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Enhanced Fluorescence from Rhodamine B Intercalated into Hydrophobized Graphite Oxides Containing Perfluoroalkyl Chains

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Fluorescence from Rhodamine B in hydrophobized graphite oxide was greatly enhanced by perfluoroalkyl chains, likely due to the lower radiationless quenching by low vibrational C–F bonds.

Recently, solid materials such as zeolites, mesoporous silicas, and layered compounds are attracting interest as matrices of photo-functional molecules for which the aggregation state and orientation are controlled.[1–3] In this context, we report that the aggregation and orientation of rhodamine B molecules can be controlled in graphite oxides hydrophobized by alkylamine.[4] Potential applications of these materials include solid lasers in which dye molecules are dispersed in thin-film intercalation compounds at high concentrations without aggregation. A large amount of rhodamine B molecules were dispersed monomerically in the system described above. However, the emission from rhodamine B was much weaker than expected from the absorption value. One reason for the low emission might be quenching by radiationless transitions caused by vibrational excitation. Emission from neodymium complexes is greatly enhanced when the ligand possesses perfluoroalkyl chains instead of alkyl chains.[5] Radiationless quenching by vibrational excitation of C–H bonds is greatly suppressed by introducing low vibrational C–F bonds into the ligand. The emission from rhodamine B molecules also can be enhanced by introducing C–F bonds into hydrophobized graphite oxide. For this study, a perfluoroalkyl group was introduced into hydrophobized graphite oxide and the effect of the perfluoroalkyl group on the emission behaviour of rhodamine B in the resulting intercalation compounds was investigated.

Graphite oxide (GO) with a composition of $C_8O_{4.0}H_{3.0}$ was used as a starting material.[6] The perfluoroalkyl group was introduced into GO via Si–O covalent bonding using a silylating reagent containing a perfluoroalkyl chain (1*H*,1*H*,2*H*,2*H*-perfluorodecyltrichlorosilane) in the same manner as that employed for the silylation of GO by octyltrichlorosilane.[6] A composition of $(C_{10}F_{17}H_4SiOH)_{0.48}C_8O_{4.0}H_{2.0}(C_4H_9NH_2)_{0.28}$ (hereafter abbreviated as C10FSi-GO) was provided by elemental analysis. Intercalation of various amounts of *n*-hexadecylamine (designated C16) was performed yielding products with C16/GO ratios of 0.5–3.5.[4] C10FSi-GO was mixed with C16 in a pestle in the presence of a small amount of hexane until the solvent evaporated. The resulting powder was dried at 60 °C for 12 h. Some weight decrease ($\approx$7%) was observed before the weight of the samples stabilized, suggesting a loss of C16 and/or substitution of residual butylamine in the starting material by C16, which are difficult to distinguish them. The sample was designated $(C16)_x$C10FSi-GO ($x = 0.5$–3.5) using nominal C16/C10FSi-GO ratios. For comparison, $(C16)_x$C8HSi-GO ($x = 1.0$ and 3.0) without fluorine also was prepared in the same manner, starting with $(C_8H_{17}SiOH)_{0.45}C_8O_{4.0}H_{2.2}(C_4H_9NH_2)_{0.24}$.[6] Thin films of rhodamine B (RhB)-intercalated $(C16)_x$C10FSi-GO samples were prepared by casting a chloroform solution of the intercalation compound and RhB molecules on a quartz substrate. Absorption and fluorescence spectra of RhB-intercalated $(C16)_x$C10FSi-GO samples were measured using Hitachi U-3010 and Hitachi F-2500 with an excitation wavelength of 510 nm. X-ray diffraction patterns of the samples were recorded with Rigaku Rint-2100 using Cu Kα radiation.

Figure 1 shows the X-ray diffraction patterns of $RhB_{0.01}$-$(C16)_x$C10FSi-GO samples with various C16 contents. Introduction of C16 molecules into C10FSi-GO increased the interlayer spacing, suggesting intercalation of C16 molecules. Two broad peaks at $2\theta = 3.8$ and 7.3° were observed for $RhB_{0.01}(C16)_{0.5}$-C10FSi-GO, indicating a layered structure with an interlayer spacing of 2.4 nm. These peaks shifted to higher angles $2\theta = 2.98°$ with an increase in C16 content. The interlayer spacing of 2.96 nm was very similar to that observed for C16-intercalated GO with a bilayer structure of C16 with a relatively small inclined angle against GO layer.[4] When C16 content became 1.5 or larger, a new and sharper peak at $2\theta = 1.76°$ appeared, suggesting the formation of new phase with an interlayer spacing of 5.0 nm. The peak at $2\theta = 2.98°$ almost disappeared in the pattern for $RhB_{0.01}(C16)_{2.5}$C10FSi-GO, indicating that the orientation of long C16 molecules (molecular length: 2.31 nm) changed to a bilayer structure with a greater inclined angle (ca. 72°) against the GO layer (thickness: 0.6 nm). The diffraction patterns of $(C16)_x$C10FSi-GO samples without RhB were very similar to those obtained above, and the diffraction peak due to RhB crystals deposited on the surface of the sample was absent, which suggests that RhB molecules were intercalated into the compounds at a low Rh B loading level.

Figure 2 shows the absorption spectra of $RhB_{0.01}(C16)_x$-

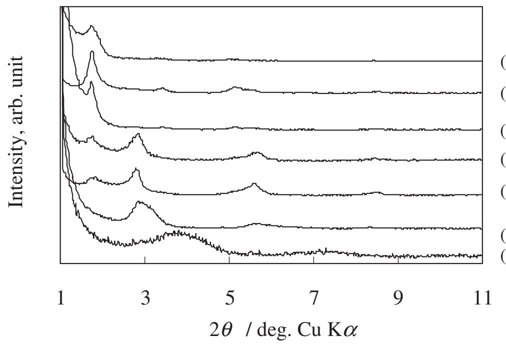

Figure 1. X-ray diffraction patterns of RhB-containing graphite oxides hydrophobized by C16 and perfluorodecyltrichlorosilane with various C16 contents. C16/GO = (A):0.5, (B):1.0, (C):1.5, (D):2.0, (E):2.5, (F):3.0, and (G):3.5 (RhB/GO = 0.01).

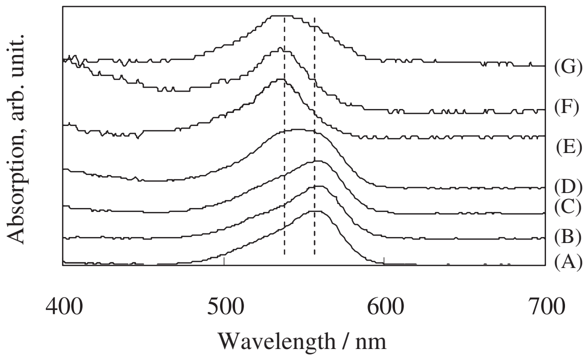

Figure 2. Absorption spectra of RhB-containing graphite oxides hydrophobized by C16 and perfluorodecyltrichlorosilane with various C16 contents. C16/GO = (A):0.5, (B):1.0, (C):1.5, (D):2.0, (E):2.5, (F):3.0, and (G):3.5 (RhB/GO = 0.01).

C10FSi-GO samples with various C16 contents. When C16 content was low, the absorption maximum was observed at 560 nm with a shoulder at 530 nm, similar to that for $(C16)_{0.6}GO$ with RhB/GO < 0.05 as reported previously.[3] However, the peak at 530 nm dominated when the RhB/GO ratio became greater than 2.0, because RhB molecules were introduced into the site with a different environment from that in $(C16)_x$C10FSi-GO with a lower C16 content. At low C16 content, the surface of the GO layer is not completely covered with C16, and polar RhB molecules with COOH groups interact with oxygen-containing groups of the GO layer, indicating a polar environment. In contrast, as the C16 content increases, the surface of GO becomes completely covered with C16 and no space between C16 molecules is available for RhB molecules. The new intercalation site for RhB molecules may be the space arising from the difference in alkyl chain lengths of C16 and C10FSi that is located far away from the polar GO surface. This space is surrounded by alkyl groups, most likely perfluoroalkl groups, and would be nonpolar. The absorption peak due to π–π^* transitions normally shifts to shorter wavelengths in a less polar environment. Therefore, the shift of the absorption peak observed can be ascribed to a change in the molecular environment.

Figure 3 shows the emission spectra of RhB intercalated into $(C16)_x$C10FSi-GO samples. The intensity was normalized by the absorption at 510 nm of each sample. When C16 content was low, a peak at 580 nm was observed. A new peak at 558 nm appeared when C16 content was greater than 1.5. The normalized intensity became almost constant for $(C16)_x$C10FSi-GO samples with C16 content larger than 2.5. Considering the X-ray and absorption data, emission peaks at 580 and 558 nm are due to RhB monomers intercalated into $(C16)_x$C10FSi-GO with small and large interlayer spacings, respectively. The normalized intensity of the latter was more than 20 times larger than that of the former.

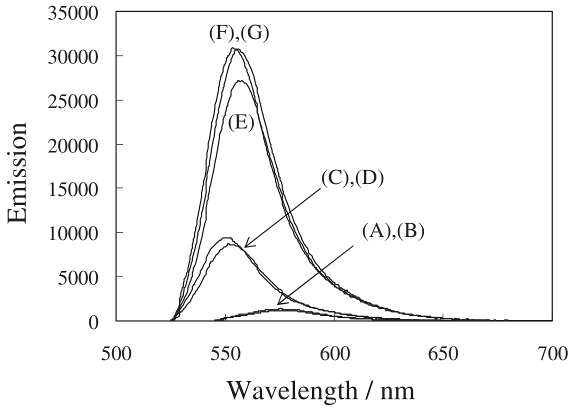

Figure 3. Normalized emission spectra of RhB-containing graphite oxides hydrophobized by C16 and perfluorodecyltrichlorosilane with various C16 contents. C16/GO = (A):0.5, (B):1.0, (C):1.5, (D):2.0, (E):2.5, (F):3.0, and (G):3.5 (RhB/GO = 0.01).

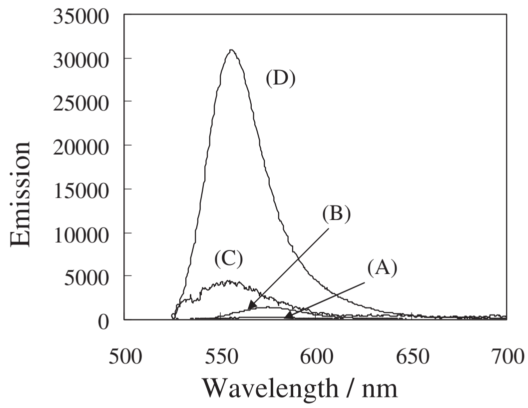

Figure 4. Normalized emission spectra of RhB in (A): $(C16)_{1.0}$C8HSi-GO, (B): $(C16)_{1.0}$C10FSi-GO, (C): $(C16)_{3.0}$C8HSi-GO, and (D):$(C16)_{3.0}$-C10FSi-GO with RhB/GO ratio of 0.01.

Figure 4 shows normalized emission spectra of RhB in $(C16)_x$C10FSi-GO samples with C16/GO ratios of 1.0 and 3.0, along with those of $(C16)_x$C8HSi-GO samples with C16/GO ratios of 1.0 and 3.0. Interlayer spacings of $(C16)_x$C8HSi-GO samples were 2.94 and 4.90 nm for samples with $x = 1.0$ and 3.0, respectively, suggesting that these compounds possess an orientation of C16 molecules similar to those in the gallery of GO. The absorption and emission maxima of RhB also were observed at positions very similar to those in $(C16)_x$C10FSi-GO samples. The larger normalized intensity (about 15-fold) for the samples with larger interlayer spacings also was observed, indicating that RhB molecules are introduced in sites of $(C16)_x$C8HSi-GO similar to those of $(C16)_x$C10FSi-GO samples. The normalized intensity observed for RhB in $(C16)_x$C10FSi-GO samples was much larger than those in $(C16)_x$C8HSi-GO samples by 5.0 and 7.4 times for the samples with small and large interlayer spacings, respectively. The higher normalized fluorescence intensity from RhB observed in $(C16)_x$C10FSi-GO compared to that in $(C16)_x$C8HSi-GO can be ascribed to lower radiationless quenching by low vibrational C–F bonds as reported for neodymium complexes.[5] Currently, the reason why normalized emission intensities from RhB increase in samples with a larger interlayer spacing is not known. However, it is interesting that emissions from organic dyes were enhanced for intercalation compounds containing perfluoroalkyl chains. The data presented here will aid in the design of new solid laser materials.

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