Self-assembling Fullerene Derivatives for Energy Transfer in Molecular Gel System

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Abstract. An L-glutamide-derived compound with a fullerene moiety was newly synthesized by the coupling of (6,6)-phenyl-C61 butyric acid with N,N'-didodecyl L-glutamide containing an amino alkyl group. In this paper, we describe that the solubility to an organic solvent was sufficiently improved by functionalization with L-glutamide and these fullerene derivatives could form ordered aggregates in organic solvents. It is also reported that the fullerene-containing derivatives were evaluated as a donor-acceptor model with the corresponding porphyrine derivative.

1. Introduction
Porphyrid and benzoquinone derivatives play as an electron donor-acceptor for light-harvesting and electron transfer in the natural photosynthesis. Recently, a porphyrin-fullerene complex has been of much concern as a mimic photosynthetic model, because the first reduction potential of fullerene is similar to that of benzoquinone and fullerene is expected to be a potential electron acceptor for a π-electron system [1]. For example, it is known that the lifetime of a charge-separated state in a porphyrin-fullerene conjugate is longer than that in the natural photosynthetic system [2].

In this paper, we wish to introduce a new porphyrin-fullerene complex system that is tuned by functionalization with L-glutamide derivatization. It has been reported that an L-glutamide-derivated moiety is a very useful tool for promoting the intermolecular hydrogen bonding to lead to suprastructural fabrications [3]. Therefore, we newly synthesized three kinds of L-glutamidederived functionalized fullerenes 1 (FC2, FC5 and FC10) (figure 1) and then they were evaluated as a donor-acceptor model with the corresponding porphyrine derivative 2 [4].
2. Experimental

N,N' -didodecyl L-glutamide containing an amino alkyl group 3 (C2, C5 or C10) was synthesized according to the previously reported method [5].

(6,6)-phenyl-C61 butyric acid (PCBA) was prepared by (6,6)-phenyl-C61 butyric acid methyl ester (PCBM) [6]. A cetic acid and HCl were added to a solution of PCBM in toluene. The mixture was stirred and refluxed. The time course of reaction was followed by TLC. All volatile components were removed in vacuo. The residue was dispersed by methanol and then washed by centrifugation with ether. The same procedure was repeated by using toluene and ether. The residue was dried in vacuo to give PCBA as dark brown powders. The chemical structures were confirmed by elemental analysis, FT-IR, UV-vis, MALDI-TOF mass and HPLC. PCBA was dissolved in pyridine and 3 (C2, C5 or C10) and N,N'-dicyclohexylcarbodiimide (DCC) were added to the PCBA solution. The mixture was stirred and refluxed. The time course of reaction was followed by HPLC. The reaction mixture was concentrated in vacuo. The residue was dissolved in dichloromethane and was filtered. The filtrate was concentrated in vacuo, and the residue was reprecipitated from toluene-acetonitrile and then dried in vacuo to give 1 (FC2, FC5 or FC10) as brown powders. The chemical structures were confirmed by elemental analysis, 1H and 13C NMR, FT-IR, UV-vis, MALDI-TOF mass and HPLC.

3. Result and Discussion

3.1. Solubility and gelation property

C60 shows limited solubility. As shown in table 1 and figure 2, the solubility of C60 is considerably modified by derivatization into PCBM and introduction of an L-glutamide moiety. Especially the L-glutamide-functionalized C60, 1 showed good solubility for THF, toluene and chloroform. However, when a solvent system was adjusted by mixing with a poor solvent such as cyclohexane, the solution of 1 changed to a gel state. Figure 2c shows that 1 (FC10) undergoes a temperature-dependent phase transition between gel and sol states in cyclohexane-THF (6 : 1) mixture. This is a typical phenomenon in a molecular gel induced by L-glutamide-derived lipids [3]. We have reported that various L-glutamide derivatives form gels through nanofibrillar network formation. As supporting this, the TEM observation indicated that 1 could form nanostructural aggregates.
Table 1. Solubility of fullerene derivatives

| solvent          | C_{60} | PCBM | PCBA | FC5 |
|------------------|--------|------|------|-----|
| toluene          | S+     | S+   | I    | S++ |
| benzene          | S+     | S+   | I    | S+  |
| dichlorobenzene  | S+     | S++  | I    | S++ |
| dichloroethane   | S     | S++  | I    | S++ |
| chloroform       | S     | S+   | I    | S++ |
| tetrahydrofuran  | I     | S    | S    | S++ |
| 1,4-dioxane      | I     | S    | I    | S+  |
| 1-propanol       | I     | S    | I    | S   |
| 2-propanol       | I     | S    | I    | S   |
| ether            | I     | I    | I    |    |
| water            | I     | I    | I    |    |
| methanol         | I     | I    | I    |    |
| acetonitrile     | I     | I    | I    |    |
| cyclohexane      | I     | I    | I    |    |

S: soluble, I: insoluble
Concentration: 1.0 mM, Temperature: 25 °C

3.2. Photophysical property
We have already reported that 2 can form a gel in organic media [4]. The typical phenomena were detected by UV-vis and CD spectral changes. For example, the Soret band of 2 appeared at 417 nm as a peak top in a solution state, but changed to a characteristic split by about 30 nm (398 nm and 428 nm) as peak tops in a gel state. In addition, the gelation was accompanied by induction of strong Cotton effect in 375 - 460 nm.

In this study, a photophysical property was investigated in a mixed system of 1 and 2. After a cyclohexane-THF (20 : 1) mixture containing 1 and 2 was kept at 60 °C for 10 min and cooled down at 10 °C, UV-vis and CD spectra were examined. A similar procedure was carried out with a 2 and C_{60} mixed system. As shown in figures 3a and b, the 2 and C_{60} (2 : 1) system showed remarkable decrease of porphyrin absorption with weak Cotton effect. This is due to precipitation because of less solubility. In contrast, the 2 and 1 (FC2) (2 : 1) mixed system showed no precipitation but also typical splitting in UV-vis spectra with induction of strong Cotton effects at the absorption band around a porphyrin
moiety as shown in figures 3c and d. These spectral changes were similar to that in 2 alone, but new Cotton effects appeared around 230 - 300 nm and 500 - 560 nm in the 2 and FC2 mixed system (figure 3d).

On the other hand, addition of 1 (FC2) to the 2 solution (0.01 mM) in acetonitrile-benzene (100 : 1) induced a bathochromic shift of the Soret band (figure 4a). It is also observed that this bathochromic behavior was temperature-dependent (figure 4b). These results indicate that the 2 and FC2 mixed system forms cooperative assemblies in mixed solvents such as cyclohexane-THF and acetonitrile-benzene at 10 °C.

Figure 3. UV-vis (a, c) and CD (b, d) spectra of a 2 and C60 (2 : 1) mixture (dotted line) and a 2 and FC2 (2 : 1) mixture (sol state: broken lines, gel state: solid line) in a cyclohexane-THF (20 : 1) mixture at 10 °C. Concentration 2: 0.5 mM.

Figure 4. Concentration-dependent UV-vis spectral change of 2 (0.01 mM) in acetonitrile-benzene (100 : 1) at 25 °C (a). Temperature-dependent UV-vis spectral change of a 2 and FC2 (1 : 1) mixture in acetonitrile-benzene (100 : 1) (b). Concentration 2: 0.01 mM.
3.3. Energy transfer system

Well-defined electron donor-acceptor arrays in the natural photosynthetic reaction center ensure highly efficient photo-induced electron transfer (PET). Therefore, we investigated fluorescence characteristic of 2 with 1 (FC2) or C60 in acetonitrile-benzene (100:1). Figure 5a shows the concentration-dependent fluorescence spectral change at 25 °C. The emission intensity of 2 decreased remarkably with increase of FC2. Similar results are observed in the presence of C60 and no significant difference is seen in both the systems. This indicates the possibility of electron transfer from 2 to FC2 and C60. On the other hand, the distinct difference between the 2 and C60 mixed systems was found in their temperature dependencies. As shown in figures 5b-5d, the 2 and FC2 (1:1) system showed remarkable temperature dependence showing the bending point at 40 °C although almost no temperature dependence was observed in the C60 mixed system at the temperature range of 10 - 60 °C. This suggests that efficiency of the electron transfer can be promoted by temperature in the mixed system with FC2. To understand these specific behaviors, we propose that co-aggregation with ordered structures was promoted by mixing with FC2 having an L-glutamide moiety. As supporting this assumption, we have reported that L-glutamide-derived lipids with hydrophobic functional head groups can form aggregates in organic media [7], showing a temperature-induced phase transition between ordered and disordered states.

Figure 5. Concentration-dependent fluorescence spectral change of emission spectra of 2 (0.01 mM) in acetonitrile-benzene (100:1) at 25 °C (a). Temperature-dependent fluorescence spectral change of a 2 and FC2 (1:1) mixture (b) and a 2 and C60 (1:1) mixture (c). Concentration 2: 0.01 mM. Excitation wavelength = 435 nm. Temperature dependence of emission intensity at 653 nm (d).
4. Conclusion
It has been described that the L-glutamide-functionalized fullerene derivative (1) can dissolve in organic media to form a molecular gel through molecular orientation. A mixed system of the fullerene (1) and porphyrin (2) derivatives was applied for an electron transfer model and it was indicated that porphyrin-fullerene complexation could be assisted by an L-glutamide moiety.

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