Self Assembly of Fluorescent Amides Containing Pyrene Units

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1. Introduction

The properties of materials depend critically on not only chemical properties of the constituent molecules but also their relative orientations and spacings in the condensed phase. Control of molecular arrangements in the condensed phase is important to realize the desired macroscopic properties of materials, such as superconductivity, ferromagnetism and nonlinear optical behavior. Hydrogen bonding and/or π-stacking interactions are much utilized to the molecular assembling.[1-2]

In these studies an amide unit has been gathering much attention because of its importance as a constituent of peptide. So, the studies of the molecular assemblies with an amide moiety have been of interest in their conformations in solid state,[3-4] hydrogen bonding patterns[5-6], and utilization to the building blocks for the supramolecular assemblies.[7-8] And recently the hydrogen bond interaction energies of identical amides were evaluated by computational methods.[9]

Intermolecular interactions in solutions remain generally unchanged as it is in the solid state. So, it is important to investigate how intermolecular interactions are affected by surroundings, such as polarity of solvents, concentration of substances, or existence of impurities. In order to examine the aggregation of compounds by spectral methods, we synthesized a novel fluorescent reagent (1) which
I. Photopolymer.


has two 1-pyrenemethyl subunits at both sides of an amide unit. As shown in the schematic figure, when the aggregation of 1 is realized in the solutions, ground state dimer or more aggregated species show strongly perturbed excimer-like fluorescence [10-11]. So, we investigated the solvent and concentration dependence of the emission spectra of reagent 1, which would show the information about the aggregation in solutions.

Furthermore, for the purpose to clarify the origin of excimer-like emission, we prepared the reference compounds 2 - 4. The measurement of the fluorescence spectra of these compounds revealed that the compound 1 showed the excimer-like fluorescence at more dilute conditions than the reference compounds, which indicated the formation of the aggregated species of 1.

2. Synthesis

Compound 1 - 4 was synthesized with 20 - 60% yield according to the scheme 1. 1 was synthesized by the coupling reaction using N,N'-carbonyldiimidazole (7) between 1-pyreneacetic acid (5) and 1-pyrenemethyamine (6), which were synthesized from pyrene by 5 steps and 3 steps reaction, respectively. Reference compounds 2 and 3 were synthesized by the coupling reaction between 6 and phenylacetyl chloride (9) and cyclohexylacetyl chloride (10), respectively. The coupling reaction using 7 was applied to the synthesis of 1, because this reagent affords the better yields than the coupling between 6 and 1-pyreneacetyl chloride. Compound 4 was synthesized by coupling reaction between 1-pyrenemethanol (12) and 6 using (7), too. The products were identified by 'H NMR and mass spectroscopic procedures.

N-(1-Pyrenemethyl)-1-pyrenemethanecarboxamide (1). A mixture of 5 (203 mg, 0.78 mmol), 6 (232 mg, 1.0 mmol) and 7 (200 mg, 1.23 mmol) in dry tetrahydrofuran (THF, 15 ml) was stirred and refluxed overnight. The mixture was cooled and extracted with chloroform several times. The combined chloroform layer was washed with water and dried over anhydrous magnesium sulfate, and the solvent was removed by evaporation under a reduced pressure. The crude product was purified by column chromatography (silica gel / chloroform-methanol): yield 140 mg (38%) yellow plates: mp 228 °C (dec.); 'H NMR δ (ppm): 7.69-8.17 (18H, m, arom H), 5.66 (1H, t, NH), 5.06 (2H, d, -CH2 NH-), 4.39 (2H, s, -CH2-CO-); MS m/z (D1) 473 [M+], 242, 228, 215.

N-(1-Pyrenemethyl)-phenylmethanecarboxamide (2). Phenylacetic acid (8) (107 mg, 0.79 mmol) was added to a distilled thionyl chloride (1.5 ml, 21 mmol) and stirred at room temperature for 3 h under nitrogen. The remaining excess thionyl chloride was removed under reduced pressure. The residue was dissolved in dry methylene chloride (10 ml) and dry triethylamine (0.3 ml), then 6 (278 mg, 1.2 mmol) was added at

\[ \text{Scheme 1} \]
once and the mixture was stirred at room temperature overnight under nitrogen. The mixture was extracted with chloroform several times. The combined chloroform layer was washed with water and dried over anhydrous magnesium sulfate, and the solvent was removed by evaporation under a reduced pressure. The crude product was purified by column chromatography (silica gel / chloroform-ethylacetate): yield 51.0 mg (19%) white plates: mp 186-187 °C; \(^1\)H NMR δ (ppm) 7.84-7.27 (9H, m, arom H (pyrenyl)), 7.23-7.27 (5H, m, arom H (phenyl)), 5.77 (1H, s, NH), 5.13 (2H, d, -CH\(_2\)-NH-), 3.64 (2H, s, -CH\(_2\)-CO-); MS m/z (DI) 349 (M\(^+\)), 215.

\(N-(1\text{-Pyrenemethyl})\text{-cyclohexylmethanecarboxamide}\) (3). Cyclohexylacetic acid (10) (50 mg, 0.35 mmol) was added to a distilled thionyl chloride (0.5 ml, 7 mmol) and stirred at room temperature for 3 h under nitrogen. The remaining excess thionyl chloride was removed under reduced pressure. The residue was dissolved in dry methylene chloride (6 ml) and dry triethylamine (0.15 ml), then 6 (116 mg, 0.5 mmol) was added at once, and the mixture was stirred at room temperature overnight under nitrogen. The mixture was extracted with chloroform several times. The chloroform layer was washed with water and dried over anhydrous magnesium sulfate, and the solvent was removed by evaporation under a reduced pressure. The crude product was purified by column chromatography (silica gel / chloroform-ethylacetate): yield 69.7 mg (56%) white powder: mp 203-204°C; \(^1\)H NMR δ (ppm) 7.94-8.27 (9H, m, arom H), 5.73 (1H, t, NH), 5.15 (2H, d, -CH\(_2\)-NH-), 2.07 (2H, s, -CH\(_2\)-CO-), 1.58-1.85 (11H, m, C\(_6\)H\(_{11}\)); MS m/z (DI) 355 (M\(^+\)), 215.

\(1\text{-Pyrenemethyl 1-pyreneacetate}\) (4). A mixture of 5 (130 mg, 0.5 mmol), 12 (143 mg, 0.62 mmol) and 7 (101 mg, 0.62 mmol) in dry THF (15 ml) was stirred and refluxed overnight. The mixture was cooled and extracted with chloroform several times. The chloroform layer was washed with water and dried over anhydrous magnesium sulfate, and the solvent was removed by evaporation under a reduced pressure. The residue was purified by column chromatography (silica gel / chloroform-ethylacetate): yield 140 mg (59%) pale yellow needles: mp 178-179°C; \(^1\)H NMR δ (ppm) 7.62-8.15 (18H, m, arom H), 5.81 (2H, s, -CH\(_2\)-O-), 4.38 (2H, s, -CH\(_2\)-CO-); m/z (DI) 474 (M\(^+\)), 260, 215.

### 3. Results and Discussion

The UV-vis spectrum of 1 shows the similar absorption curve to that of pyrene, which indicates no through bond intramolecular interaction exists between two pyrene subunits. The reference compounds 2 - 4 showed the similar UV-vis spectra with 1 (Table 1).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\lambda_{\text{max}} / \text{nm})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>345.5, 329.5, 278.0, 267.5, 244.5</td>
</tr>
<tr>
<td>2</td>
<td>344.5, 328.0, 277.5, 267.0, 246.5</td>
</tr>
<tr>
<td>3</td>
<td>344.5, 328.0, 277.5, 267.0, 245.5</td>
</tr>
<tr>
<td>4</td>
<td>345.5, 328.5, 278.0, 267.0, 244.0</td>
</tr>
<tr>
<td>pyrene</td>
<td>333.3, 320.2, 273.2, 262.6, 242.9</td>
</tr>
</tbody>
</table>

In chloroform at 1 \(\times 10^{-3}\)M 1 showed an emission band among 380 and 400 nm assigned to a monomer emission, and a further emission band at 425 nm (Fig. 1. Bottom). As the concentration of 1 increased, the emission band at 425 nm increased and the emission band at 390 nm decreased. Further increase of concentration gave a new emission band at 480 nm. These spectral changes indicated that the emission band at 425 nm was assigned to the excimer-like emission from the ground state aggregated species and the emission at 480 nm was considered to be the excimer emissions from the excited state aggregated species, ordinarily observed for pyrene in concentrated solutions.

![Emission Intensity vs Wavelength](image_url)

Fig. 1 Concentration dependence of the fluorescence spectrum of 1 in chloroform at 25°C. \(\lambda_{\text{ex}} = 375\) nm. Concentrations are 1 \(\times 10^{-3}\)M (top), 1 \(\times 10^{-4}\)M (middle), 1 \(\times 10^{-5}\)M (bottom).

To clarify the existence of the species aggregated by hydrogen bonding, the concentration dependence of the fluorescence spectra of the compounds 2 - 4
were measured in a similar manner. In chloroform at concentration of $1 \times 10^{-3}$M, at which concentration the emission band at 425 nm was observed for 1, compounds 2 - 4 showed the monomer emission only among 380 and 400 nm, as shown in Fig 2. Compound 4 had two pyrene units and the four-membered bridging unit as same as compound 1 but didn’t show the excimer emission until the concentration reached to $1 \times 10^{-3}$M. It is reasonable that the amide proton is important for the aggregation. The cyclohexyl unit of 3 seemed to be large enough to prevent the pyrene units from encountering. But, in spite of the easy piling structure of benzene units, 2 didn’t show the excimer emission, neither. As the benzene unit did not have enough stabilizing energy by a face-to-face piling interactions between the adjacent molecules and took a random edge-to-face interactions, this randomness would prevent the pyrene units from piling up.

![Fluorescence spectra of compounds 1, 2, 3, and 4 in chloroform at 25°C.](image)

**Fig. 2** Fluorescence spectra of 1, 2, 3 and 4 in chloroform at 25°C ([1] = [2] = [3] = [4] = $1 \times 10^{-3}$M, $\lambda_{ex} = 375$ nm.)

4. **Conclusion**

We prepared the fluorescent reagents 1 and reference compounds 2 - 4. Fluorescence spectra of compound 1 showed the concentration and solvent dependence described as the formation of aggregated species. We revealed that the aggregating behavior of 1 was detected by the spectral method. The measurements of fluorescence spectra of 2 - 4 confirmed the possibility of the formation of the aggregated species of 1.

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**References**