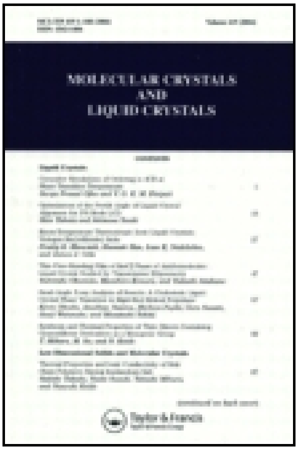

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Development of New D-A Systems Based on Fullerene and TTF for Organic Devices

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Development of New D-A Systems Based on Fullerene and TTF for Organic Devices

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*New C_{60}-TTF dyads with several substituents on the TTF moiety were prepared to examine the substituent effect on the intramolecular charge transfer interaction. Cast films of the dyads with long alkyl chains were obtained with high quality and characterized. In X-ray diffraction study for the cast film of the derivative with -$SC_{16}H_{33}$ groups (**1g**), high ordered reflection peaks were observed. Analysis of the diffraction pattern revealed that **1g** forms the multibilayer structure in condensed film.*

Keywords: bilayer structure; cast film; donor-acceptor system; fullerene; intramolecular charge transfer interaction; tetrathiafulvalene

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INTRODUCTION

Donor-acceptor (D-A) dyad systems have attracted current interest from the viewpoint of the application to molecular devices such as organic thin film transistors and photovoltaic devices. Particularly, D-A dyads based on C_{60} fullerene as an acceptor unit have been extensively examined because C_{60} retains its unique physical properties even in the derivatives; relatively low reorganization energy of C_{60} core realizes long-lived charge separation states for several donor-linked C_{60} derivatives [1]. Consequently, C_{60}-based D-A systems with several donor molecules showed photovoltaic properties. Among the donor components of C_{60}-based D-A systems, tetrathiafulvalene (TTF) derivatives are also regarded as a useful unit due to their remarkable redox properties. Namely, the redox core of TTF gains aromaticity upon oxidation, which is considered to stabilize the charge separation states in D-A systems [2]. A number of C_{60}-TTF dyads have already been synthesized and their electrochemical and photophysical properties have been investigated [3]. These studies have revealed that very weak or no charge transfer (CT) interaction between C_{60} and TTF moieties exists in the ground states of the C_{60}-TTF dyads hitherto known. On the other hand, we have developed a new methanofullerene (**1a**) bearing a tetrathiafulvalene derivative and reported that the dyad showed strong intramolecular charge-transfer (CT) interaction even in the ground state [4]. The dyad, however, showed very rapid charge separation and recombination process due to the fairly strong intramolecular interaction, and gave a thin film with poor quality. These factors are fatal to the application to organic thin-film devices, particularly organic photovoltaic devices. In order to improve the quality of the thin film composed of the C_{60}-TTF dyads, we introduced long alkyl chains (-$SC_{12}H_{25}$ and -$SC_{16}H_{33}$) to the C_{60}-TTF dyad as substituents on the TTF moiety and investigate the formation of thin films by a cast method. In relation to this purpose, we also investigate the effect of the substituents on the intramolecular interaction by preparing C_{60}-TTF derivatives with several substituents (**1b–g**).

EXPERIMENTAL

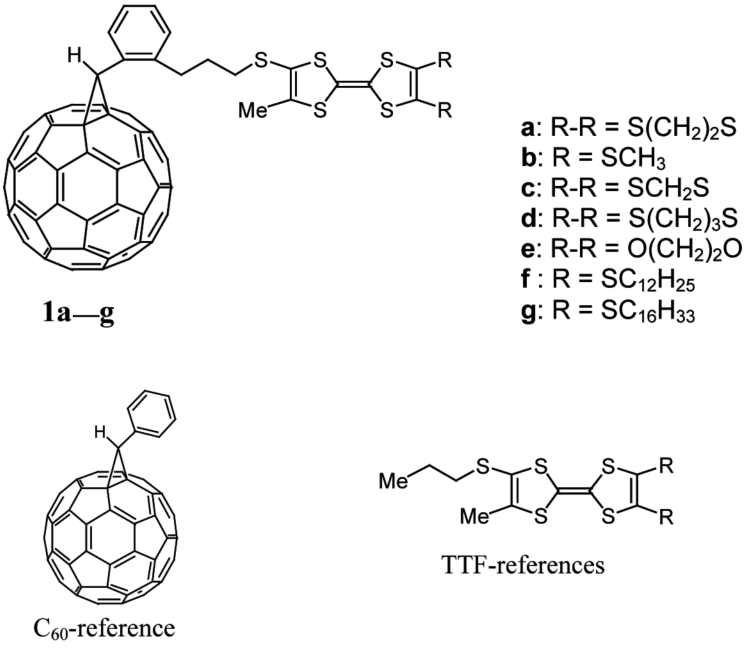
Synthesis of C_{60}-TTF dyads (**1b–g**) was carried out according to the method reported previously [4]. Cyclic voltammetry was performed through the application of an electrochemical analyzer (ALS model 600 A) at 25°C in benzonitrile containing n-Bu_4NClO_4 as a supporting electrolyte (0.1 M) at a scan rate of 50 mV s^{-1}, using platinum working and counter electrodes and a saturated calomel electrode (SCE) as a reference electrode. The solution was deaerated with N_2 bubbling before measurements. Absorption spectra of **1a-g** in toluene were measured on a Hitachi model U-3500 spectrophotometer.

The films of **1f** and **1 g** were prepared by a cast method from carbon disulfide solution onto the quartz substrate coated with amorphous carbon made by the plasma polymerization equipment. X-ray diffraction (XRD) measurement of the cast film of **1g**, which was annealed at 100°C for 24 hours before measurements, was carried out on a Rigaku Denki RU-300 by using Cu Kα radiation of 50 kV, 200 mA. The diffractions were measured in the 2θ–θ scan mode with 0.01° steps in 2θ.

RESULTS AND DISCUSSION

Synthesis, Electrochemical Properties and Absorption Spectra

Synthesis of **1b–g** was performed via the cycloaddition of diazo compounds to C_{60} similarly to the synthetic method of **1a** as shown in



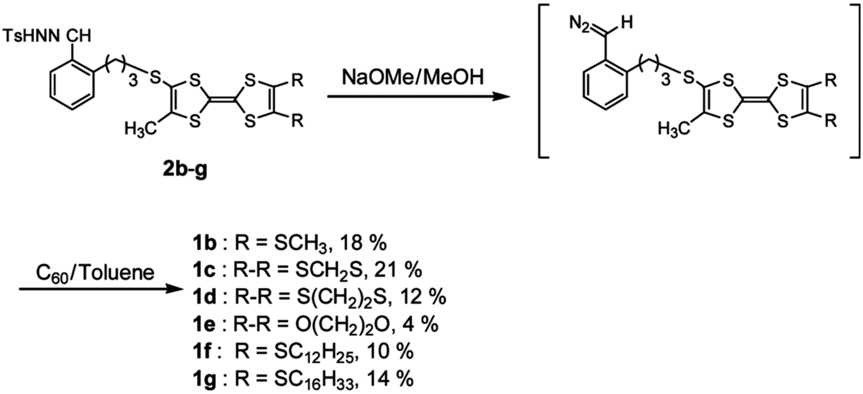
1a—g

a: R-R = $S(CH_2)_2S$
b: R = SCH_3
c: R-R = SCH_2S
d: R-R = $S(CH_2)_3S$
e: R-R = $O(CH_2)_2O$
f : R = $SC_{12}H_{25}$
g: R = $SC_{16}H_{33}$

C_{60}-reference

TTF-references

SCHEME 1 Molecular structures of C_{60}-TTF dyads (**1a–g**), C_{60}-Reference, and TTF-References.



SCHEME 2 Synthesis of C_{60}-TTF dyads (**1a–g**).

Scheme 2. Yields of **1b–g** in the scheme were calculated based on reacted C_{60}. The diazo compounds were generated in situ from *p*-tosylhydrazones (**2b-g**) which were prepared from cyanoethyl-protected TTFs in three steps. Redox potentials of **1b–g** are summarized in Table 1, together with those of **1a**, C_{60}-reference, and TTF-references. Similarly to **1a**, all the new dyads exhibited three and two pairs of reversible redox waves on the reduction and oxidation side, respectively, except for the fourth reduction wave which was not observed clearly for **1b–g**. The redox steps on the reduction side correspond to the reduction of C_{60} moiety, while those on the oxidation side correspond to the oxidation of TTF moiety. The first oxidation potentials of

TABLE 1 Redox Potentials of **1a–g**, C_{60}-Reference and TTF-References[a]

Compounds	E_1^{ox}	E_2^{ox}	E_1^{red}	E_2^{red}	E_3^{red}	E_4^{red}
1a	0.52 (0.45)	0.84 (0.83)	−0.54	−0.95	−1.44	−2.00[b]
1b	0.52 (0.49)	0.81 (0.79)	−0.51	−0.94	−1.43	
1c	0.50 (0.47)	0.79 (0.78)	−0.54	−0.95	−1.44	
1d	0.51 (0.50)	0.83 (0.83)	−0.53	−0.96	−1.44	
1e	0.43 (0.41)	0.77 (0.76)	−0.55	−0.95	−1.44	
1f	0.50 (0.49)	0.80 (0.78)	−0.53	−0.96	−1.44	
1g	0.50 (0.49)	0.80 (0.78)	−0.53	−0.96	−1.44	
C_{60}-reference			−0.52	−0.95	−1.43	−2.03[b]

[a] Given in volt versus a SCE; 0.1 M n-Bu_4NClO_4 in benzonitrile; platinum electrode; redox potentials of TTF-references are presented in parentheses.

[b] Irreversible step.

1b–g slightly shift to more-positive values compared with those of the corresponding TTF-references, suggesting the decrease of donor ability which may be caused by the partial CT from the TTF to the C_{60} moieties.

As shown in Figure 1, absorption spectra of **1b–g** show broad absorption maxima with a clear peak around 750 nm, in addition to the local excitation of the TTF moiety at 460 nm and the C_{60} moiety at 550 and 600 nm. This behavior is exactly same to that observed in **1a**, and suggests that a substantial intramolecular interaction between the C_{60} and TTF moieties in the ground state also exists in **1b–g**. The absorption coefficients of these CT bands are independent of the concentration in the range of 0.02–1.0 mM for **1b** and **1e**, thus the CT interaction should intrinsically originate in an intramolecular interaction. The results of the electrochemical and spectroscopic studies indicate that the redox potential of the donor moiety does not affect the intramolecular CT interaction but the proximity of the donor moiety to C_{60} core plays a significant role in the intramolecular interaction.

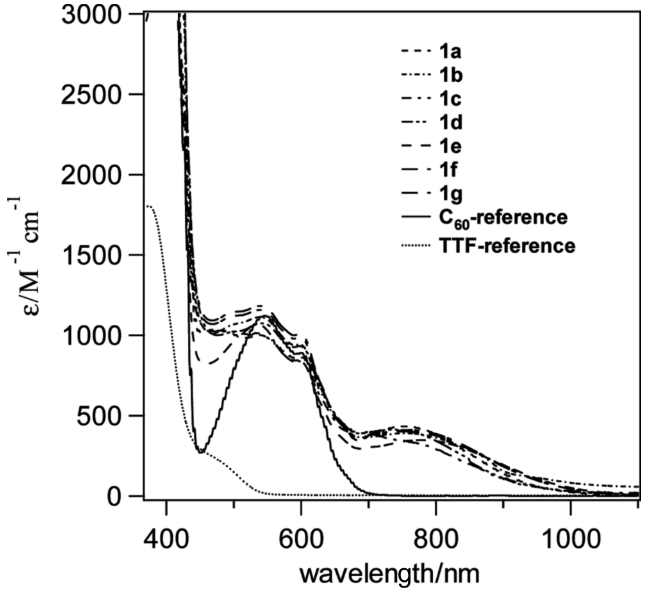


FIGURE 1 Absorption spectra of **1a–g**, C_{60}-reference, and TTF-reference in toluene. As the TTF-reference, spectra of derivative with thiomethyl groups was indicated as a representative.

X-ray Diffraction and Structure of Thin Film

In order to investigate the electronic state in condensed film, absorption spectra of cast films and spin-coat films of **1f** and **1g** were measured. Broad absorption bands corresponding to the intramolecular CT interaction were observed in both the cast and spin-coat films of **1f** and **1g** in the region of 700–1000 nm. In all the case, intensity maxima were observed around 800 nm, which shift to longer wavelength by ca. 50 nm compared to those in the solution of **1f** and **1g**. The red-shift in the condensed state is probably due to polarizability of the surrounding molecules, which is often seen for the films of C_{60} derivatives.

XRD were measured on the cast film of **1g** made onto the amorphous carbon coated quartz substrate after annealing for 24 hours at 100°C. Without annealing, no diffraction peak was observed for the films both of **1f** and **1g**. Thus, the XRD should be measured for the film of **1f** with annealing under the same condition. The XRD pattern shown in Figure 2 was obtained by subtracting the background diffraction from the quartz substrate. Reflections of 001 were observed up to fifth and no other reflection was observed, which indicate that the film of **1g** takes moderately well-ordered layer structure and the crystallites are preferentially oriented with (001) plane parallel to the substrate. The spacing of (001) plane of the film of **1g** is calculated to be 39.6 Å according to Bragg's law.

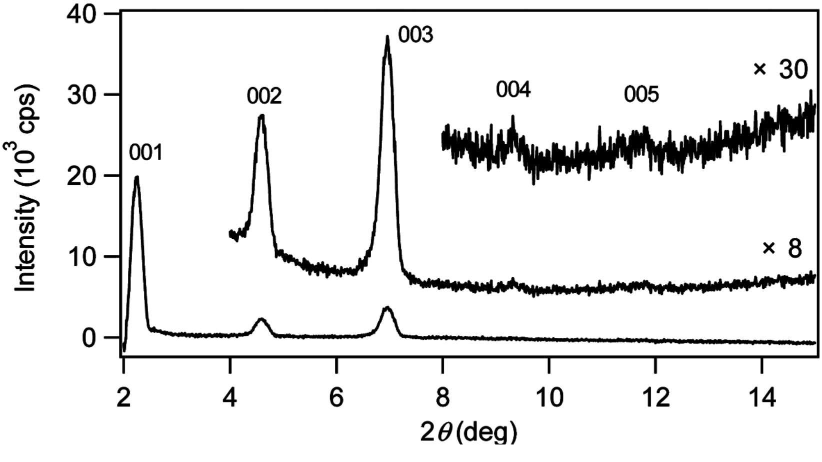


FIGURE 2 X-ray diffraction pattern of the cast film of **1 g** on amorphous carbon coated quartz substrate.

The minimum energy conformation of **1 g** was examined by a molecular mechanics calculation (MM2) in order to obtain structural insight on the condensed film. We adopted the optimized structure of **1a** calculated at the Hartree-Fock theory with a 3-21G basis set for the conformation of C_{60} and TTF moieties [8]. Only the part of the long alkyl chains was optimized by the MM2 calculation, and the other part of the molecule was fixed during the calculation. The calculated molecular length is found to be 32.5Å for **1 g**, which is shorter than the spacing of (001) plane. Thus multibilayer structure as shown in Figure 3 is plausible for the structure of the cast film of **1 g** where the long alkyl chains are interdigitated and tilt by ca. 20° from the z-axis. It is reported that cast films of C_{60} derivatives with long alkyl chains took the multibilayer structures by the precise analyses of intensities of XRD patterns of the cast films by calculating the structural factors using the electron densities of the molecules [5]. In this context, it should be reasonable that the cast film of **1 g** takes multibilayer structure.

Since **1 g** formed the well-ordered cast film, we examined the photovoltaic property for the film of **1 g** using ITO (indium tin oxide) and Mg/Ag electrodes. However, no photovoltaic property was observed probably due to the very short lifetime of the excited state with partial charge separation. To improve the device properties, we are currently investigating the C_{60}-TTF derivatives with dendrimer structures, and the results will be reported elsewhere.

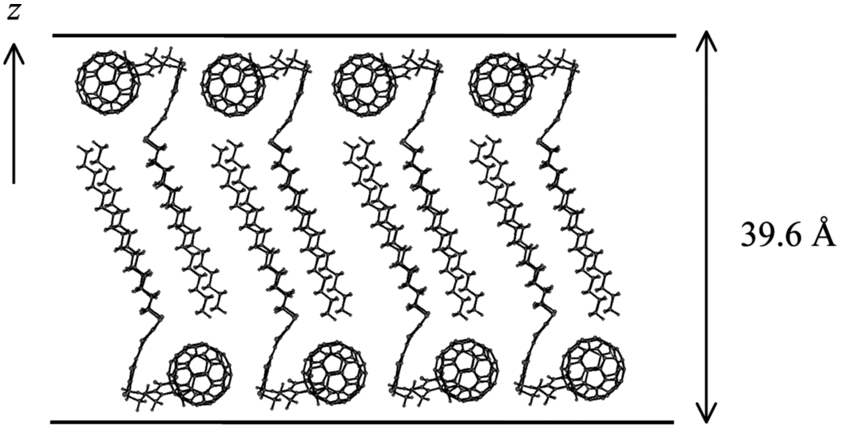


FIGURE 3 Illustration of one-period of multibilayer structure in the cast film of **1 g**.

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