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# Chromophore end-labelled long chain perfluoropolyether as probes to study the formation of aggregates in aqueous organic solvent and their asymmetrical coaggregation with hydrocarbons

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## Abstract

The emission spectra of 2-naphthyl and 9-anthryl ester terminated perfluoropolyether compounds (NpOF and AnOF) in aqueous organic binary solvents were investigated. The fluorescence spectra of NpOF in dimethyl sulfoxide–water mixture (DMSO–$H_2O$) are dominated by the excimer emission. Addition of methyl perfluoropolyether carboxylate ($CH_3OF$) to the solution results in a reduction in the excimer emission and an enhancement of monomer emission. Selective excitation of the naphthalene moiety in the mixture solution of NpOF and AnOF leads to strong emission from AnOF. All these observations suggest the formation of perfluoropolyether aggregates in the aqueous organic binary solvents.

Both NpOF and dodecyl 2-naphthoate (NpHC12) in 1,4-dioxane–$H_2O$ exhibit the excimer emission exclusively. Addition of a high concentration of $n$-$C_{18}H_{38}$ to the NpOF solution results in a reduction in the excimer emission and an enhancement of monomer emission, suggesting that chromophores of NpOF are diluted by the $C_{18}H_{38}$ aggregates. Addition of a high concentration of $CH_3OF$ to the NpHC12 solution, however, has only slight effect on the fluorescence of NpHC12 emission. These observations indicate that when coaggregation of hydrocarbon and perfluoropolyether occurs, these coaggregates contain much more hydrocarbons than perfluoropolyether compounds.

*Keywords:* Hydrophobic; Perfluoropolyether; Aggregate; Photochemistry; Chromophores

## 1. Introduction

In aqueous or aqueous organic binary solvents the electrically neutral long chain hydrocarbons can form aggregates at very low concentrations, driven by hydrophobic interactions [1]. The aggregates thus formed may serve as simple models for molecular assemblies and may have valuable applications in macrocyclic synthetic chemistry, medicine design and other disciplines [2,3].

Perfluorocarbon molecules are well known to be significantly different from hydrocarbons due to the differences in the nature of the hydrophobic moiety. It is also well known that fluorocarbons and hydrocarbons exhibit pronounced mutual phobicity [4,5]. The miscibility of fluorocarbon and hydrocarbon surfactants has been the subject of numerous investigations [6–13]. Among various approaches employed to explore the structural and dynamic features of molecular assemblies, photophysical and photochemical probe analysis has been an important method for the study of the microscopic environment around a chromophore [14–16]. Recently we have used a chromophore end-labelled hydrocarbon and fluorocarbon molecules as fluorescence probes to investigate their excimer formation and energy transfer in aqueous organic mixed solvents. The results showed that the effect of hydrophobic forces in the fluorocarbons is significantly greater than in the hydrocarbons of the same chain length [17]. We have also obtained straightforward evidences of ideal and nonideal mixing of fluorocarbon and hydrocarbon molecules in aggregate systems, depending on the chain lengths of the perfluorocarbons [18].

Perfluoropolyether (PFPE) is a class of material showing several typical properties of perfluoriated molecules, such as low hydrophilic character, thermal and chemical inertness, and ease of formation of micelle aggregates and microemulsions [19–24]. Moreover, these compounds can be prepared with different chain length and branching, and the presence of the ether bridge provides a higher degree of

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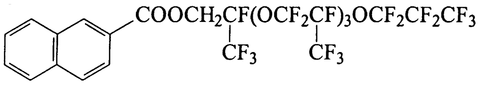
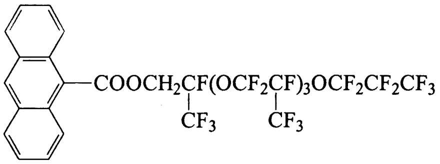
conformational freedom than in perfluorocarbons. It is of interest to know whether perfluropolyether could form aggregates in aqueous organic solvents, driven by the hydrophobic interactions. Their miscibility or immiscibility with hydrocarbons is also an attractive problem to study that may contribute to improving our comprehension of phobicity between the fluorocarbons and hydrocarbons and drug designs.

In the present work, we investigated the behavior of PFPE 2-naphthoates and PFPE 9-anthracenecarboxylate in aqueous organic solvents. Through the examination of excimer formation, energy transfer, diluted effect, we obtained evidence for aggregation of perfluoropolyether molecules in aqueous organic solvents and their mutual miscibility or immiscibility with the hydrocarbons.

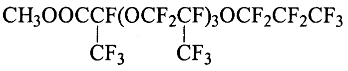
The molecules we studied have the following structures.



NpOF



AnOF



$CH_3OOC\underset{CF_3}{C}F(OCF_2\underset{CF_3}{C}F)_3OCF_2CF_2CF_3$

CH3OF

## 2. Experimental

### 2.1. Materials

Methyl 2,5,8,11-tetra(trifluoromethyl)-3,6,9,12-tetraoxa-perfluoropentadecano-ate ($CH_3OF$) was donated by Shanghai Organic Institute, Chinese Academy of Sciences. 2,5,8,11-tetra(trifluoromethyl)-3,6,9,12-tetraoxa-perfluoropentadecanol was synthesized by reduction of the $CH_3OF$ with $LiAlH_4$. 2-Naphthoyl chloride was prepared by reaction of 2-naphthoic acid with thionyl chloride and the product was distilled at reduced pressure. 2,5,8,11-tetra(trifluoromethyl)-3,6,9,12-tetraoxa-perfluoropentadecyl 2-naphthoate (NpOF) was synthesized by esterification of 2-naphthoyl chloride with the 2,5,8,11-tetra(trifluoromethyl)-3,6,9,12-tetraoxa-perfluoropentadecanol. 2,5,8,11-tetra(trifluoro-methyl)-3,6,9,12-tetraoxa-perfluoropentadecyl 9-anthracenecarboxylate (AnOF) was synthesized by esterification of 9-anthracene-carbonyl chloride with the 2,5,8,11-tetra(trifluoromethyl)-3,6,9,12-tetraoxa-perfluoropentadecanol [25]. The synthesized compounds were characterized by IR, MS and $^1H$ NMR as well as $^{19}F$ NMR spectra. Spectral-grade dimethyl sulfoxide (DMSO) (Aldrich, 99.9%), 1,4-dioxane (DX) (Aldrich, 99%) and ethanol were used for fluorescence measurements without further purification. Doubly distilled water was used in all the experiments.

### 2.2. Instrumentation

$^1H$ NMR spectra were determined with a Varian XL-400 (400 MHz) instrument in $CDCl_3$ using TMS as the internal standard. The $^{19}F$ NMR spectra were recorded on a Varian XL-400 (400 MHz) instrument using TFA as the internal standard. Mass spectra were determined with a Finnigan 4021C mass spectrometer with an electron impact source at 25 or 70 eV. Steady-state fluorescence spectra were run on either a Hitachi-850 or Hitachi MPF-4 spectrofluorimeter.

### 2.3. Fluorescence measurements

The samples were purged with presaturated nitrogen with water or aqueous-organic binary solvents for at least 30 min before the measurements. The excitation wavelength was 280 nm both for the excimer formation and the energy transfer studies. The spectra were fully corrected for instrument response. Of particular interest for NpOF excimer formation is the excimer to monomer intensity ratio $I_E/I_M$, which was calculated from the peak heights at 420 and 360 nm for excimer ($I_E$) and monomer ($I_M$), respectively. The peak height and peak areas were proportional to one another.

## 3. Results and discussion

### 3.1. Excimer formation of NpOF and AnOF

The fluorescence spectra of $1 \times 10^{-5}$ mol dm$^{-3}$ solution of NpOF in 1,4-dioxane–water (DX–$H_2O$) are shown in Fig. 1, where $\Phi$ represents the volume fraction of water in the solvent mixture. This compound exhibits the structured fluorescence characteristic of naphthoate monomer 370 nm for $\Phi = 0$. As the $\Phi$ value increases, the monomer fluorescence intensity decreases and a new structureless excimer emission, centered at, ca. 408 nm is observed. At $\Phi > 0.5$ the excimer emission dominates the fluorescence spectrum. This is a behavior typical of the aggregate formation of long chain hydrocarbon or perfluorocarbon compounds [17]. In order to measure the critical aggregation concentration (CAC) of NpOF in various aqueous organic solvents, we examined the ratio $I_E/I_M$ of the fluorescence intensity of the excimer (at 420 nm) to that of the monomer (at 360 nm) as a function of NpOF concentration at a constant $\Phi$ value as described before [17]. As shown in Fig. 2, the plot of $I_E/I_M$ versus [NpOF] displays a break and the concentration corresponding to the break point is defined as the CAC. Fig. 3 shows the plot of $I_E/I_M$ as a function of $\Phi$ at constant NpOF concentration. This plot also exhibits a break. The $\Phi$ value corresponding to the break is defined as the critical solvent composition for aggregation ($\Phi_C$). A small $\Phi_C$ suggests that the solvent possesses a large aggregation power.

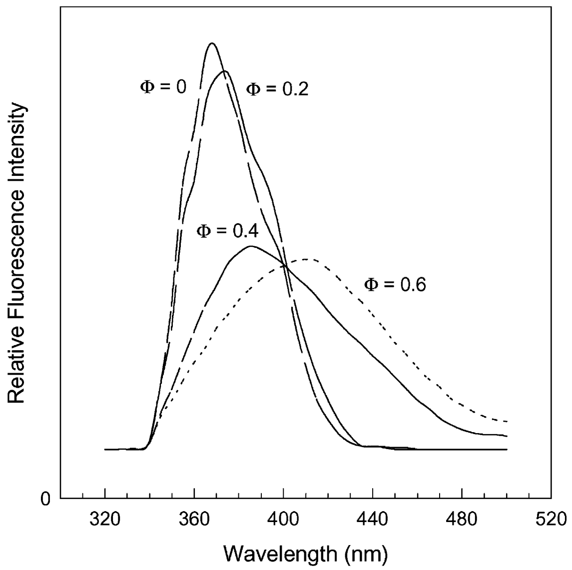


Fig. 1. Fluorescence spectra of NpOF in DX–$H_2O$ for various volume fractions ($\Phi$) of water in the solvent mixture ($[NpOF] = 1 \times 10^{-5}$ mol dm$^{-3}$, $\lambda_{ex} = 280$ nm) for $\Phi = 0$; $\Phi = 0.2$; $\Phi = 0.4$ and $\Phi = 0.6$.

It is expected that the driving force for aggregate formation for NpOF in aqueous organic solvents is hydrophobic interactions. The probe molecule used in the our experiment contains a large, planar building moiety, naphthyl. This hydrophobic moiety may make a contribution to the formation of aggregates. To estimate the extent of the importance of these moieties in the formation of aggregates, we examined the fluorescence spectra of a short chain perfluorocarbon, $NpCOO(CF_2)_3CF_3$, which exhibits monomer fluorescence even in aqueous organic mixtures having a large proportion of water. Another fluorescent probe, AnOF, that contains a bigger anthryl moiety was also studied and the spectra are shown in Fig. 4. AnOF can also form aggregates in DX–$H_2O$

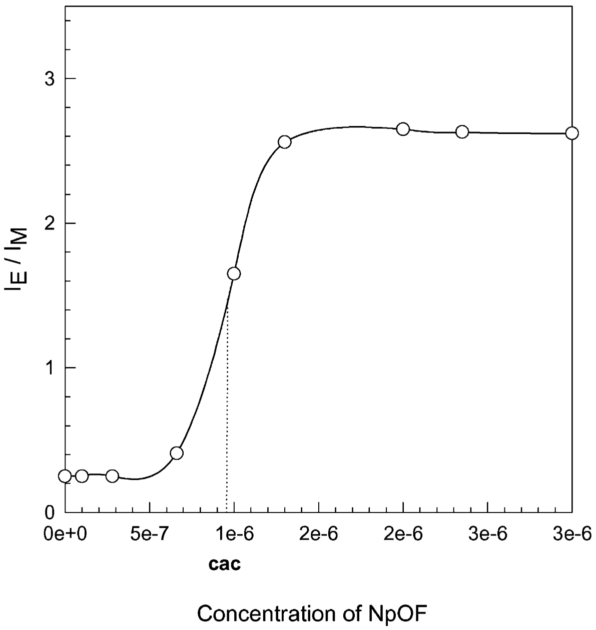


Fig. 2. The plot of the ratio $I_E/I_M$ of fluorescence intensities of excimer (at 420 nm) to monomer (at 360 nm) for NpOF in DX–$H_2O$ mixed solvents at a constant volume fraction of water ($\Phi = 0.6$) as a function of the concentration ($\lambda_{ex} = 280$ nm).

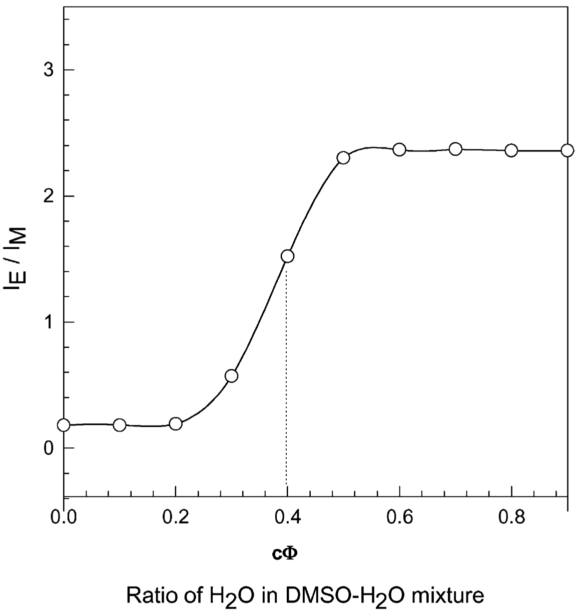


Fig. 3. The plot of the ratio $I_E/I_M$ of fluorescence intensities of excimer (at 420 nm) to monomer (at 360 nm) for NpOF in DX–$H_2O$ mixed solvents at a constant concentration ($1 \times 10^{-5}$ mol dm$^{-3}$) as a function of the volume fraction of water in the solvent mixture ($\lambda_{ex} = 280$ nm).

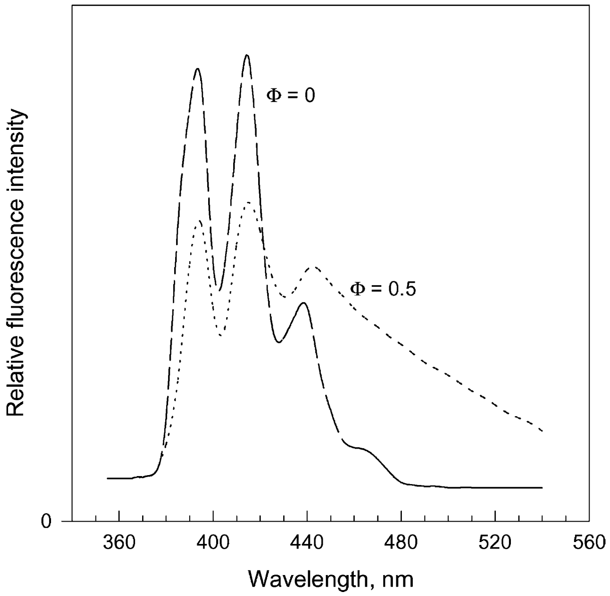


Fig. 4. Fluorescence spectra of AnOF in DX–$H_2O$ for various volume fractions ($\Phi$) of water in the solvent mixture ($[AnOF] = 1 \times 10^{-5}$ mol dm$^{-3}$, $\lambda_{ex} = 350$ nm) for $\Phi = 0$ (– –); $\Phi = 0.5$ (---).

Table 1
$\Phi_C$ and the CAC values of NpOF and NpFC12[a] in various aqueous organic solvents

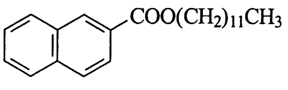
| | $\Phi_C$ [b] | | | CAC[c] | | |
|---|---|---|---|---|---|---|
| | DMSO–$H_2O$ | DX–$H_2O$ | EtOH–$H_2O$ | DMSO–$H_2O$ | DX–$H_2O$ | EtOH–$H_2O$ |
| NpOF | 0.20 | 0.40 | 0.55 | $<10^{-7}$ | $9.6 \times 10^{-7}$ | $6 \times 10^{-6}$ |
| NpFC12 | 0.30 | 0.50 | 0.65 | $4 \times 10^{-7}$ | $4 \times 10^{-6}$ | $5 \times 10^{-5}$ |

[a] NpFC12 = 2-Naphthyl-$COOCH_2(CF_2)_{10}CF_3$.
[b] [NpOF or NpFC12] = $1 \times 10^{-5}$ mol/dm$^3$.
[c] $\Phi = 0.6$.

($\Phi = 0.5$) and an excimer fluorescence centered at 490 nm is observed after normalization. The CAC or $\Phi_C$ values obtained from the AnOF is just the same as from NpOF using the above method. These results suggest that the hydrophobic interactions relating to the naphthyl or anthryl groups are not large enough to induce aggregate formation and they make little or no contribution to the aggregation process. Considering the fact that the polyethers are hydrophilic but perfluoropolyethers are hydrophobic, it is concluded that the lone pair electrons on the oxygen atoms in PFPE are shielded by the big fluorine atoms in PFPE and they are unable to form hydrogen bonds with the water molecules in the solution.

The excitation spectra for the excimer and monomer emission are identical, and the maximum peak wavelength corresponds to that in the UV absorption spectrum, suggesting the absence of strong interactions between the naphthoate chromophores in the ground state. Obviously, within the aggregates the local concentration of the chromophores is high, but the chromophores do not associate with each other to form a complex in the ground state.

The behavior of NpOF in dimethyl sulfoxide–water (DMSO–$H_2O$) and ethanol–water (EtOH–$H_2O$) mixed solvents is analogous to that in DX–$H_2O$. The values of $\Phi_C$ at fixed concentration and the CAC at fixed $\Phi_C$ are listed in Table 1. It is shown that the CAC and $\Phi_C$ of NpOF at the same $\Phi$ or concentration, respectively, are much smaller than those of the perfluorinated compound, such as perfluorotridecanoate 2-naphthoates (NpFC12), which has the same carbon chain length as studied in our previous work [18]. These results suggest that the PFPE molecules are more hydrophobic than the straight chain perfluorcarbons with the same chain length. This effect may arise from the $CF_3$ branches in the perfluoropolyether that make PFPE more hydrophobic. It maybe the case that besides hydrophobicity, bulkier groups also contribute to other factors that affect aggregation. However, lack of the non-branch perfluoropolyether materials in the industry restrict our further study of whether the side chain contributes exclusively to stronger hydrophobicity of PFPE materials.



NpHC12

### 3.2. Coaggregates of NpOF and $CH_3OF$

To provide more evidence for aggregation, we studied the effect of unlabelled PFPE molecule $CH_3OF$ on the excimer formation of NpOF in DX–$H_2O$ with a $\Phi$ value of 0.5. In the absence of the unlabelled fluorocarbon $CH_3OF$, NpOF emits mainly excimer fluorescence at concentration of $1 \times 10^{-5}$ mol dm$^{-3}$ (Fig. 5) owing to the formation of aggregates. Addition of $CH_3OF$ to the solution results in an enhancement of the monomer emission and a reduction of the excimer fluorescence. In the presence of sufficient $CH_3OF$, the fluorescence spectrum of this NpOF is dominated by the structured monomer emission. Obviously this is because $CH_3OF$ molecules coaggregate with NpOF and the chromophores are diluted in the coaggregates.

### 3.3. Energy transfer from NpOF to AnOF

The evidence for aggregation is further strengthened by the observation of energy transfer from NpOF to AnOF. The absorption spectra of NpOF and AnOF indicate that one can

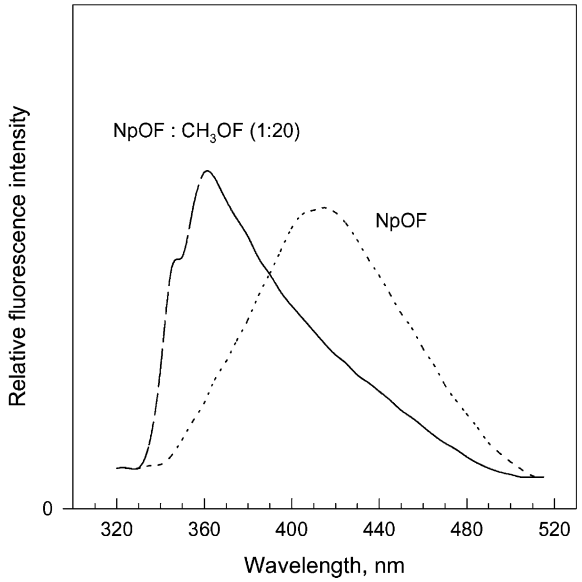


Fig. 5. The effect of $CH_3OF$ on the fluorescence spectrum of NpOF in DX–$H_2O$ mixed solvents ($\Phi = 0.5$; [NpOF] = $1 \times 10^{-5}$ mol dm$^{-3}$; $\lambda_{ex} = 280$ nm); [$CH_3OF$] = 0 (– –); [$CH_3OF$] = $2 \times 10^{-4}$ mol dm$^{-3}$ (---).

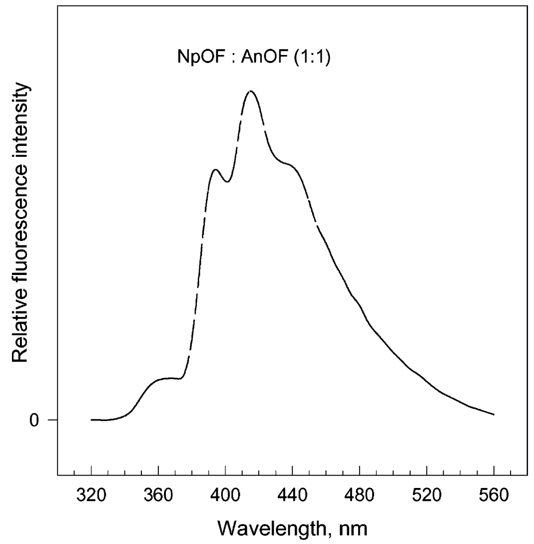


Fig. 6. Fluorescence spectra of NpOF and AnOF in DX–$H_2O$ mixed solvents ([NpOF] = [AnOF] = $1 \times 10^{-5}$ mol dm$^{-3}$, $\lambda_{ex} = 280$ nm).

use 280 nm light selectively to excite the naphthalene moiety in the mixture of NpOF and AnOF. Excitation at 280 nm of the mixed solution of NpOF ($1 \times 10^{-5}$ mol dm$^{-3}$) and AnOF ($1 \times 10^{-5}$ mol dm$^{-3}$) in organic solvents such as DX only leads to the monomer fluorescence of NpOF, the emission from AnOF is hardly detected, indicating the absence of energy transfer between NpOF and AnOF due to the low concentration of the donor and acceptor in organic solvent. However, in aqueous organic mixed solvents significant energy transfer is observed. As shown in Fig. 6, the fluorescence of NpOF is almost diminished and the structured emission of AnOF dominates the fluorescence spectrum of the mixed solution of $1 \times 10^{-5}$ M of NpOF and $1 \times 10^{-5}$ M of AnOF in DX–$H_2O$ with $\Phi$ equal to 0.5. Obviously, NpOF and AnOF coaggregate and within the coaggregates the mutual chromophore separation favors singlet energy transfer.

### *3.4. Asymmetrical coaggregation behavior between PFPE and hydrocarbons*

To obtain information about the miscibility of PFPE compounds with the hydrocarbons in the aggregate systems, we examined the effect of unlabelled hydrocarbon $n$-$C_{18}H_{38}$ on the excimer formation of NpOF and the effect of unlabelled PFPE compounds $CH_3OF$ on the excimer formation of dodecyl 2-naphthoate (NpHC12). As shown in Fig. 7, $1 \times 10^{-5}$ M of NpOF in DX–$H_2O$ solvents with $\Phi = 0.5$ emits excimer fluorescence due to aggregation. Addition of $2 \times 10^{-4}$ M of $n$-$C_{18}H_{38}$ to the solution results in an enhancement of the monomer emission and a reduction of the excimer fluorescence.

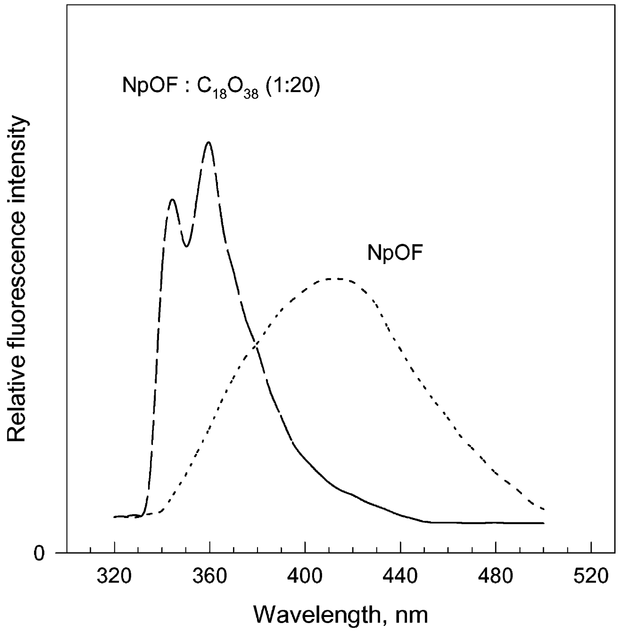


Fig. 7. The effect of non-labelled hydrocarbons $n$-$C_{18}H_{38}$ on the fluorescence spectrum of NpOF in DX–$H_2O$ mixed solvents ($\Phi = 0.5$; [NpOF] = $1 \times 10^{-5}$ mol dm$^{-3}$; $\lambda_{ex} = 280$ nm); [$C_{18}H_{38}$] = 0 (---); [$C_{18}H_{38}$] = $2 \times 10^{-4}$ mol dm$^{-3}$ (– –).

The effect of $CH_3OF$ on the emission spectra of NpHC12 in aqueous organic mixed solvents is shown in Fig. 8. A solution of $1 \times 10^{-5}$ M of NpHC12 in DX–$H_2O$ ($\Phi = 0.5$) exhibits exclusively excimer fluorescence at high concentration due to aggregation.

Surprisingly, addition of $2 \times 10^{-4}$ M $CH_3OF$ to the solution of NpHC12 shows almost no change in the fluorescence of NpHC12.

These two significantly different observations indicate an asymmetrical coaggregation behavior between the PFPE compounds and hydrocarbons. This asymmetrical behavior

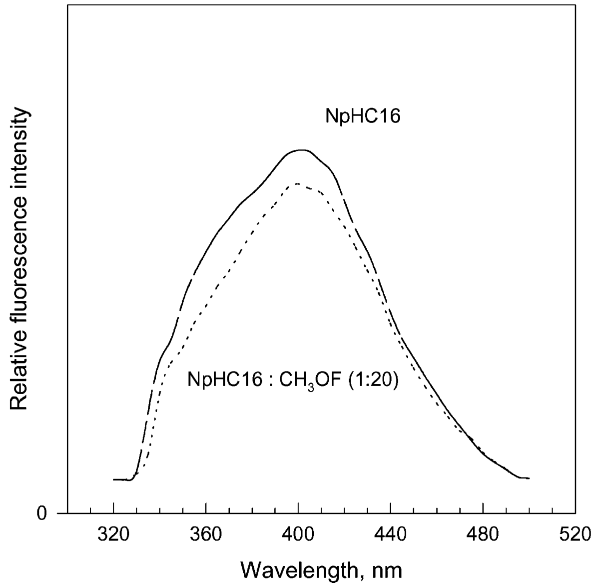


Fig. 8. The effect $CH_3OF$ on the fluorescence spectrum of NpHC12 in DX–$H_2O$ mixed solvents ($\Phi = 0.5$; [NpHC12] = $1 \times 10^{-5}$ mol dm$^{-3}$; $\lambda_{ex} = 280$ nm) [$CH_3OF$] = 0 (– –); [$CH_3OF$] = $2 \times 10^{-4}$ mol dm$^{-3}$ (---).

has already been studied in other types of aggregation systems [22–24] and in line with our present work. These asymmetrical coaggregation behavior could be explained by the nonmiscibility between PFPE and hydrocarbons [22–24]. In aqueous organic binary solvents, both PFPE and hydrocarbon molecules would keep their own aggregates because of mutual phobicity. However, a small amount of coaggregates could occur and these coaggregates contain much more hydrocarbons than PFPE [22–24]. Thus, when a high concentration of $C_{18}H_{38}$ ($2 \times 10^{-4}$ M) is added into the NpOF solution ($1 \times 10^{-5}$ M), since the concentration of NaOF is very low as compared to $C_{18}H_{38}$, most of the NpOF coaggregates with $C_{18}H_{38}$ rather than keeping their own aggregates. The consequence is that the naphthyl groups of NpOF are diluted by $C_{18}H_{38}$ resulting in an enhancement of the naphthyl monomer emission and a reduction of the excimer fluorescence. On the contrary, when a large amount of $CH_3OF$ ($2 \times 10^{-4}$ M) is added into the NpHC12 solution ($1 \times 10^{-5}$ M), two types of aggregates occur in the solution, a large number of $CH_3OF$ aggregates and a smaller number of coaggregates (containing mainly NpHC12) in aqueous organic binary solvents. In the coaggregates, the ratio of PFPE is too low to affect the fluorescence profile of NpHC12.

## Acknowledgements

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