

## Control of photochemical dimerization of acenaphthylene in graphite oxides intercalated by n-alkylamines with different alkyl chain lengths

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Photochemical dimerization of acenaphthylene in hydrophobized graphite oxide was controlled by using two n-alkylamines with different alkyl chain lengths (n-tetradecylamine; C14 and n-hexadecylamine; C16). X-ray diffraction data showed that both C16 and C14 were well mixed in the interlayer spacing of graphite oxide. More than 0.6 equivalent acenaphthylene was introduced into these intercalation compounds. The interlayer spacing did not change much as the result of intercalation of acenaphthylene. The  $I_1/I_3$  ratios of vibrational fine structure of pyrene molecules introduced in the nanospace of the intercalation compounds were between 0.75 and 0.88, indicating low micro-polarity like hydrocarbon solvents. The micro-polarity of the nanospace varied depending on the content of C14 and it became maximum when the C14 content was 82 %. The syn/anti ratio of acenaphthylene dimer photochemically formed in the intercalation compounds changed in a complicated way. Considering that relatively higher micro-polarity of the nanospace in the intercalation compound with C14 content of 82 % would reduce the diffusion of excited acenaphthylene molecules, causing higher syn/anti ratio.

Key words: Photochemical dimerization, acenaphthylene, graphite oxide, alkylamine, polarity

### 1. INTRODUCTION

Recently, solid matrices such as zeolites, liquid crystals and layered materials are attracting much interest as photochemical reaction media<sup>1-6</sup>. In these media, reaction was controlled by changing the electronic field, direction of diffusion and molecular orientation. In this context, we have reported that neutral aromatic molecules can be easily introduced into graphite oxides hydrophobized by cationic surfactant or alkylamine<sup>7-10</sup>. Photochemical dimerization of acenaphthylene occurred easily in these hydrophobized graphite oxides and syn/anti ratio of the formed acenaphthylene dimers varied greatly depending on the alkyl chain length of amine and the contents of amine or cationic surfactant. The highest syn/anti ratio of 9 was obtained when octylamine was used.<sup>11-13</sup> The change of syn/anti ratio was suggested to be due to that of the diffusion behaviour of excited acenaphthylene molecules. In order to control the photochemical reaction in hydrophobized graphite oxides furthermore, it would be necessary to control the orientation of acenaphthylene molecules in the intercalation compounds or to control diffusion behavior of the excited molecules in the hydrophobized graphite oxides in different manners. In this study, we show the control of photochemical dimerization of acenaphthylene in n-alkylamine-intercalated graphite oxide by using two alkylamines with different alkyl chain lengths at the same

time. The results were discussed in terms of the size of the nanospace of hydrophobized graphite oxides and the micro-polarity determined based on the fluorescence spectra of pyrene introduced in them.

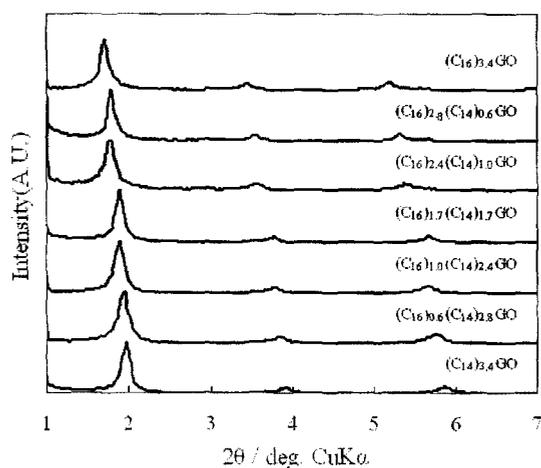
### 2. EXPERIMENTAL

Graphite oxide (GO) was prepared from natural graphite powder (57-74  $\mu\text{m}$ ) based on the Brodie's method<sup>14</sup> and the composition of  $\text{C}_8\text{O}_{3.2}\text{H}_{2.4}$  was obtained. Intercalation of various amounts of n-hexadecylamine (C16) into GO was performed as reported previously<sup>11,12</sup>. Then, n-tetradecylamine (C14) was added to the resulting C16-intercalated GO in a similar manner and  $(\text{C16})_x(\text{C14})_{3.4-x}\text{GOs}$  ( $x=0-3.4$ ) were obtained. Thin film sample of acenaphthylene or pyrene-intercalated  $(\text{C16})_x(\text{C14})_{3.4-x}\text{GO}$  samples were prepared by casting the chloroform solution of intercalation compound and the above organic molecules on quartz substrate. Fluorescence spectra of pyrene-intercalated  $(\text{C16})_x(\text{C14})_{3.4-x}\text{GO}$  samples were measured using Hitachi F-2500 fluorescence spectrophotometer with the excitation wavelength of 330nm. In order to avoid the aggregation of pyrene, the content of pyrene molecules was 0.01 mol per GO unit and the ratios of the peak intensity at 373 and 383 nm ( $I_1/I_3$  ratio) were calculated. X-ray diffraction patterns of the samples were recorded by Rigaku Rint-2100 using  $\text{CuK}\alpha$  radiation.

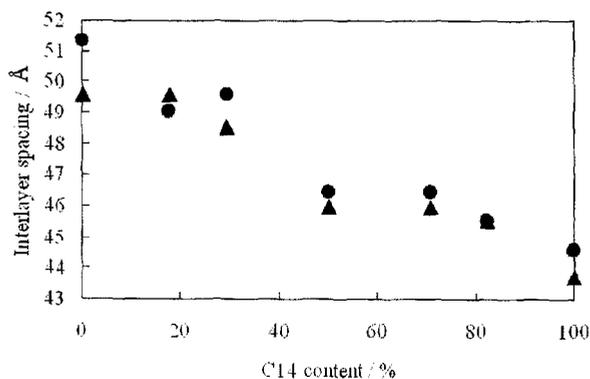
Photochemical dimerization of acenaphthylene was performed as reported previously<sup>3</sup>, using ultra high pressure mercury lamp ( $\lambda > 340$  nm by using Corning CS-052 filter). The acenaphthylene content in the intercalation compounds were 0.6 mol/GO, except for (C16)<sub>3,4</sub>GO (0.3 mol/GO). Syn/anti ratio of the formed acenaphthylene dimer was determined from the ratio of the peak area at 4.09ppm (syn) and 4.84ppm (anti) in <sup>1</sup>H NMR spectra obtained by Bruker 500RX for the sample extracted from intercalation compound with cyclohexane<sup>12,13</sup>.

### 3. RESULTS AND DISCUSSIONS

Fig. 1 shows the X-ray diffraction patterns of (C16)<sub>x</sub>(C14)<sub>3,4-x</sub>GO samples with various C14 contents. In all cases, a series of (00 $\ell$ ) peaks were clearly observed, indicating that the products were consist of a



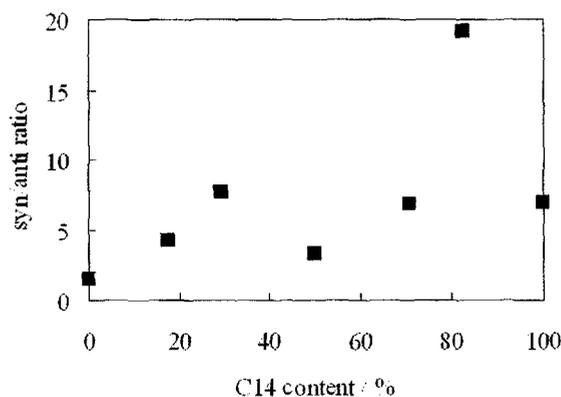
**Fig.1** X-ray diffraction patterns of graphite oxides intercalated by *n*-hexadecylamine and *n*-tetradecylamine with various C14 contents.



**Fig.2**  $I_c$  values of (C16)<sub>x</sub>(C14)<sub>3,4-x</sub>GO (●) and acenaphthylene-intercalated (C16)<sub>x</sub>(C14)<sub>3,4-x</sub>GO (▲) as a function of C14 contents.

single phase, and therefore, C16 and C14 were well mixed in the interlayer gallery of GO. The interlayer spacings ( $I_c$  values) decreased almost linearly with the increase of C14 content, which shows that the free volume in (C16)<sub>x</sub>(C14)<sub>3,4-x</sub>GO samples available between alkylamines for the inclusion of acenaphthylene decreased, because the alkylamine contents are the same for all the samples. However, the maximum amounts of acenaphthylene molecules introduced in the nanospace of (C16)<sub>x</sub>(C14)<sub>3,4-x</sub>GO samples without excess acenaphthylene crystal which was determined from the data of X-ray diffraction measurement as previously reported<sup>3,5</sup> were more than 0.6 mol/GO, almost twice of that in (C16)<sub>3,4</sub>GO (0.3 mol/GO). Since the  $I_c$  values of (C16)<sub>x</sub>(C14)<sub>3,4-x</sub>GO samples after intercalation of acenaphthylene molecules as shown in Fig.2 decreased similarly to those of pristine samples, the increase of maximum amount of acenaphthylene could be because introduction of two alkylamines with different alkyl chain lengths into GO created new adsorption sites for acenaphthylene.

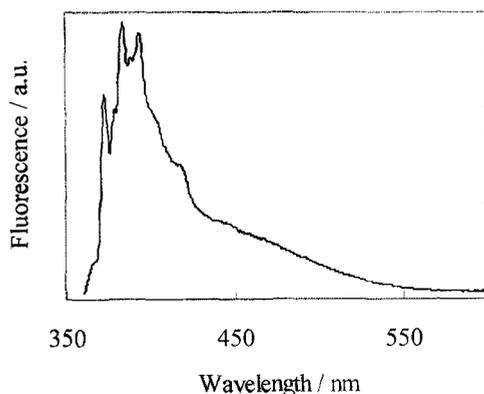
Fig.3 shows the syn/anti ratio of acenaphthylene dimer formed in the nanospace of (C16)<sub>x</sub>(C14)<sub>3,4-x</sub>GO samples as a function of C14 content. By introducing two alkylamines with different alkyl chain lengths, syn/anti ratio became larger than those of acenaphthylene dimers formed in graphite oxide containing only C16 and varied in a complicated way. When the C14 content was low, it increased up to 7.7 for (C16)<sub>2,4</sub>(C14)<sub>1,0</sub>GO with the increase of C14 content and then decreased to 3.3 for



**Fig.3** Syn/anti ratios of acenaphthylene dimers formed in graphite oxides intercalated by *n*-hexadecylamine and *n*-tetradecylamine with various *n*-tetradecylamine (C14) contents. The acenaphthylene content in (C16)<sub>3,4</sub>GO was 0.3 mol/GO.

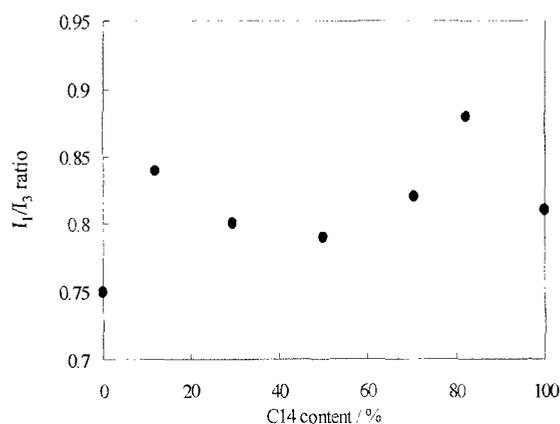
(C16)<sub>1.7</sub>(C14)<sub>1.7</sub>GO. It increased again and became maximum (19.2) for (C16)<sub>0.6</sub>(C14)<sub>2.8</sub>GO (C14 content of 82%). It has been reported that more than 95% and about 50% of acenaphthylene molecules in the singlet and triplet excited states, respectively provide syn-isomer<sup>15,16</sup>. As the result, syn/anti ratios of the dimers are more than 19 and about 1, when they are exclusively formed from the singlet and triplet excited states, respectively. Therefore, in the present case, it is possible to conclude that almost all the acenaphthylene dimers formed in (C16)<sub>0.6</sub>(C14)<sub>2.8</sub>GO were from singlet excited state. It is very interesting to control the syn/anti ratio of acenaphthylene dimer simply by changing the C14 content in graphite oxide intercalated by n-alkylamines.

Fig.4 shows the emission spectrum of pyrene introduced in the layer of (C16)<sub>3.4</sub>GO with pyrene/GO ratio of 0.01. The emission peaks at around 370-390 nm which were attributed to the monomerically dispersed pyrene molecules was clearly observed, while that at 450 nm due to pyrene dimer was almost absent, as was reported in our previous paper<sup>8</sup>.  $I_1/I_3$  ratio is a good indication of micro-polarity of the media surrounding pyrene molecules<sup>17</sup>. The  $I_1/I_3$  ratios of pyrene in the intercalation compounds were rather low and comparable to those in hydrocarbon solvents. This is in contrast with the case of micelles in aqueous solution, which would be because water molecules were excluded in the nanospace of hydrophobized graphite oxide. Fig.5 shows the  $I_1/I_3$  ratio of fluorescence of pyrene monomer in the nanospace of (C16)<sub>x</sub>(C14)<sub>3.4-x</sub>GOs as a function of C14 content in GO. It changed in a similar manner to that of syn/anti ratio of acenaphthylene dimers formed in the intercalation compounds, except that at the C14 content of 11%. The



**Fig.4** Fluorescence spectrum of pyrene in (C16)<sub>3.4</sub>GO. Pyrene/GO ratio was 0.01.

larger  $I_1/I_3$  ratios at the C14 content of 11% and 82% are not well understood at this moment. However, it is noteworthy to point out that at the C14 content of 82%, syn/anti ratio of acenaphthylene dimers was very large; 19.2, as shown in Figure 2. Higher micro-polarity of the nanospace would make more difficult for the excited acenaphthylene molecules to diffuse and collide with other molecules, therefore, acenaphthylene dimer did not form from triplet excited state with longer life time. In other words, pairs of two acenaphthylene molecules with relatively short inter-molecular distance exclusively



**Fig.5**  $I_1/I_3$  ratios of pyrene in graphite oxides intercalated by n-hexadecylamine and n-tetradecylamine with various n-tetradecylamine (C14) content.

reacted. On the other hand, when the  $I_1/I_3$  ratio was small, diffusion of excited molecules would be easier, leading the formation of triplet excited state and consequently giving more anti dimers. Since the molecular size of acenaphthylene is different from that of pyrene and the adsorption site of them in hydrophobized graphite oxide would be different, direct comparison of the syn/anti ratio of acenaphthylene dimer formed in intercalation compounds and micro-polarity of the nanospace in them might be difficult. However, the complicated change of syn/anti as a function of C14 content would be qualitatively explained as follows. The increase of syn/anti ratio for the (C16)<sub>x</sub>(C14)<sub>3.4-x</sub>GO with lower C14 content would lead the decrease of distance between adjacent acenaphthylene as the result of the decrease of  $I_c$  value, assuming that acenaphthylene molecules are dispersed uniformly. This causes the increased of the formation of syn-dimers. On the other hand, the decrease of micro-polarity in the intercalation compound increases

the mobility of excited acenaphthylene molecules, giving more anti-dimers. These two competing effects determined the syn/anti ratio of the acenaphthylene dimers.

In conclusion, by introducing n-alkylamines with different alkyl chain lengths into graphite oxide at the same time, both the size and the micropolarity of nanospace available in the intercalation compound were changed. As the result, the distance between acenaphthylene molecules and the diffusion rate of the excited molecules varied, therefore, the syn/anti ratio of acenaphthylene dimer was controlled in a wide range. The authors believe that the present results would be good information to design photochemical reaction media with high selectivity and efficiency.

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