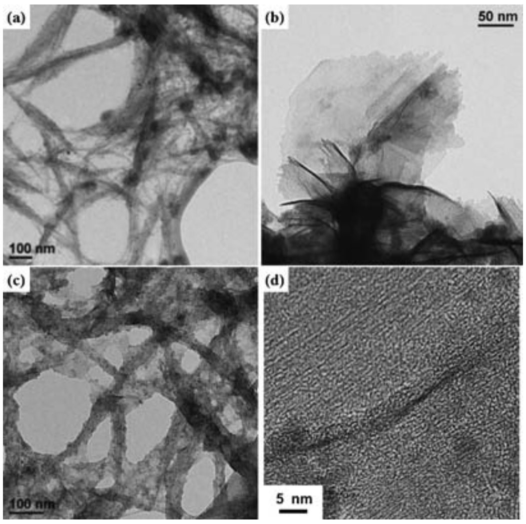

Figure 3. TEM images of (a) TPySPG/SWNT composite, (b) TPySPG/SWNT composite with Fe^{2+}, and (c) SPG/SWNT composite with Fe^{2+}. (d) High-resolution TEM image of the sheet-like structure from the TPySPG/SWNT composite with Fe^{2+}.

Figure 3 shows TEM images of the TPySPG/SWNT composite (using a 100 times diluted solution) incubated for 12 h at 20 °C with and without $FeCl_2$ (1.0 mmol dm^{-3}). In the absence of $FeCl_2$, the TEM image shows amorphous assemblies of the TPySPG/SWNT composite (Figure 3a). In the presence of $FeCl_2$, in contrast, a well-grown sheet-like structure is observed (Figure 3b). From high-resolution TEM observation of this picture, one can confirm that SWNTs are aligned in the same direction to form a sheet-like morphology (Figure 3d). In addition, the EDS analysis of this sample indicated that the sheet-like structure is composed of SWNTs, sugar, and iron (Figure S4).[12] In contrast, no sheet-like structure was observed when $FeCl_2$ was mixed with unmodified-SPG/SWNT composite (Figure 3c), again supporting the importance of the Fe^{2+}–TPy interaction. When the Fe^{2+} concentration was lowered to 0.01 or 0.1 mmol dm^{-3} in the TPySPG/SWNT composite dispersion, no sheet-like structure or only a very minute oriented domain was obtained. This Fe^{2+} concentration dependence is consistent with the result of Fe^{2+} titration for TPySPG. These results support the view that the regular assembling of SWNTs was achieved by the metal–ligand interaction between Fe^{2+} and pendant TPy groups. Further evidence for the importance of the Fe^{2+}–TPy interaction was obtained from the fact that the sheet-like morphology disappeared when 0.1 mol dm^{-3} of ethylenediamine-*N*,*N*,*N′*,*N′*-tetraacetic acid (EDTA) disodium salt was added to the sample solution (Figure S5).[12] This is clear due to the competitive binding of EDTA with Fe^{2+} which destroys the aligned structure supported by the coordination bonds. We also tested other metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}): although some of them afforded the very minute oriented domain, they were all much smaller than that constructed by Fe^{2+}.

We have considered what the origin of this difference is for metal ions. It is well known that Fe^{2+} ion has a smaller stability constant than other metal ions in the Irving–Williams series.[9] In addition, the stability of 1:1 complex between Fe^{2+} and tridentate tpy ligand is lower than other metal ions because of its strained electron orbital of the coordination axis.[8] Consequently, the 1:2 complex, rather than the 1:1 complex, is obtained predominantly. One may regard that this complexation characteristic of $K_{1:2} > K_{1:1}$ is a sort of "homotropic allosterism."[10] In our previous studies, it was demonstrated that "aligners" bearing such allosteric functions are capable of organizing stiff polymers into 2D sheet structures.[11] We now consider, therefore, that the Fe^{2+}–TPy interaction bearing such allosteric functions is particularly useful to create the sheet-like structure from the TPySPG/SWNT composite.

In conclusion, we have shown that the sheet-like morphology, in which SWNTs are oriented into the one direction, can be constructed by the metal–ligand interaction between Fe^{2+} and the TPySPG/SWNT composite. Although the cross-linking points consisting of the coordination bond seem to be relatively low, it exerts the sufficient capability to arrange the TPySPG/SWNT composite in a 2D fashion. We now consider that introduction of coordination complexes showing fluorescence emission or redox activity will provide new functional materials in conjugation with oriented SWNT sheets.

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References and Notes

1 K. Miyoshi, K. Uezu, K. Sakurai, S. Shinkai, *Chem. Biodivers.* **2004**, *1*, 916.

2 K. Sakurai, K. Uezu, M. Numata, T. Hasegawa, C. Li, K. Kaneko, S. Shinkai, *Chem. Commun.* **2005**, 4383.

3 M. Numata, K. Sugikawa, K. Kaneko, S. Shinkai, *Chem.—Eur. J.* **2008**, *14*, 2398.

4 S. Tamesue, M. Numata, K. Kaneko, T. D. James, S. Shinkai, *Chem. Commun.* **2008**, 4478.

5 E. C. Constable, *Chem. Soc. Rev.* **2007**, *36*, 246.

6 A. Winter, A. M. J. van den Berg, R. Hoogenboom, G. Kickelbick, U. S. Schubert, *Synthesis* **2006**, 2873.

7 H. Wolpher, S. Sinha, J. Pan, A. Johansson, M. J. Lundqvist, P. Persson, R. Lomoth, J. Bergquist, L. Sun, V. Sundström, B. Åkermark, T. Polívka, *Inorg. Chem.* **2007**, *46*, 638.

8 R. H. Holyer, C. D. Hubbard, S. F. A. Kettle, R. G. Wilkins, *Inorg. Chem.* **1966**, *5*, 622.

9 H. Irving, R. J. P. Williams, *J. Chem. Soc.* **1953**, 3192.

10 M. Takeuchi, M. Ikeda, A. Sugasaki, S. Shinkai, *Acc. Chem. Res.* **2001**, *34*, 865.

11 Y. Kubo, Y. Kitada, R. Wakabayashi, T. Kishida, M. Ayabe, K. Kaneko, M. Takeuchi, S. Shinkai, *Angew. Chem., Int. Ed.* **2006**, *45*, 1548.

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