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Preparation of self-assembled fluorinated molecular aggregates, fluorescein nanocomposites: an extremely enhanced light absorption in nanocomposites

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Abstract Self-assembled fluorinated molecular aggregates formed by fluoroalkyl end-capped *N*-(1,1-dimethyl-3-oxobutyl)acrylamide oligomers, *N*,*N*-dimethylacrylamide oligomers, and acrylic acid oligomers in methanol could selectively recognize fluoresceins as guest molecules to form a new class of fluorinated aggregates-fluorescein nanocomposites. These fluorinated fluorescein nanocomposites that are obtained exhibit an extraordinarily enhanced light absorption (λ_{max} ca. 440 nm) compared to that (λ_{maxs} 452, 480 nm) of the parent fluorescein in the absence of fluorinated aggregates.

Introduction

Metal and inorganic semiconductor nanoparticles have recently been receiving increased attention due to both their unique properties originating from quantum-size effects and a variety of potential applications including optical, electronic and magnetic device, biomedical fields, and light-emitting diodes [1–6]. From the viewpoint of the higher applicable potential in material syntheses, the development of the preparation of novel organic nanomaterials is much interesting. In fact, much attention has been focused on the systematic research works through the preparation of nanoparticles by a precipitation method [7–14]. There has hitherto been an active interest in organofluorine compounds due to their exhibiting quite different unique properties from the corresponding non-fluorinated ones [15]. Therefore, it is in particular of interest to explore the novel synthetic systems of organic nanomaterials using organofluorine compounds. In our comprehensive studies on the synthesis and application of fluoroalkyl end-capped oligomers [16–21], we demonstrated that these fluoroalkyl end-capped oligomers can form self-assembled molecular aggregates with the aggregations of end-capped fluoroalkyl segments in aqueous and organic media, although longer fluoroalkylated compounds in general exhibit a strong repellent property against water and hydrocarbons [22–31].

In the course of our study on the preparation of organic nanomaterials using organofluorine compounds, the surprise find was that self-assembled fluorinated molecular aggregates formed by fluoroalkyl end-capped oligomers in methanol can interact selectively with fluorescein as guest molecules to form a new class of fluorinated aggregates—fluorescein nanocomposites with a mean diameter of 46 nm. More surprisingly, it was found that these fluorinated fluorescein nanocomposites lead to a dramatic increase in light absorption compared to that of the parent fluorescein.

UV-Vis spectra of methanol solution of fluorescein (0.1 mmol/dm^3) show absorption band at 452 nm (enol form) and 480 nm (keto form); however, these absorption bands completely disappeared by the addition of fluoroalkyl end-capped *N*-(1,1-dimthyl-3-oxobutyl)acrylamide oligomer [R_F–$[CH_2CHC(=O)NCMe_2CH_2C(=O)Me]_n$–$R_F$ [R_F–$(DOBAA)_n$–R_F], $R_F = CF(CF_3)OC_3F_7$ (Mn = 5710; 2.0 g/dm^3)], and interestingly, an intense narrow absorption band was observed afresh at 440 nm as shown in Fig. 1. In this case, (Fig. 1) the parent R_F–$(DOBAA)_n$–R_F oligomer showed no absorption band from 350 nm to 550 nm. In contrast, such anabsorption band was not observed in the presence of the corresponding non-fluorinated DOBAA oligomer [Mn = 18300], and UV-Vis spectra showed the same two absorption bands as with the parent fluorescein (see Fig. 1).

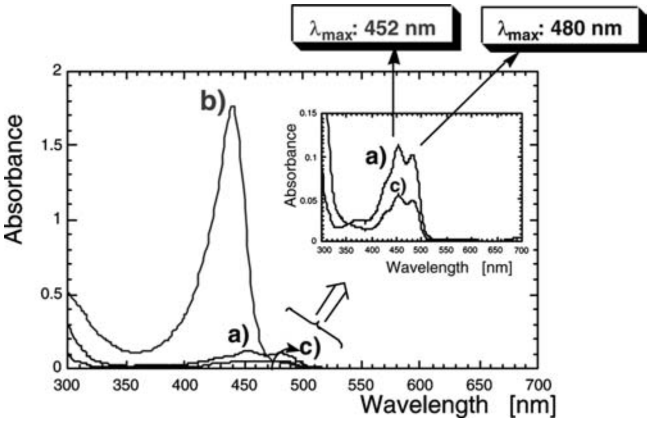

Fig. 1 UV-vis. spectra of methanol solution of fluorescein in the presence of R_F–$(DOBAA)_n$–R_F oligomer **a** fluorescein (0.1 mmol/dm^3) in MeOH. **b** R_F–$(DOBAA)_n$–R_F (2g/dm^3): fluorescein (0.1 mmol/dm^3) in MeOH. **c** –$(DOBAA)_n$–(2g/dm^3): fluorescein (0.1 mmol/dm^3) in MeOH

Additionally, we tried to measure the ultraviolet absorption for a variety of fluorescein derivatives such as uranine, fluoresceinamine, carboxyfluorescein, fluorescein diacetate, fluorescein isothiocyanate under similar conditions, and the results are shown in Table 1.

As shown in Table 1, each absorption band of the parent fluorescein derivatives disappeared completely in the presence of R_F–$(DOBAA)_n$–R_F oligomer, and intense narrow absorption bands around 440 nm were observed in these fluoresceins. It is of interest that uranine and fluorescein diacetate, in which –OH groups are substituted for –ONa and –OC(=O)Me, respectively, were not able to afford such intense narrow absorption bands around 440 nm, and the ratio of absorbance [$A_{oligomer}$(ca. 440 nm)/A(ca. 450 nm)] [the ratios of the absorbance around 440 nm based on that (around 450 nm) of the parent fluorescein] became significantly decreased. On the other hand, fluorescein and fluoresceinamine had remarkably higher values (14.5 and 13.9). These findings suggest that fluorinated self-assembled molecular aggregates formed by R_F–$(DOBAA)_n$–R_F oligomer in methanol could provide suitable host moieties to selectively recognize fluorescein derivatives bearing hydroxyl groups as guest molecules. The intermolecular hydrogen bonding between hydroxyl groups in fluoresceins and amido segments in fluorinated oligomers would become dominant for the interaction of the fluorinated host moieties with fluoresceins.

Calcein bearing two bulky substituents on aromatic nuclei, which is one of the fluorescein derivatives, failed to exhibit the enhanced absorption band around 440 nm. This would be due to the steric hindrance of calcein. In addition, common organic dyes such as indigo carmine, tropaeolin O, lucigenin, eriochrome black T, ethidium bromide, aminophthalic acid, methyl red, 4-methylumbelliferone, phenyl acridine-9-carboxylate, 4-hydroxyazobenzene-4′-sulfonic acid, rhodamine B, methylene blue, acridine hydrochloride, methyl orange, 4-hydroxyazobenzene-4′-sulfonic acid sodium salt, and acriflavine hydrochloride, which possess no fluorescein's skeletons, were not able to interact with fluorinated molecular aggregates at all, and only the original absorption bands related to parent organic dyes were observed.

To calculate the maximum number of fluorescein that could occupy the fluorinated aggregate core, experiments were conducted with varying molar ratios of fluorescein in methanol, and the results are shown in Fig. 2.

The absorbance of 440 nm in the presence of R_F–$(DOBAA)_n$–R_F oligomer increased remarkably with the

Table 1 Absorbance (A) of fluorescein derivatives in methanol in the presence of 2.0 g/dm^3 R_F–(DOBAA)$_n$–R_n [R_F = CF(CF$_3$)OC$_3$F$_7$; Mn = 3710]

Fluorescein derivatives (mmol/dm^3)	In the absence of oligomer	In the presence of oligometer	
	λ_{max}(nm)[A]	λ_{max}(nm)[A]	$A_{oligometer}$(ca. 440 nm)/ A(ca. 450 nm)
Fluorescein (0.1)	452 [0.101] 480 [0.095]	440 [1.467]	14.5
Uranine (0.03)	457 [0.512] 489 [0.678]	440 [0.392]	0.8
Fluoresceinamine (0.10)	452 [0.204] 479 [0.190]	435 [2.834]	13.9
Fluorescein Isothiocyanate (0.20)	442 [0.601]	442 [2.834]	4.7
Carboxyfluorescein (0.10)	443 [0.569]	443 [1.366]	2.4
Fluorescein Diacetate (1.0)	450 [0.081] 477 [0.068]	440 [0.108]	1.3

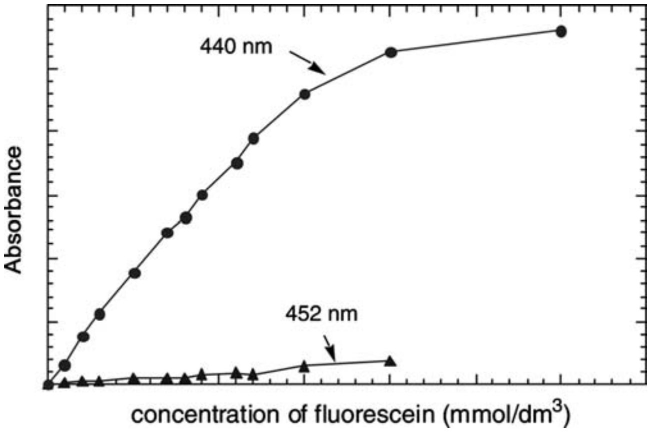

Fig. 2 Relationship between the absorbance of fluorescein and the concentrations of fluorescein in the presence of oligomers (2 g/dm^3) in methanol. *Filled circle* R_F–(DOBAA)$_n$–R_F:R_F = CF(CF$_3$)OC$_3$F$_7$ (Mn = 3710). *Open triangle* –(DOBAA)$_n$–: (Mn = 5820)

increase in the concentration of fluorescein, and the almost constant values were obtained above 0.2 mmol/dm^3. On the other hand, the absorbance of 452 nm related to the parent fluorescein (enol isomer) in the presence of –(DOBAA)$_n$– oligomer increased slightly with the increase in the concentration of fluorescein. This experimental result shows that 1 mol of R_F–(DOBAA)$_n$–R_F oligomer could interact with ca. 0.37 mol of fluorescein. Thus, it is suggested that the fluorinated molecular aggregate [32] could occupy around three fluorescein molecules per aggregate core; because this fluorinated molecular aggregate is considered to consist of around eight fluorinated oligomeric molecules since the molecular weight of the aggregates formed by the fluorinated oligomer determined by the static light scattering measurements and the molecular weight of the fluorinated oligomer determined by GPC measurements are 30310 and 3720, respectively.

Hitherto, organic dyes such as 5,5′,6,6′-tetrachloro-1,1′-diethyl-3,3′-bis(4-sulfobutyl)-benzimidazolocarbocyanine sodium salt have been known to exhibit the J-aggregation band [33–34]. This band is distinctly red-shifted and appears as an intense narrow absorption band to the motional narrowing related to the interaction of "edge to edge" [33–36]. Herz [35] and Tanaka [36], individually, reported on the aggregation numbers (n) of this organic dye (n = 4 and 8, respectively). Our present result in the extraordinarily enhanced narrow blue-shifted band compared to the parent fluorescein seems to be quite different from the previously reported J band. Thus, we were interested in measuring the association number (n) of fluorescein according to the method reported by Herz [35] and Tanaka et al. [36]. Self-assembled molecular aggregates formed not only by R_F–(DOBAA)$_n$–R_F oligomers but also as fluoroalkyl end-capped acrylic acid oligomers [R_F–(ACA)$_n$–R_F] and *N*,*N*-dimethylacrylamide oligomers [R_F–(DMAA)$_n$–R_F] could interact strongly with fluoresceins to exhibit new absorption bands around 440 nm under similar conditions. In contrast, the corresponding non-fluorinated –(ACA)$_n$– oligomer and –(DMAA)$_n$– oligomer could not interact with fluorescein at all as well as –(DOBAA)$_n$– oligomer. We have measured the UV-Vis spectra of fluorescein in the presence of R_F–(ACA)$_n$–R_F oligomers under similar conditions as in Fig. 1, and the obtained association number (n) of fluorescein (0.05–0.20 mmol) in fluorinated molecular aggregates (concentrations of fluorinated oligomers: 0.3, 0.6, 0.9 and 1.5 g/dm^3) at 30 °C is around 1.0 in each case. This finding suggests that fluoresceins in fluorinated molecular aggregates are unable to fall into the well-known J aggregates. In order to clarify this unique behavior of fluoresceins in fluorinated molecular aggregates, we have measured SEM (scanning electron microscopy) photographs of methanol solution of fluorescein in the presence of R_F–(DOBAA)$_n$–R_F oligomer, and the results are shown in Fig. 3.

Surprisingly, the electron micrograph shows the formation of self-assembled fluorinated molecular aggregates—fluorescein nanocomposites. The size distributions of fluorinated aggregates—fluorescein nanocomposites show that fluorinated nanocomposites are very fine spheres with a mean diameter of 46 nm. The

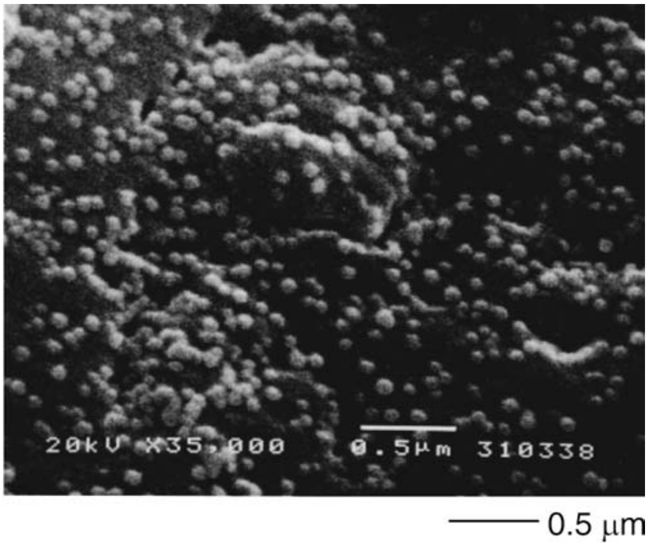

Fig. 3 SEM(scanning electron microscopy) images of methanol solution of R_F–$(DOBAA)_n$–R_F [$R_F = CF(CF_3)C_3F_7$; 2 g/dm^3] and fluorescein (0.1 mmol/dm^3)

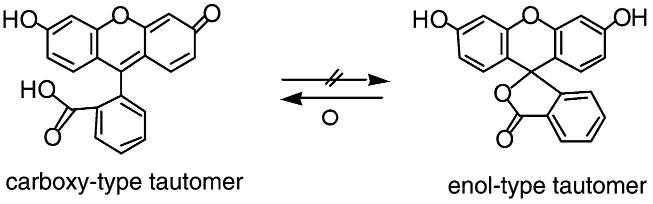

Fig. 4 Tautomeric equilibria of fluorescein

insides of fluorinated molecular aggregate cores consist of the solvophobic environment, and in addition, the host moieties in these cores could selectively recognize fluoresceins as guest molecules. Thus, under such specific conditions, fluoresceins with only enol-form, especially carboxy-type tautomer possessing –OH and –C(= O)OH groups (see Fig. 4) could interact strongly with fluorinated [Fig. 4] aggregate cores through the intermolecular hydrogen bonding to afford fluorinated nanocompsoites. In fact, the ZINDO molecular orbital theoretical studies (programs: Gaussian 03 W) [37] suggested that the carboxy-type tautomer in Fig. 4 could absorb the light effectively through the HOMO-LUMO (π–π^* transition) interaction to exhibit the absorption at λ_{max}: 412 nm (theoretical) [experimental λ_{max}: 437 nm (see Refs. [38], [39]) owing to the increased flatness of this tautomer. Hence, the molecular motions of fluoresecins in the nanocomposites would be remarkably restricted, and an extraordinarily enhanced light absorption would be observed in the carboxy-type fluorescein nanocomposites. Our present fluorinated fluorescein naocomposites, which possess an extraordinarily enhanced light absorption ability around 400 nm, are expected to have a high potential to apply into the recording materials for blue semiconductor laser.

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