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Photoinduced Electron Transfer (PET) between C_{60} and Amines in Micelle Solution —A Kinetic ESR Study

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Abstract: As indicated by kinetic ESR measurements, the key factor to affect electron recombination in the process of PET between C_{60} and amines is the space between donor and C_{60}. To increase solubility of C_{60} in water, it was incorporated into micelle of surfactants.

]Keywords: C_{60}, ESR, photoinduced electron transfer (PET), micelle.

Fullerene chemistry has been one of the most exciting research subjects in the recent decade[1,2]. However, the predominant hydrophobic character and the spherical carbon allotrope of C_{60} hinder its solubility in an aqueous solution. In order to efficiently slow down charge recombination in the PET system containing C_{60}, water was selected as optimal polar media to stabilize charge separation state. Accordingly, solubility of fullerene in water had to be achieved by incorporating it into the hydrophobic cavity of several macromolecule hosts[3-4] or micelle of surfactants[5]. Here, kinetics of electron recombination in the PET between both primary amines ($PrNH_2$, $BuNH_2$, $HexNH_2$, $OctNH_2$) and tertiary amines ($(HOEt)_3N$, Et_3N, Bu_3N) and C_{60} were just systematically studied by means of ESR method in combination with the technique to increase solubility of C_{60} in water upon the addition of some bipolar non-ionic Triton surfactants.

When micelle solution containing C_{60} and amine donors was irradiated with YAG laser (532 nm), a single line ESR spectrum immediately appeared. Afterwards, another new single line peak became detectable at lower field position of the first peak while the irradiation period was continually extended. Two successively produced ESR signals can be respectively recognized as $C_{60}^{-\cdot}$ (g = 2.0000) and $C_{60}^{2-\cdot}$ (g = 2.0006) by comparing their g factors with the references in literature[6]. In other words, $C_{60}^{2-\cdot}$ and $C_{60}^{-\cdot}$ radicals can be photo-generated one after the other through two single electron transfer steps.

$$C_{60} + \text{Amines} \xleftrightarrow{h} C_{60}^{-\cdot} + \text{Amines} \xleftrightarrow{h} C_{60}^{2-\cdot}$$

Half-life of $C_{60}^{2-\cdot}$ in photo-irradiated C_{60}/amines/Triton system are listed in **Table 1**. In the PET systems composed by either C_{60}/RNH_2 or C_{60}/R_3N, variation in half-life of $C_{60}^{2-\cdot}$ at different Triton micelle solution follows the order of:

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Triton X-114 < Triton X-100 < Triton X-405

The order is clearly related to the length of the corresponding Triton surfactant chain in micelle. The shorter the length of surfactant chain is, the shorter the half-life of $C_{60}^{2-\cdot}$ dianion radicals is. Amine electron donors can be self-assemblingly embedded nearby the hydrophilic surface of surfactants in the micelle according to their hydrophilic characters[7]. Therefore, the distance between C_{60} molecule and amine donors is in accordance with the radium of the micelle. By this way, when Coulomb action and solvent effect are ignored, the rate of the electron recombination inside charge separation state could be proportional to the radius of the micelle.

Table 1 Half-life of $C_{60}^{2-\cdot}$ in photo-irradiated C_{60}/amines/Triton system

$_{1/2}$, (S) Tritons	$PrNH_2$	$BuNH_2$	$HexNH_2$	$OctNH_2$	$(HOEt)_3N$	Et_3N	Bu_3N
Triton X-114	84.3	69.4	42.2	38.1	69.4	50.3	42.2
Triton X-100	91.1	74.8	51.7	40.8	72.1	54.4	45.1
Triton X-405	446.0	424.3	380.7	342.7	89.7	81.6	

Half-life of $C_{60}^{2-\cdot}$ also exhibits distinct difference in the PET system containing same micelle solution but different amine donors. Extra comparison of data in the **Table 1** can further reveal that half-life of $C_{60}^{2-\cdot}$ varies with various primary amine donors and tertiary amine donors in the following orders respectively:

$PrNH_2 > BuNH_2 > HexNH_2 > OctNH_2$ and $(HOEt)_3N > Et_3N > Bu_3N$

The orders seem to correlate with hydrophobic behavior of the amines. Being more hydrophobic means that the amine donors can be more deeply embed inside micelle, and the longer distance between C_{60} and electron donors is, the more stable the charge separation state and the lower kinetic rate of the electron recombination are.

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