doi:10.1246/cl.2011.538

Facile Evaluation of Interactions between Carbon Nanotubes and Phthalocyanines Using Silica Spheres Coated with Ultrathin-layers of Single-walled Carbon Nanotubes

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A simple and versatile method to evaluate the interactions between four different phthalocyanine dyes and carbon nanotube surfaces using silica spheres coated with ultrathin-layers of single-walled carbon nanotubes (SWNTs) is described. The well-isolated SWNTs immobilized on the silica spheres acted as effective adsorption sites for the dye molecules, and the interactions between them were evaluated by measuring the absorbance change in the supernatant solutions after simple mixing.

Significant efforts have been made in fundamental studies and applications of carbon nanotubes (CNTs).[1] The exfoliation of strong bundles of CNTs is a primary step to initiate these investigations. The adsorption of molecules onto the CNT surfaces is often utilized for the exfoliation of CNT bundles, resulting in the dispersion/solubilization of the CNTs in solution.[2] A systematic study for understanding the interactions between molecules and CNTs may provide useful indications for the fundamental science of CNTs and their applications. Several methods have been proposed to evaluate the degree of CNT–molecule interaction including the assessments of dispersed CNTs in analyte solutions[3,4] Raman shifts occurring after molecular adsorption on the CNTs[5] and fluorescent quenching of the molecules upon adsorption onto the surfaces of the CNTs.[6–8] However, a clear analysis for the interactions using these methods is difficult. Recently, we reported a simple, quick, and qualitative method to evaluate the CNT–molecule interactions based on a chromatography technique using CNT-coated silica spheres as the stationary phase[9] that enables systematic studies to rank the CNT–molecule interactions depending on the molecular structures. During the study, we found that molecules having an extremely strong interaction on the CNT surfaces remain on the column for quite a long time, resulting in a difficult analysis.

Here we describe a simpler method than chromatography to evaluate the CNT–molecule interactions using CNT-coated silica spheres; namely, the CNTs adsorbed onto silica spheres acted as an adsorption site, and after mixing, the amount of remaining molecules in the supernatant solution was evaluated. Homogeneous and ultrathin-layer (monolayer-level)-coated CNTs on silica required a very small amount of CNTs for the evaluations. As shown in Figure 1, in this study, four different phthalocyanine derivatives (PCs) were used as the analyte.[10] We have already found that the PCs possess a strong affinity for the CNT surfaces, and we were unable to obtain an eluent for the chromatography experiment due to the very strong binding to the CNT-coated silica.

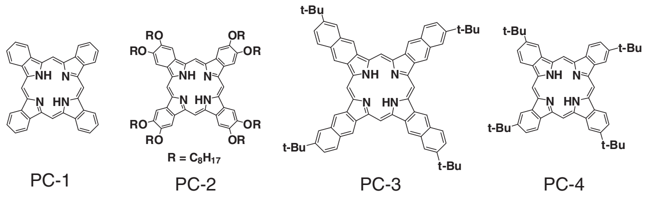

Figure 1. Chemical structures of PC-1, PC-2, PC-3, and PC-4.

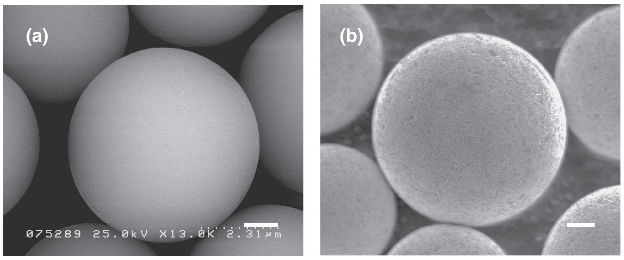

Figure 2. Scanning electron microscope images of (a) silica sphere and (b) SWNT–silica. Scale bars: 1 µm.

Single-walled carbon nanotube (SWNT)-coated silica spheres were prepared according to our previous paper.[11] Simply, SWNTs dispersed in 1-methyl-2-pyrrolidinone (NMP) were mixed with silica spheres (ca. 5.0 µm diameter). The obtained SWNT-coated silica spheres (SWNT–silica) possessed a rather homogeneous monolayer-leveled SWNT layer on the silica spheres (Figure 2). The PCs were simply mixed with the SWNT–silica in THF. After the addition of the SWNT–silica to the PC solutions, the mixture was shaken for 60 min to produce a sediment. The grayish SWNT–silica was found to become darker, suggesting the adsorption of the PCs on the SWNT–silica surfaces. On the other hand, the color of the supernatant solution became lighter. Figure 3 shows the vis-absorption spectra of the supernatant solutions, in which the characteristic Q-band peaks of the PCs decrease with the increasing amounts of the added SWNT–silica. On the other hand, the addition of the silica spheres (120 mg) not coated with the SWNTs induced no substantial change in the absorbance.[12] In Figure 4a, the absorbance of the PCs in the supernatant solutions at the maximum peaks is plotted as a function of the amount of the SWNT–silica added to the solution. A linear decrease in the absorbance was observed for all the PCs. Of interest, the slopes

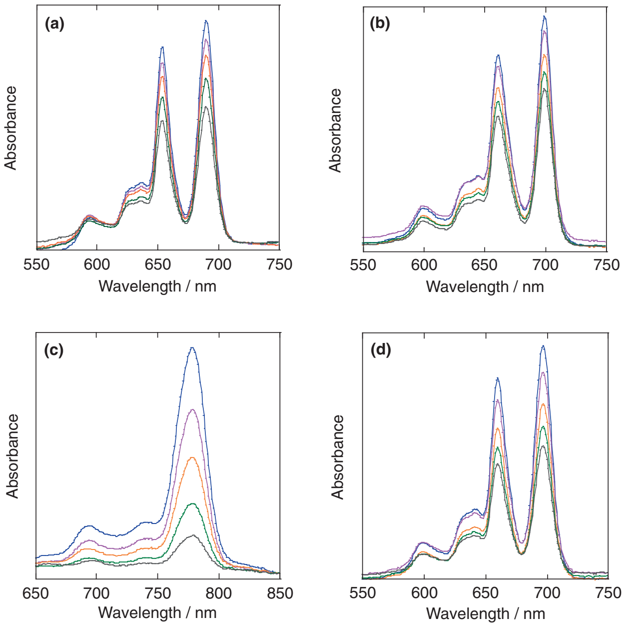

Figure 3. Absorption spectra of PC-1 (a), PC-2 (b), PC-3 (c), and PC-4 (d) in THF after the addition of 0 (blue), 30 (red), 60 (orange), 90 (green), and 120 mg (blown) of SWNT–silica.

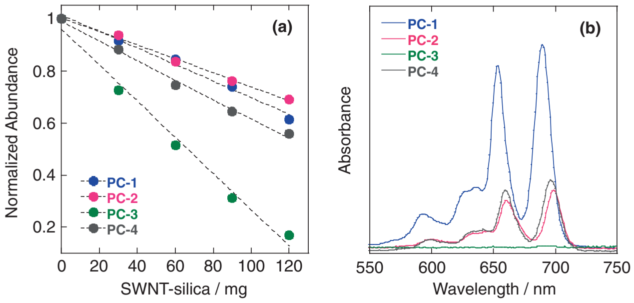

Figure 4. (a) Plots of normalized absorption of PC-1 (blue), PC-2 (red), PC-3 (green), and PC-4 (gray) as a function of the SWNT–silica addition. (b) Absorption spectra of SWNT–silica supernatant adsorbed by PC-1 (blue), PC-2 (red), PC-3 (green), and PC-4 (gray) in THF.

for each PC differed; namely, the slopes showed a strong PC chemical dependence. Since a stronger interaction between the PCs and the SWNT–silica leads to an efficient adsorption of the PCs onto the SWNT surfaces, the higher slope indicates stronger SWNT–PC molecular interactions. Based on the plots, it was revealed that the order of the PCs for the interaction with the SWNTs is: PC-3 > PC-4 > PC-1 ≈ PC-2. We have reported that the longer linear polyacene shows a stronger interaction compared to the nonlinear analogs due to the parallel stacking onto the one-dimensional SWNT structure. Therefore, the strongest interaction of PC-3 having the longest conjugation structure agreed with the previous chromatographic evaluation. The strongest interaction of PC-3 was also confirmed by redissolution of the SWNT–silica in THF after the adsorption experiments. As shown in Figure 4b, the characteristic Q-band peaks were observed in the supernatant of the redissolution solutions of PC-1, PC-2, and PC-4, while no such peak was detected from the PC-3 solution. This suggests that PC-3 strongly and nondynamically adsorbs onto the SWNT surfaces. In the chromatographic evaluation, such a static adsorption provides no eluent and, what is worse, may contaminate the stationary phase of the column. The present method is superior since it enables the evaluation of both the static and dynamic adsorption on the SWNT surfaces and only requires an absorption measurement after simple shaking. Therefore, this method is a promising tool to evaluate other static adsorption systems, such as the DNA–SWNT hybrids.[13] It should be emphasized that an extremely small amount of SWNTs is sufficient for the evaluation. For instance, only 76 µg of the SWNTs was used for the preparation of the 120 mg SWNT–silica. In addition, the as-produced SWNTs are not suitable for use in the evaluation since they form different degrees of bundles and may have lower surface areas, resulting in data variation depending on the types of SWNTs used for the evaluations. Silica spheres homogeneously coated by the SWNTs are reproducible, and therefore, the present method is reliable to evaluate the SWNT–molecular interactions.

In conclusion, we have developed a facile method to evaluate the interactions between aromatic molecules and SWNTs using SWNT-coated silica spheres. Simple mixing of the analyte solution with the SWNT–silica resulted in an absorption change of the analyte solution, which was analyzed to evaluate the interactions. The present method is applicable for both nondynamic and dynamic molecular adsorption processes on the SWNT surfaces and enables the analysis of a variety of molecules. This simple and versatile evaluation method is powerful enough to investigate the affinity between molecules and SWNTs, which is important in order to understand the fundamental features of SWNTs.

This work was supported by the Global COE Program "Science for Future Molecular Systems" and Nanotechnology Network Project (Kyushu-area Nanotechnology Network) from the Ministry of Education, Culture, Sports, Science and Technology, Japan.

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