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–H2O) are dominated by the excimer emission. Addition of methyl perfluoropolyether carboxylate (CH3OF) 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–H2O exhibit the excimer emission exclusively. Addition of a high concentration of n-C18H38 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 C18H38 aggregates. Addition of a high concentration of CH3OF 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.

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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 photophysical 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
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-anthracene carboxylate in aqueous organic solvents. Through the examination of excimer formation, energy transfer, diluted effect, we obtained evidence for aggregation of perfluropolyether molecules in aqueous organic solvents and their mutual miscibility or immiscibility with the hydrocarbons.

The molecules we studied have the following structures.

2. Experimental

2.1. Materials

Methyl 2,5,8,11-tetra(trifluoromethyl)-3,6,9,12-tetraoxa-perfluoropentadecanoate (CH$_3$OF) 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$_3$OF with LiAlH$_4$. 2-Naphthoyl chloride was prepared by reaction of 2-naphtholic acid with thionyl chloride and the product was distilled at reduced pressure. 2,5,8,11-tetra(trifluoromethyl)-2-naphthoic acid with thionyl chloride and the product was distilled at reduced pressure. 2,5,8,11-tetra(trifluoromethyl)-2-naphthoate (NpOF) was synthesized by esterification of 2-naphthoyl chloride with the 2,5,8,11-tetra(trifluoromethyl)-3,6,9,12-tetraoxa-perfluoropentadecyl 2-naphthoate (NpOF).

2.2. Instrumentation

$^1$H 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$_2$O) 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 as the solvent mixture. This compound exhibits the structured fluorescence characteristic of naphthoate monomer 370 nm and peak areas were proportional to one another.

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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 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, \( \text{NpCOO(CF}_2\text{)}_3\text{CF}_3 \), 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\(_2\)O...
Table 1

<table>
<thead>
<tr>
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<th>DMSO–H₂O</th>
<th>DX–H₂O</th>
<th>EIOH–H₂O</th>
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<tbody>
<tr>
<td>NpOF</td>
<td>0.20</td>
<td>0.40</td>
<td>0.55</td>
</tr>
<tr>
<td>NpFC12</td>
<td>0.30</td>
<td>0.50</td>
<td>0.65</td>
</tr>
</tbody>
</table>

ΦC and the CAC values of NpOF and NpFC12 in various aqueous organic solvents

ΦC; CAC

DMSO–H₂O | DX–H₂O | EIOH–H₂O
0.20      | 0.40    | 0.55
9.6 × 10⁻⁷ | 4 × 10⁻⁷ | 5 × 10⁻⁷

NpOF 0.20 0.40 0.55 < 10⁻⁷ 9.6 × 10⁻⁷ 6 × 10⁻⁶
NpFC12 0.30 0.50 0.65 4 × 10⁻⁷ 4 × 10⁻⁶ 5 × 10⁻⁵

NpFC12 = 2-Naphthyl-COOCH₂(CF₂)₁₀CF₃.

1 [NpOF or NpFC12] = 1 × 10⁻⁵ mol/dm³.

Φ = 0.6.

3.2. Coaggregates of NpOF and CH₃OF

To provide more evidence for aggregation, we studied the effect of unlabelled PFPE molecule CH₃OF on the excimer formation of NpOF in DX–H₂O with a Φ value of 0.5. In the absence of the unlabelled fluorocarbon CH₃OF, NpOF emits mainly excimer fluorescence at concentration of 1 × 10⁻³ mol dm⁻³ (Fig. 5) owing to the formation of aggregates. Addition of CH₃OF to the solution results in an enhancement of the monomer emission and a reduction of the excimer fluorescence. In the presence of sufficient CH₃OF, the fluorescence spectrum of this NpOF is dominated by the structured monomer emission. Obviously this is because CH₃OF 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...
use 280 nm light selectively to excite the naphthalene moiety in the mixture of NpOF and AnOF. Excitation at 280 nm 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 mol dm$^{-3}$ of NpOF and 1 mol dm$^{-3}$ of AnOF in DX-H$_2$O 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$_3$OF on the excimer formation of dodecyl 2-naphthoate (NpHC$_{12}$). As shown in Fig. 7, 1 mol dm$^{-3}$ of NpOF in DX-H$_2$O solvents with $\Phi = 0.5$ emits excimer fluorescence due to aggregation. Addition of 2 mol dm$^{-3}$ of \( n-C_{18}H_{38} \) to the solution results in an enhancement of the monomer emission and a reduction of the excimer fluorescence.

The effect of CH$_3$OF on the emission spectra of NpHC$_{12}$ in aqueous organic mixed solvents is shown in Fig. 8. A solution of 1 mol dm$^{-3}$ of NpHC$_{12}$ in DX-H$_2$O (\( \Phi = 0.5 \)) exhibits exclusively excimer fluorescence at high concentration due to aggregation.

Surprisingly, addition of 2 mol dm$^{-3}$ CH$_3$OF to the solution of NpHC$_{12}$ shows almost no change in the fluorescence of NpHC$_{12}$. These two significantly different observations indicate an asymmetrical coaggregation behavior between the PFPE compounds and hydrocarbons. This asymmetrical behavior...
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 \( \text{C}_{18} \text{H}_{38} \left( 2 \times 10^{-4} \text{M} \right) \) is added into the \( \text{NpOF} \) solution \( \left( 1 \times 10^{-5} \text{M} \right) \), since the concentration of NaOF is very low as compared to \( \text{C}_{18} \text{H}_{38} \), most of the \( \text{NpOF} \) coaggregates with \( \text{C}_{18} \text{H}_{38} \) rather than keeping their own aggregates. The consequence is that the naphthyl groups of \( \text{NpOF} \) are diluted by \( \text{C}_{18} \text{H}_{38} \) resulting in an enhancement of the naphthyl monomer emission and a reduction of the excimer fluorescence. On the contrary, when a large amount of \( \text{CH}_{3} \text{OF} \left( 2 \times 10^{-4} \text{M} \right) \) is added into the \( \text{NpHC}_{12} \) solution \( \left( 1 \times 10^{-5} \text{M} \right) \), two types of aggregates occur in the solution, a large number of \( \text{CH}_{3} \text{OF} \) aggregates and a smaller number of coaggregates (containing mainly \( \text{NpHC}_{12} \)) in aqueous organic binary solvents. In the coaggregates, the ratio of PFPE is too low to affect the fluorescence profile of \( \text{NpHC}_{12} \).

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