Reversible gelation in cyclohexane of pyrene substituted by dialkyl L-glutamide: photophysics of the self-assembled fibrillar network

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Abstract

L-Glutamic acid-derived compound with pyrenyl group was able to form organic gels in benzene, cyclohexane, and so on. The gels were produced through the formation of highly oriented aggregates and a remarkable development of their fibrous polymer networks. Our scopes of this study are to present the salient features of the photophysics of pyrene in the highly oriented fibrillar network in cyclohexane and to describe spectroscopic measurements used either to detect pyrene association prior to excitation or to confirm the absence of aggregated pyrenes. The concentration and the temperature affected the gel-formation. The sol in the concentration below critical gel concentration includes nanoassemblies with highly oriented aggregates of the compound. Functionalization of L-glutamide derivative with different head groups using electron accepting pyrene and electron-donating *N,N*-dimethylaniline (DMA) chromophores was also performed to detect the exciplex formation as the mimicry of the photoinduced electron transfer process in the photosynthesis. Upon cooling from 60 to 10 °C, red shifted fluorescence from 446 to 456 nm ascribed to the charge transfer from DMA to pyrene was observed in the mixed system of pyrene- and DMA-containing L-glutamide derivatives in cyclohexane.
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1. Introduction

In recent years, various kinds of low molecular weight compounds have been found to assemble in organic solvents [1–3]. Self-aggregation of the gel-forming systems through intermolecular interactions, such as hydrogen bonding, the solvophobic effect, and so on leads to the formation of fibrous networks in most cases. Particularly, we have had a great interest in lipophilic L-glutamide derivatives as gel-forming materials in the past decade [4–6]. The L-glutamide moiety as a chiral source, double long-chain alkyl groups as lipophilic parts, and a head group as a functional part can characterize these compounds. The unique properties are emphasized by the facts that the gel formation is observed at a low concentration and this is brought through the network formation with microfibrous aggregates based on highly-oriented structure in organic media such as benzene, ethanol, cyclohexane, and so on. Formation of organic gels can be visually observed and microfibrous aggregates can be detected by using transmission electron microscopics (TEM). In order to evaluate the exact critical aggregation concentration (cac), we previously reported on the direct evaluation of an aggregation threshold prior to the sol–gel phase transition applied to protoporphyrin IX- and/or pyrene-functionalized L-glutamide derivatives in benzene [7]. Chromophoric probes of porphyrin and pyrene moieties enabled evaluation of their assembling behavior photophysically even at a low concentration below the critical gel concentration (cgc) through UV–vis, circular dichroism (CD), and fluorescence spectroscopic characterization. These spectroscopic characterizations were able to

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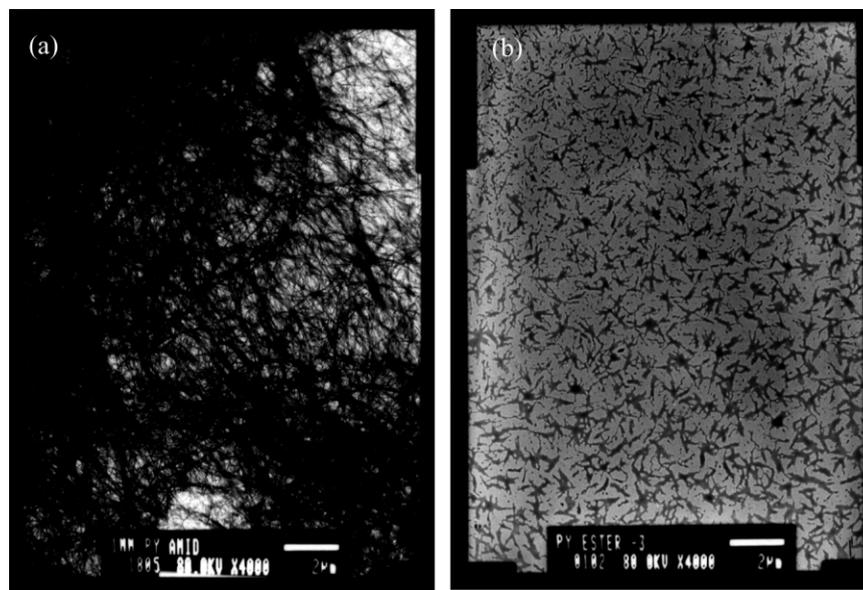
Fig. 1. Transmission electron micrographs of **1** {(a) 1.0 mmol dm^{-3}} and **2** {(b) 1.0 mmol dm^{-3}} aggregates in the cast films from cyclohexane solutions. Stained by 2 wt.% ammonium molybdate.

compensate the lack of TEM observation for the aggregation in the dilute solution. We also examined the steady-state fluorescence spectral changes caused by the singlet–singlet energy migration from pyrene to porphyrin in the mixed microfibrous assemblies in benzene to mimic the energy transfer process in the photosynthetic antenna complex [7]. Although a precise evaluation of intrinsic quantum yield for energy transfer is not clear-cut, at least, energy transfer from the excimer–pyrene complex to the ground-state free base porphyrin was realized. Benzene is good solvent to dissolve the porphyrin- and pyrene-containing L-glutamide derivatives, however, the aromatic solvent of benzene tends to be intercalated between the pyrene and the porphyrin and it disturbs the energy migration.

In this paper, we report photophysical re-evaluation of an aggregation behavior of pyrene-containing L-glutamide derivative in cyclohexane {or 50:1 (v/v) cyclohexane/ethanol} instead of benzene and the further functionalization of L-glutamide derivative with different head group using electron-donating N,N-dimethylaniline (DMA). Steady-state fluorescence spectroscopic measurements to detect the charge transfer from DMA to pyrene in the mixed microfibrous assemblies were performed as the mimicry of the photoinduced electron transfer process in the photosynthesis.

2. Experimental

A pyrene containing didodecylamide-type compound (**1**) was prepared according to the procedure reported previously [7]. Didodecylester-type (**2**) was prepared according to the procedure reported previously [4] with slight modification. mp 65–66 °C. Found: C, 77.9; H, 9.4; N, 1.8. Calc. for $C_{49}H_{71}NO_5$: C, 78.0; H, 9.5; N, 1.9%. An L-glutamic acid derived compound with DMA head group (**3**) was prepared by the condensation of 4-(dimethylamino)-phenylacetic acid and N',N'-didodecyl-L-glutamide [6] by using triethylamine and diethyl cyanophosphonate in THF. mp 156–159 °C. Found: C, 70.9; H, 10.6; N, 8.2. Calc. for $C_{39}H_{70}N_4O_3$: C, 72.8; H, 11.0; N, 8.7%. **1** and **3** dissolved in cyclohexane at 70 °C were gradually cooled to 20 °C to form gels.

Preparation of samples for UV–vis, CD, Fluorescence spectroscopic measurements, TEM observation, and cgc determination was performed in a similar manner as reported in Refs. [6,7].

3. Results and discussion

Pyrene-containing didodecylamide-type (**1**) formed organic gels in cyclohexane at the concentration of more than 1.0 mmol dm^{-3}. TEM observation showed a self-assembled and well-developed fibrous network as seen in Fig. 1a. The diameters are around several tens to hundreds of nanometers. Their lengths will be at least in the order of hundreds of micrometers. While, as shown in Fig. 1b, the didodecylester-type **2** produced a different type of aggregates with shorter lengths (approx. 1 μm) than those of **1**. Thus, hydrogen bonding between amide groups in these systems is effective to form and develop the fibrous network with longer length.

The plots of the molecular coefficient at 343 nm (ε_{343}) vs. log[**1**] (Fig. 2a) and the molecular ellipticity at 359 nm (θ_{359}) vs. log[**1**] (Fig. 2b) in 50:1 (v/v) cyclohexane/ethanol showed that θ_{359} increased (ε_{343}
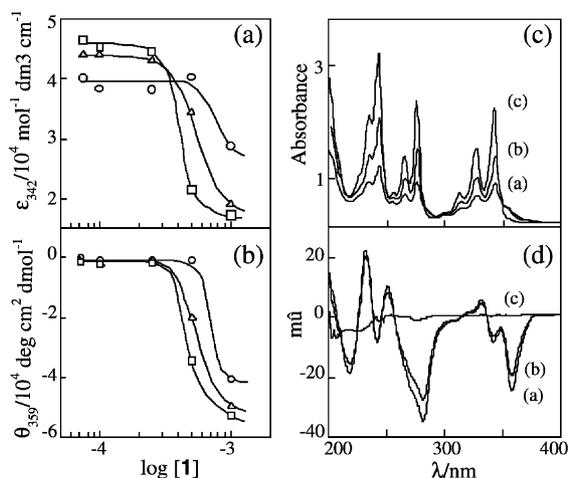
Fig. 2. (a) Molecular coefficient (ε_{343}) and (b) molecular ellipticity (θ_{359}) of **1** in 50:1 (v/v) cyclohexane/ethanol at 60 (circle), 25 (triangle) and 10 °C (square). (c) UV–vis and (d) CD spectral changes of **1** (0.5 mmol dm^{-3}) in 50:1 (v/v) cyclohexane/ethanol at (A) 10, (B) 25 and (C) 60 °C using a 1 mm quartz cell.

decreased) remarkably in the concentrations above 0.3 mmol dm^{-3}. The electronic transition of pyrene is likely to be ^1L_a (allowed) at 343 nm; there is a transition at a longer wavelength (^1L_b) [8]. In the case of a cyclohexane-ethanol solution (50:1,v/v) containing 0.5 mmol dm^{-3} of **1**, the gel was not visually observed. Critical gel concentration of **1** in 50:1 (v/v) cyclohexane/ethanol was determined as over 1.0 mmol dm^{-3}. Therefore, we consider that the increase of θ_{359} is not related to the gel formation, but indicates micro-environmental change such as highly oriented aggregation. The critical points (concentration) of Fig. 2a,b will be attributable to the cac of **1** in cyclohexane/ethanol (50:1). It is also proved that **1** can form oriented aggregates even at the sol-forming concentration. The value of A_{343} decreased as lowering the temperature from 60 to 10 °C as shown in Fig. 2c. However, θ_{359} increased drastically for temperatures below 25 °C in their CD spectra as seen in Fig. 2d. On the contrary, no UV–vis- and CD-spectral changes were observed in the case of a cyclohexane-ethanol solution (50:1,v/v) containing 0.5 mmol dm^{-3} of **2** at 10–60 °C. In the case of **2**, there was no molecular ellipticity ($\theta = 0°$ cm^2 dmol^{-1}) from 250 to 400 nm. These results also support that the importance of the hydrogen bonding between amide groups in **1** to aggregate with highly oriented structure.

It is known that the monomer fluorescence of pyrene is very sensitive to its surroundings [9]. This effect is also expected in our case. When the didodecylester-type of **2** (1.0 mmol dm^{-3}) was dissolved in cyclohexane-ethanol (50:1,v/v), the emission band was observed at 398 nm {curve (E) of Fig. 3a}. This band is assigned to be the monomer fluorescence of a pyrene moiety [8]. The shape and maximum position of the emission band

did not change at the temperature range of 10–60 °C. This implies that **2** disperses as a monomeric state at these temperatures. However, emission band of **1** was affected by the temperature. Upon cooling to 10 °C, new band centered at 450 nm (E$_2$) is observed, and this is assigned to be the excimer formation [8] as seen in Fig. 3a {curves (A–D)}. In marked contrast with benzene [7], the excimer band appears even at 40 °C in cyclohexane/ethanol (50:1). Therefore, cyclohexane well meets the purpose of the photoinduced electron transfer, since the aromatic benzene tends to be intercalated between the two pyrenes and it disturbs the charge transfer.

The fluorescence behavior in the **1** and **3** mixed system was also examined as shown in Fig. 3b. Red-shifted fluorescence from 446 to 456 nm was observed with decreasing the temperature from 60 to 10 °C. This result indicates to be the exciplex formation of **1** and **3** mixed system caused by the charge transfer from DMA to pyrene. The emission intensities at 456 nm increased with increasing the [**3**]/[**1**] ratio. There is no absorbance at the wavelength 350–400 nm from the UV spectrum of **3** as shown in Figs. 4 and 3 does not fluoresce when exposed to the light of wavelength 350–500 nm. Therefore, despite of the relatively high concentration of **3** (10^{-3} mol dm^{-3}), possibility of the serious inner cell effect in this fluorescence experiment is low. It was found by the inverse fluid method [6,10] that aggregation of **1** occurs more easily than that of the DMA-containing **3**, although **3** can also form similar organic gel. This result implies that phase-separation of **1** from mixed system of **1** and **3** occurs predominantly to that of **3** because the aggregation of **1** occurs more easily than that of **3** as described above.
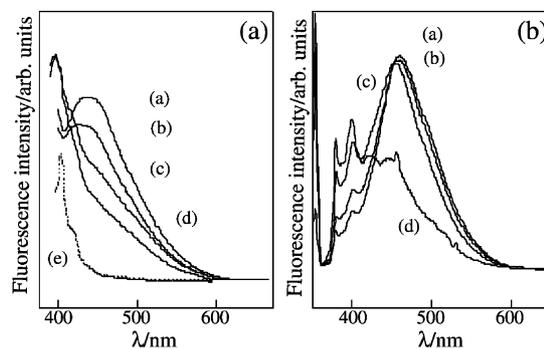
Fig. 3. (a) Fluorescence spectra of **1** (1.0 mmol dm^{-3}) in 50:1 (v/v) cyclohexane/ethanol at (A) 10, (B) 25, (C) 40 and (D) 60 °C and **2** {1.0 mmol dm^{-3}; curve (E)} in 50:1 (v/v) cyclohexane/ethanol at 10 °C. (b) Fluorescence spectra of mixed system of **1** (0.05 mmol dm^{-3}) and **3** (2.5 mmol dm^{-3}) in cyclohexane at (A) 10, (B) 25, (C) 40 and (D) 60 °C with excitation at 350 nm.
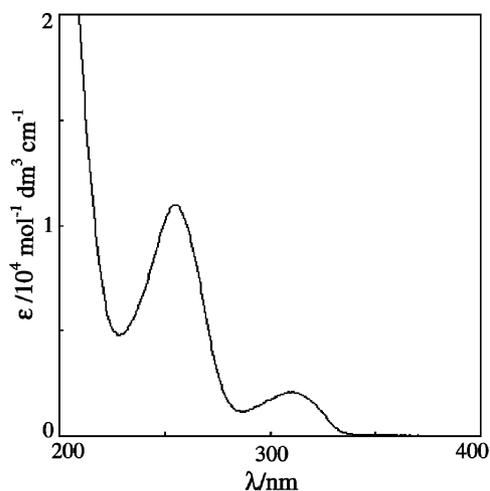
Fig. 4. Molecular coefficient (ε) of **3** in cyclohexane at 25 °C.

4. Conclusions

In conclusion, assembling behavior of L-glutamide derivative with pyrene head group was re-evaluated conveniently through photophysical analysis of chromophoric probe in cyclohexane. In particular, cyclohexane well meets the purpose of the photoinduced electron transfer system for the fluorescence spectroscopic measurement. The extent of charge transfer for pyrene–pyrene and/or DMA-pyrene could be controlled effectively by changing the concentration and the temperature through gel-formation of dialkyl L-glutamide derivative systems in cyclohexane.

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