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Porphyrin / Single-Walled Carbon Nanotubes Composites in DMF

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Our interest is the preparation of *noncovalent sidewall-functionalized soluble carbon nanotubes*,[1,2] which would enable further chemical and physicochemical applications of carbon nanotubes. Porphyrins are dyes, which act as a photoexitation center in an electron transfer system, and their composites with carbon nanotubes are expected as an effective photoelectron material. We present here the solubilization and functionalization of single-walled carbon nanotubes (SWNTs) with zinc protoporphyrin IX (ZnPP) in organic solvents.[3]

Sonication of SWNTs in a DMF solution of ZnPP gave a reddish black-colored transparent DMF dispersion/solution, which was used for measurements.

AFM images of p-SWNTs-ZnPP dispersion/solution showed dispersed SWNTs with 0.5 - 1 μm in length and ca. 1 nm in height (Figure 1), indicating the existence of individually dissolved SWNTs in the ZnPP solution.

UV-visible-near IR (NIR) spectra of p-SWNTs-ZnPP dispersion/solution showed characteristic absorption come from the nanotubes dissolved in the ZnPP solution in the visible-NIR region (Figure 2a), which is almost identical with that of the reported HiPco SWNTs.

In order to remove the ZnPP which is not concerned with the solubilization of the SWNTs, filtration and resolubilization procedure were carried out.

UV-visible-NIR spectrum for the resolubilized SWNTs in DMF showed the characteristic absorption of the nanotubes in visible-NIR region again whereas exiguous absorption was observed for Soret band of the ZnPP in the UV-visible region (Figure 2c), which could be concerned with the solubilization of the SWNTs. Fluorescence of the ZnPP in the resolubilized SWNTs-DMF dispersion/solution was quenched compared with that of the almost same concentration of a DMF solution of ZnPP. This is the direct evidence indicating the interaction between the nanotube sidewall and ZnPP in DMF solution.

1) N. Nakashima, et al., *Chem. Lett.*, **32**, 456-457 (2003).
2) N. Nakashima, Y. Tomonari, H. Murakami, *Chem. Lett.*, **2002**, 638-639.
3) H. Murkami, et al., *Chem. Phys. Lett.*, **378**, 481-485 (2003).

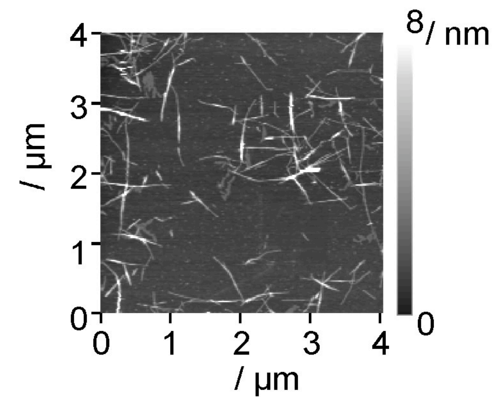

Figure 1. Typical AFM image for a p-SWNTs-ZnPP DMF dispersion/solution.

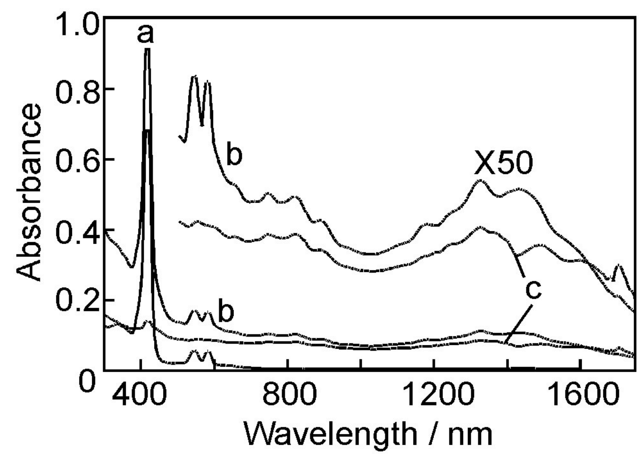

Figure 2. UV-visible-NIR spectra forDMF solutions of (a) ZnPP, (b) p-SWNTs-ZnPP, and (c) resolubilized p-SWNTs.

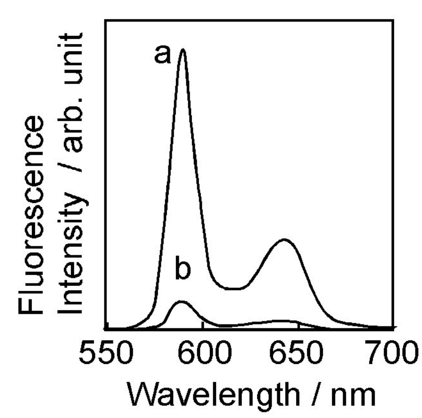

Figure 3. Fluorescence spectra of (a) ZnPP DMF solution ([ZnPP]=1.3μM) and (b) resolubilized p-SWNTs DMF solution ([ZnPP]= ca.1.3μM). Excitation, 420 nm.