

# INTERACTION OF ORGANIC DYES WITH CROSS-LINKED FLUOROALKYL END-CAPPED OLIGOMERIC NANOCOMPOSITES AND PHOTODEGRADATION OF ORGANIC DYES IN THESE COMPOSITES

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## Introduction

Considerable efforts have been recently devoted to the studies involving hybrids based on blends of silica and organic polymers dispersed at a molecular level for the aim of the development of high performance [1]. During our comprehensive studies on the development of novel organic/inorganic hybrid materials possessing unique characteristics imparted by fluorine [2, 3], we have recently found that cross-linked fluoroalkyl end-capped oligomeric nanocomposites possessing aromatic siloxane segments as core units [ $R_F$ -oligomer/ $Ar-SiO_2$ ] can be prepared by the sol-gel reactions of the corresponding oligomers with aromatic silanes [ $Ar-Si(OEt)_3$ ] under alkaline conditions [4]. Here we report not only the selective encapsulation-release characteristics of organic dyes such as methylene blue (MB), rhodamine B (RB), 4-hydroxyazobenzene-4'-sulfonic acid sodium salt (4-HABSNa), and methyl orange (MO) but also the novel photodegradation characteristic of encapsulated organic dyes into these fluorinated nanocomposites.

## Experimental

### Materials

Acrylic acid (ACA), *N,N*-dimethylacrylamide (DMAA), and *N*-(1,1-dimethyl-3-oxobutyl)acrylamide (DOBAA) were used as received from Toagosei Co., Ltd., Kojin Co., Ltd. and Kyowa Hakko Chemical Co., Ltd., respectively. 1,4-bis(triethoxysilyl)benzene and 4,4'-bis(triethoxysilyl)-1,1'-biphenyl were purchased from Sigma Aldrich Japan Co., Ltd.. Cross-linked fluoroalkyl end-capped oligomeric nanocomposites possessing aromatic siloxane segments as core units were prepared according to our previously reported method [4].

### *Interaction of Organic Dyes with Fluorinated Nanocomposites and Photodegradation of Organic Dyes in These Composites*

The procedure of encapsulation and release of methylene blue (MB) in water by the use of cross-linked fluoroalkyl end-capped oligomeric nanocomposites possessing aromatic siloxane segments as core units is as follow: to

an aqueous solution of MB ( $0.01 \text{ mmoldm}^{-3}$ , 10.0 ml) was added fluorinated nanocomposites (1.0 mg). The mixture was stirred with a magnetic stirring bar at room temperature for 1 day. The aqueous solution thus obtained was centrifuged for 30 min. The relative amounts of encapsulated MB in water were estimated by the encapsulated ratio at 664 nm (UV-vis spectra, Shimadzu UV-1600 UV-vis spectrophotometer). In contrast, water (10.0 ml) was added into the isolated fluorinated nanocomposite after the above-mentioned centrifugal separation, and the mixture was stirred with a magnetic stirring bar at room temperature for 1 day. After the centrifugal separation for 30 min of this mixture, the amounts of released MB into the supernatant were estimated by UV-vis spectra. The amounts of encapsulated and released other organic dyes in water and organic media were also estimated under similar conditions.

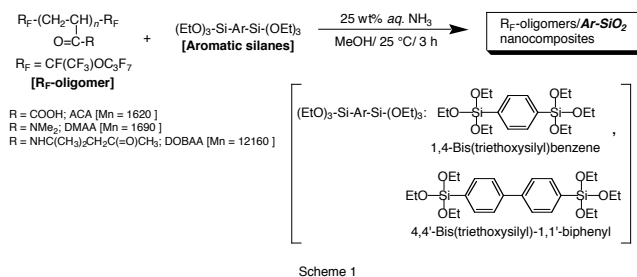
The procedure of photodegradation of methyl orange (MO) in the presence of fluorinated nanocomposites is as follow: to an aqueous solution of MO ( $0.02 \text{ mmoldm}^{-3}$ , 5.0 ml) was added  $R_F-(ACA)_n-R_F/Ar-SiO_2$  nanocomposites (2.0 mg). The mixture was stirred with a magnetic stirring bar at room temperature for 1 day. The aqueous solution thus obtained was found to exhibit an absorption band around 464 nm related to MO. The photodegradation of MO was examined by illuminating this solution, as well as the parent MO in water, with the UV-lamp ( $\lambda_{\text{max}}$ : 254 nm) for 0 ~ 8 hours at room temperature.

## Results and Discussion

A variety of cross-linked fluoroalkyl end-capped oligomeric nanocomposites possessing aromatic siloxane segments as core units were prepared by the hydrolysis of alkoxy silanes containing aromatic groups in the presence of the corresponding oligomers under alkaline conditions (see Scheme 1) [4].

The fluorinated composites thus obtained were nanometer size-controlled very fine particles (42 ~ 81 nm), and exhibited good dispersibility and stability in not only water but also traditional organic solvents such as

methanol, ethanol, isopropyl alcohol and acetone.



We have studied the encapsulation of organic dyes such as methylene blue (MB) and methyl orange (MO) into water by cross-linked fluoroalkyl end-capped oligomeric nanocomposites possessing aromatic siloxane segments as core units in Scheme 1, and the results were shown in Fig. 1. As shown in Fig. 1, R<sub>F</sub>-(DMAA)<sub>n</sub>-R<sub>F</sub>/Ar-SiO<sub>2</sub> [Ar: biphenylene] nanocomposites was able to encapsulate MB, completely, as a guest molecule to exhibit no absorption band around 664 nm (see Fig. 1-(b)), and this composite also afforded an effective encapsulation ability toward MO as shown in Fig. 1-(e). On the other hand, other R<sub>F</sub>-(DMAA)<sub>n</sub>-R<sub>F</sub>/Ar-SiO<sub>2</sub> [Ar: phenylene and Ar-SiO<sub>2</sub>: SiO<sub>2</sub>] nanocomposites exhibited an extremely lower encapsulation ability toward MO (see Fig. 1-(d), (f)).

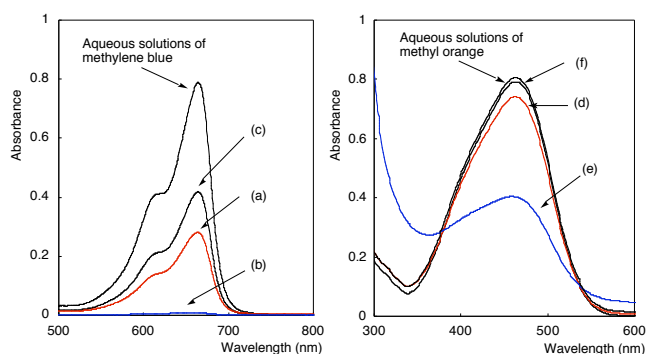


Fig. 1 UV-vis spectra of aqueous solutions of 0.01 mmol dm<sup>-3</sup> methylene blue in the presence of 0.10 g dm<sup>-3</sup> R<sub>F</sub>-(DMAA)<sub>n</sub>-R<sub>F</sub>/Ar-SiO<sub>2</sub> nanocomposites and aqueous solutions of 0.03 mmol dm<sup>-3</sup> methyl orange in the presence of 1.0 g dm<sup>-3</sup> R<sub>F</sub>-(DMAA)<sub>n</sub>-R<sub>F</sub>/Ar-SiO<sub>2</sub> nanocomposites [(a), (d): phenylene (b), (e): biphenylene (c), (f): Ar-SiO<sub>2</sub>: SiO<sub>2</sub>]

Additionally, R<sub>F</sub>-oligomer/Ar-SiO<sub>2</sub> nanocomposites-encapsulated organic dyes were found to exhibit a controlled releasing characteristic toward these encapsulated dyes, and encapsulated MO was not released into water, however, this encapsulated dye was smoothly released into acetone under similar conditions. Fig. 2 shows that R<sub>F</sub>-oligomer/Ar-SiO<sub>2</sub> nanocomposites possessing biphenylene segments as core units were able to exhibit not a photostable characteristic but an extremely higher photodegradation ability toward MO under UV light irradiation. R<sub>F</sub>-(ACA)<sub>n</sub>-R<sub>F</sub>/Ar-SiO<sub>2</sub> [Ar: biphenylene] nanocomposite was found to exhibit an

extraordinarily high photodegradation ability corresponding to the residual MO: 3 % under similar conditions, and MO decomposed completely after 3 hr UV-illumination at room temperature.

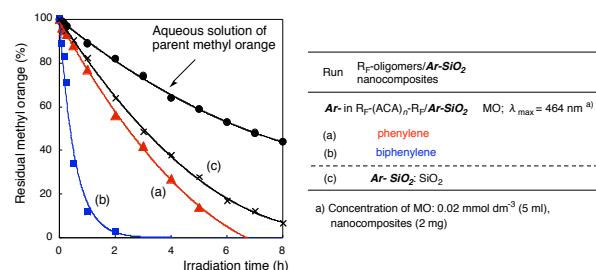


Fig. 4 Relationship between the amounts of residual methyl orange and the irradiation time (λ<sub>max</sub> = 254 nm) for aqueous solutions of methyl orange in the presence of R<sub>F</sub>-(ACA)<sub>n</sub>-R<sub>F</sub>/Ar-SiO<sub>2</sub> nanocomposites

In general, there have been numerous reports on the photocatalytic degradation of organic compounds by the use of titanium oxide; however, studies on the photodegradation of organic compounds by the use of organic/inorganic nanocomposites have been hitherto very limited except for our present study [5]. Thus, our present R<sub>F</sub>-oligomer/Ar-SiO<sub>2</sub> [Ar: biphenylene] nanocomposite would be applicable to the novel removal system of toxic organic compounds.

## Conclusion

We succeeded in preparing cross-linked fluoroalkyl end-capped oligomeric nanocomposites possessing aromatic siloxane segments [R<sub>F</sub>-oligomer/Ar-SiO<sub>2</sub>] - encapsulating organic dyes such as MB, MO, RB and 4-HABSNa by the treatment of the corresponding nanocomposites with these dyes in aqueous and organic media. R<sub>F</sub>-oligomer/Ar-SiO<sub>2</sub> nanocomposites-encapsulated MO were found to exhibit a releasing characteristic into aqueous and organic media. Interestingly, it was demonstrated that our present R<sub>F</sub>-(ACA)<sub>n</sub>-R<sub>F</sub>/Ar-SiO<sub>2</sub> [Ar: biphenylene] nanocomposite cannot show the photostable property for MO but extremely higher photodegradation characteristic for MO by the UV-irradiation.

## References

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