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Citation	電気材料技術雑誌. 2001, 10(2), p. 45-48
Version Type	VoR
URL	https://hdl.handle.net/11094/81655
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Photocurrent Enhancement in Conducting Polymer Device by Doping of Tetra(amino)fullerene Epoxides

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Conducting polymers with extended π -conjugation in their main chains have attracted much attention not only from a fundamental viewpoint but also for a practical interest [1] as materials suitable for electronic and optoelectronic devices such as photodiodes and solar cells. [2-4]

Previously, fabrication of conducting polymer/fullerene composite devices based on the effective photoinduced charge transfer between conducting polymers and C_{60} has been demonstrated. C_{60} was found experimentally to be an optically active acceptor for conducting polymers, causing quenching of photoluminescence (PL) [2,4] and enhancements of photoconductivity. [3-5] That is, composites consisting of a polymer and C_{60} layer exhibited a strong donor-acceptor type photovoltaic effect. [2-5]

Molecular structural modifications of C_{60} with a substituent improve the solubility and the photovoltaic properties in conducting polymer films. [6] Multi-substitution of C_{60} should be one of attempts for achieving the high efficient properties in conducting polymer photovoltaic cells.

Recently, C_{60} derivatives, tetra(amino)fullerene epoxide (TAFE) were developed by Isobe *et al.*, and were found to be soluble in typical organic solvents such as chloroform, tetrahydrofuran (THF) and toluene. [7] They could be dissolved in these solvents with high concentration, therefore, the high density doping into conducting polymer films as well as the efficient photocurrent generation is expected.

In this study, we report on the optical properties and photoconductivity of poly(3-octylthiophene) (PAT-8) - TAFE composite film. The unique properties of the optical absorption, PL and photoconduction have been discussed taking the charge transfer into consideration.

The molecular structures of TAFEs used in this study are shown in Fig. 1. These four kinds of TAFEs, that is, tetra(pyrrolidine)fullerene epoxide (TAFE-Py), tetra(morpholine)fullerene epoxide (TAFE-Mo), tetra(1-methyl-piperazine)fullerene epoxide (TAFE-MPi), and tetra(1,4-dioxo-8-aza-spiro[4.5]decane)fullerene epoxide (TAFE-DOASp) were synthesized from C_{60} with pyrrolidine, morpholine, 1-methyl-piperazine or 1,4-dioxo-8-aza-spiro[4.5]decane under photochemical aerobic condition, respectively. PAT-8 was synthesized using a conventional method [8] and dissolved in toluene. PAT-8/TAFE composites at an appropriate weight ratio were dissolved in toluene. A thin film of mixture of PAT-8 and TAFE was fabricated by spin coating onto the cleaned substrates, the typical

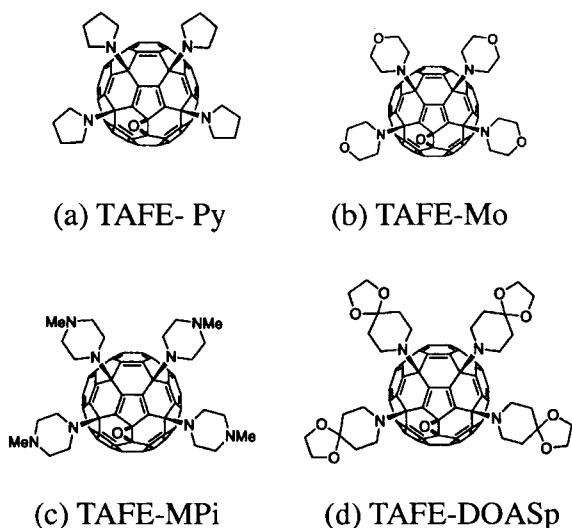


Fig. 1. The molecular structures of TAFEs used in this study.

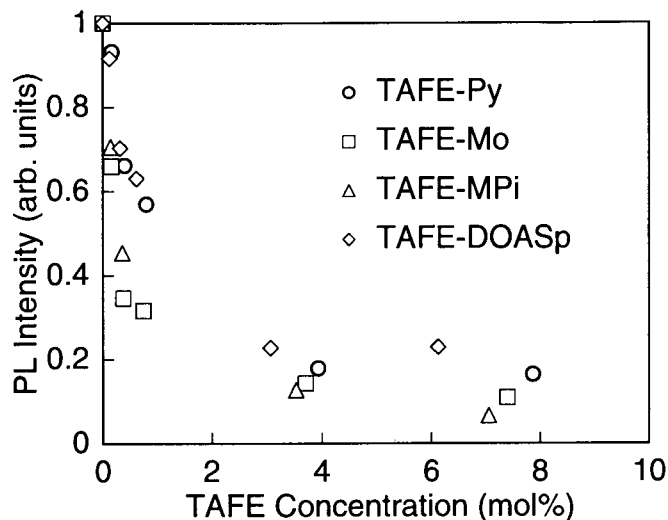


Fig. 2 PL intensity in composite films of PAT-8 and TAFE as a function of TAFE concentration.

thickness of which was 120 nm.

TAFEs could be doped into conducting polymer over 20 mol% easily, because of their high solubility in typical solvents. In the absorption spectra of PAT-8 doped with TAFE-MPi at the various concentrations upto 21.4 mol%, the absorption peaks at around 500 nm, which correspond to the π - π^* transition of PAT-8, were suppressed upon doping of TAFE-MPi. The peak wavelength was shifted to the higher energy with increasing the TAFE-MPi concentration. It should be noted that the large peak shift could be observed only at higher concentration of TAFE-MPi over 10 mol%.

In the case of C_{60} doping into poly(3-hexylthiophene) (PAT-6) films, similar peak shift was reported previously, which has been interpreted by the electron transfer from the conjugated chain of PAT-6 to C_{60} in the ground state. [2-4] That is, the density of states in the higher energy level of the valence band of PAT-6 decreases in the composite of PAT-6 and C_{60} , resulting in the suppression of the interband transition corresponding to π - π^* transition. The composite system of PAT-8 and TAFEs exhibited the similar results with the composite of PAT-6 and C_{60} . It should be noted that as also be reported by us, [3] in PATs with longer alkyl chains than PAT-6, that is, in PAT-8 and PAT-12, the electron transfer in the ground state was negligible. However, the heavy doping of TAFEs into PAT-8 might induce the electron transfer from the conjugated chain of PAT-8 to TAFEs in the ground state as observed in this experiment.

The PL intensity of PAT-8 was suppressed markedly with increasing the density of TAFE-MPi. The

doping of the other TAFEs into PAT-8 also demonstrated the similar PL quenching as shown in Fig. 2. Each TAFE plays a role as an efficient dopant for the PL quenching, and the PL suppression could be observed even at the dopant concentration of 1 mol%. In the case of heavy doping of TAFE, such as 21.4 mol%, the PL of PAT-8 was extremely weak, which should be due to the dissociation of excitons upon encountering a TAFE and the decreasing of the density of states of the valence band originated from the electron transfer between PAT-8 and TAFE in the ground state. From the results of PL quenching in Fig. 2, TAFEs must also be efficient dopants for enhancing the photoconductivity in PAT-8.

Figure 3 shows the photocurrent spectra of photocells with single-layer structures of ITO /composite film of PAT-8 and TAFE-MPi/ Al under short circuit condition. The photocurrent response was enhanced markedly upon TAFE doping. Such a photocurrent enhancement could be obtained by introduction of small amount of TAFE. Photocurrent intensity in composite films of PAT-8 and TAFE-MPi increased with increasing TAFE-MPi concentration as shown in Fig. 4. However, further increase of TAFE-MPi concentration above 4 mol% suppressed the photoconductivity gradually.

From current-voltage measurements under irradiation of 600-nm-light, typical value for the open circuit voltage, V_{oc} , was 0.35 V, and a typical filling factor (FF) was 0.3 in the case of TAFE-MPi doping of 3.8 mol%, resulting in a photoconversion efficiency of $\eta = I_{sc} \cdot V_{oc} \cdot FF/W = 0.24\%$, where I_{sc} and W mean a short circuit current and an input light power, respectively.

Comparing the doping properties of TAFE and C_{60} , resemble phenomena such as PL quenching and photocurrent enhancement could be noticed. Such PL quenching and photocurrent enhancement should be probably due to the photoinduced charge transfer [2-4] to TAFE. The electronic band structures of

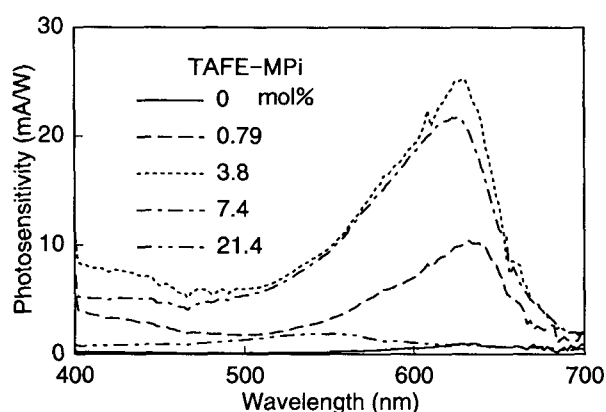


Fig. 3. Photocurrent spectra of photocells with single-layer structures of ITO /composite film of PAT-8 and TAFE-MPi/ Al under short circuit condition.

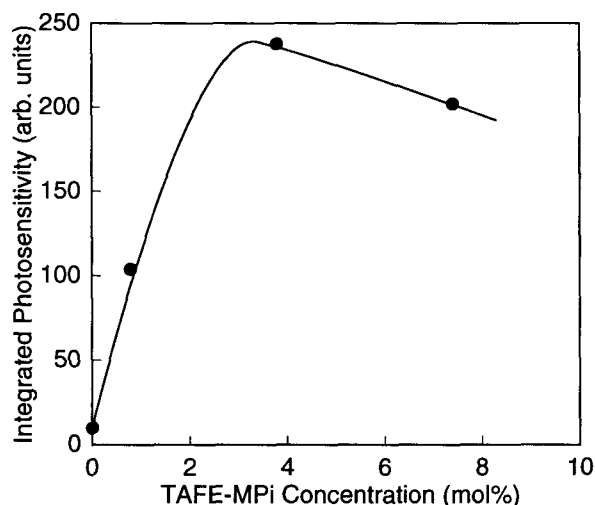


Fig. 4. Photocurrent intensity in composite films of PAT-8 and TAFE-MPi as a function of TAFE-MPi concentration.

TAFEs are not clear at this stage, however, TAFEs might be efficient acceptors for the appropriate conducting polymers.

At 21.4 mol% concentration, the photocurrent spectrum became different from those of the composite devices with the lower concentration of TAFE-MPi, and the photocurrent intensity decreased. The photocurrent peak appeared at around 550 nm, which was much shorter than those of the composite devices with the lower concentration of TAFE-MPi. The situation of such a heavy TAFE doping induces the charge transfer in the ground state as described above. The density of states in the higher energy level of the valence band of PAT-8 decreases in the composite of PAT-8 and TAFE because of the charge transfer in the ground state. Hence, it is considered that the photocurrent intensity decreased involving with the suppression of the interband transition corresponding to π - π^* transition and therefore the optimum doping concentration appeared at around 4 mol%.

In conclusion, optical properties of the composites of PAT and novel C_{60} derivatives, TAFEs, such as optical absorption, PL and photoconduction, were studied. TAFEs had high solubility, and the heavy doping into conducting polymers was easy in the wet process. PL intensity of PAT-8 was quenched and photocurrent intensity was enhanced markedly with increasing the concentration of TAFEs, which must be explained by the photoinduced charge transfer from PAT-8 to TAFEs. In the case of heavier doping of TAFEs above 4 mol%, the charge transfer from PAT-8 to TAFEs in the ground state caused spectral changes of absorption and photoconduction spectra.

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