Synthesis of Copolymers Containing C_{60}, Cyclododecyl, and Sulfonate Groups: Photophysical Behavior of C_{60} in Highly Constrained Microenvironments

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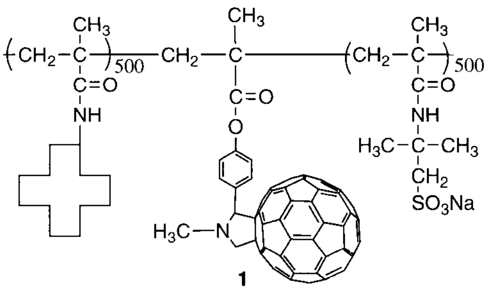
C_{60} was covalently incorporated into hydrophobic cluster of amphiphilic polysulfonates. In this cluster C_{60} chromophores showed extremely blue-shifted fluorescence and no thermally activated delayed fluorescence.

Since the first discovery of C_{60}, its unique π system with round shape has attracted much attention and the photophysical properties have been investigated in various conditions.[1] Recently, one of the authors succeeded in producing highly constraining hydrophobic microenvironments in amphiphilic polymers and observed unusual luminescence of Zn(II) tetraphenylporphyrin in such circumstances.[2] Here we report on the incorporation of C_{60} chromophores into the similar hydrophobic clusters and on its luminescence behavior.

The synthesis of C_{60}-containing copolymer **1** was carried out by heating a mixture of monomers **2**,[3] **3**, and **4** with a ratio of 0.1, 49.95, and 49.95 mol%, respectively, in DMF in the presence of AIBN at 60 °C for 12 h.[4] The crude polymer was purified by reprecipitation from a methanol solution into excess ether for three times and by dialysis against pure water for three weeks. The conversion was 33.3% on the basis of the total monomers. Reference compound **5** was prepared under the same conditions to be used for the synthesis of **2**. A long alkyl chain was introduced into **5** to improve the poor solubility of C_{60} residue in usual organic solvents. The structures of **2**[5], **3**[4], and **5**[5] were confirmed on the basis of spectroscopic data.



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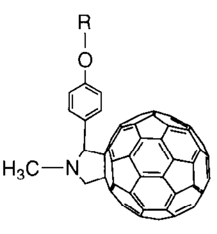
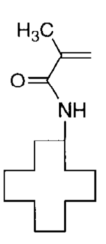


2: R= $-CO-C(CH_3)=CH_2$
5: R= $-(CH_2)_{21}-CH_3$



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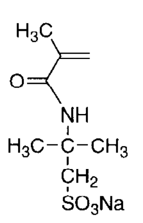

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The weight-average molecular weight of copolymer **1** was estimated to be 1.6 x10^5 by a Zimm plot analysis of static light-scattering data. The average diameter of **1** in water was estimated to be 13 nm by a dynamic light-scattering technique on assuming a spherical shape for the polymer. These values are close to those reported for similar polymers.[6] The existence of C_{60} chromophores in **1** was supported by FT-IR on the basis of typical absorptions for pyrrolidine-fused C_{60}. Thus, **1** shows peaks at 520, 477, and 419 cm^{-1}, which are close to the values of **5** (526, 479, and 416 cm^{-1}) and to those of similarly modified C_{60}-fullerenes.[7]

In order to get information on the aggregation of C_{60} chromophores in **1**, the quantum yield of singlet oxygen production was determined. Thus, $^1O_2$ formation by energy transfer from the triplet state of C_{60} chromophores in **1** and **5** and C_{60} itself in oxygen saturated solutions was measured by comparing the singlet oxygen emission intensity at 1270 nm immediately after the laser excitation[8] of the fullerene samples as a function of laser pulse energy. Assuming that the value for C_{60} itself is unity,[9] the quantum yields of singlet oxygen production for **1** and **5** were obtained to be 0.49±0.03 and 0.93±0.05, respectively. If strong aggregation or close interactions between the fullerenes were involved, the value would be close to zero. Therefore, the present results clearly indicate that the C_{60} chromophores in **1** produce triplet states and are almost isolated.

Absorption and fluorescence spectra were measured for **1** in water at a concentration of 3g/dm^3 and for **5** in THF in 1.0

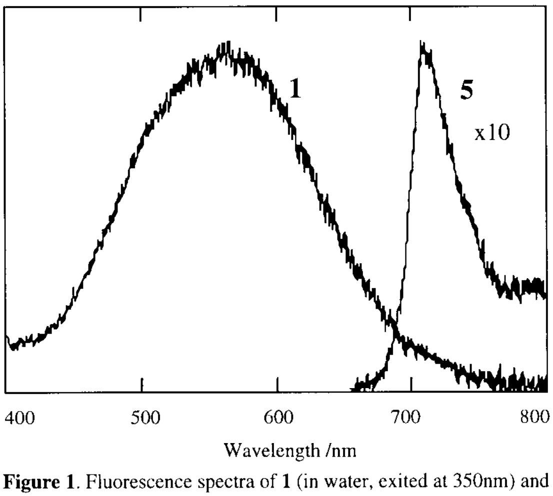

Figure 1. Fluorescence spectra of **1** (in water, exited at 350nm) and **5** (in THF, exited at 290nm).

x10^{-5} mol/dm^3. The absorption spectrum of **5** is similar to that reported for the corresponding analogs with peaks at 431 nm.[3] On the other hand, **1** showed a broad spectrum in the whole region of 240-700 nm with a peak around 420 nm, which is characteristic of the C_{60} chromophore. The fluorescence spectra of **1** and **5** were shown in Figure 1. Marked blue shift (150 nm) of the maximum as well as higher intensity were observed for **1** as compared with those of **5**. Although the tendency of the blue shift for the fluorescence of C_{60} chromophores incorporated in polymers is reported,[10] the shortest fluorescence maximum so far remains 600 nm. The much larger blue shift in the present case (maximum at 560 nm) probably reflects the constraining hydrophobic microenvironments in the polymer.

Fluorescence lifetime was measured by Nd^{3+} YLF laser exciting at 349 nm and monitoring at 580 nm for **1** and at 710 nm for **5**. The decay curves were analyzed by a single exponential component and lifetimes were obtained to be 2.2 ns for **1** and 1.2 ns for **5**. The value of **5** is in good agreement with reported values.[11] Since thermally activated delayed fluorescence is reported for C_{60},[12] the somewhat longer lifetime of **1** could be associated with the similar phenomenon. Therefore, we checked the temperature dependence of fluorescence of **1** in a degassed aqueous solution. As shown in Figure 2, the fluorescence intensity was decreased with an increase of temperature, contrary to the behavior of C_{60} itself, probably due to increased thermal deactivation pathways in the polymer at higher temperature. This explanation is supported by the fact that the fluorescence quantum yield of **1** at room temperature is 10 times higher than that of **5** (Figure 1). The photophysical properties of **1** are quite different from those of a porphyrin chromophore in the same environment, where the porphyrin showed delayed fluorescence as well as phosphorescence at room temperature.[2] This indicates that the C_{60} chromophore is not frozen in the same conditions as for the porphyrin. The different behavior of the two chromophores may be ascribed to the difference in the energy gap between the singlet and triplet states or to the shape of chromophore i.e., round for C60 and flat for porphyrin.

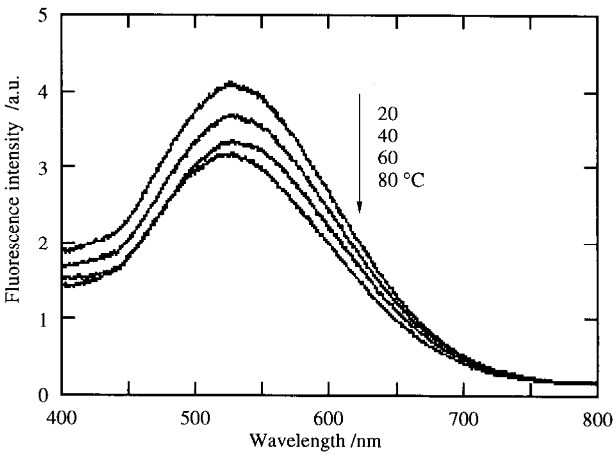

Figure 2. Fluorescence spectra of a degassed solution of **1** in water at 20, 40, 60, and 80 °C. Excitation wavelength is 350 nm.

In summary, the photophysical properties of C_{60} in highly constraining hydrophobic microenvironments are quite different from those in usual organic solvents.

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5 Spectral data for **2** : ^{1}H-NMR ($CDCl_3$, 270 MHz) δ= 7.78 (d, 2H, J=7.9 Hz), 7.14 (d, 2H, J=7.9 Hz), 6.28 (s, 1H), 5.70 (br.s, 1H), 4.96 (d, 1H, J=9.5 Hz), 4.93 (s, 1H), 4.25 (d, 1H, J=9.5 Hz), 2.80 (s, 3H), 2.03 (s, 3H). **5**: δ= 7.69 (d, 2H, J=8.2 Hz), 6.93 (d, 2H, J=8.2 Hz), 4.97 (d, 1H, J=9.6 Hz), 4.87 (s, 1H), 4.23 (d, 1H, J=9.6 Hz), 3.95 (t, 2H, J=6.9 Hz), 2.79 (s, 3H), 1.73 (m, 2H), 1.5-1.2 (m, 38H), 0.88 (t, 3H, J=6.9 Hz): Mass (MALDI-TOF) 1178 (M^+).

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