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Photoinduced charge separation and charge recombination in terthiophene-acetylene-fullerene linked dyads

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Abstract

Charge separation (CS) and recombination (CR) processes in terthiophene-fullerene linked dyads with bridges (3T-br*n*-C_{60}-R, bridge-1 (br1) = −C≡C−, and bridge-2 (br2) = −$(CH_2)_5$−C≡C−; R = CN or Me) were investigated by fluorescence up-conversion method and transient absorption measurement in benzonitrile (PhCN) and toluene. With photoexcitation of the 3T moiety in 3T-br*n*-C_{60}-R, the CS process takes place fast in the region of $(0.14–3.5) \times 10^{12}\ s^{-1}$ via ^{1}3T*-br*n*-C_{60}-R. In the case of 3T-br1-C_{60}-R, the CS process takes place fast via one step before the vibrational relaxation of the ^{1}3T* moiety, whereas in the case of 3T-br2-C_{60}-R, the CS process occurs two steps competing with the vibrational relaxation and after the relaxation. Such difference can be interpreted by the rigidity of the bridges. The $3T^{\bullet+}$-br*n*-$C_{60}{}^{\bullet-}$-R states were confirmed by the transient absorption spectra in the $(1.0–3.6) \times 10^3$ ps region. The lifetimes of the radical ion-pair (τ_{RIP}) were evaluated to be 10–25 ps for $3T^{\bullet+}$-br1-$C_{60}{}^{\bullet-}$-R in PhCN. In toluene, the τ_{RIP} values became longer ($(1.2–4.7) \times 10^2$ ps) than those in PhCN. In both solvents, the τ_{RIP} values are longer for R = Me than that for R = CN. In the case of 3T-br2-C_{60}-R in which the methylene chain inserted between 3T and acetylene bridge, the τ_{RIP} values are longer than the corresponding values for of $3T^{\bullet+}$-br1-$C_{60}{}^{\bullet-}$-R, i.e., $(0.91–1.2) \times 10^3$ ps in PhCN and $(1.5–3.6) \times 10^3$ ps in toluene for R = CN and Me, respectively. It is revealed that the radical ion pairs last for longer in toluene than those in PhCN, suggesting that the CR process in the inverted region of the Marcus parabola, which was also supported by the substituent effect, i.e., unstable $3T^{\bullet+}$-br*n*-$C_{60}{}^{\bullet-}$-Me prolongs longer than stable $3T^{\bullet+}$-br*n*-$C_{60}{}^{\bullet-}$-CN. Drastic prolongation of τ_{RIP} for $3T^{\bullet+}$-br2-$C_{60}{}^{\bullet-}$-R indicates that the electronic coupling for CR through the normal methylene group in 3T-br2-C_{60}-R is smaller than the π-conjugated system in 3T-br1-C_{60}-R.

Keywords: Terthiophene; C_{60}; Electron transfer

1. Introduction

Organic materials with a π-conjugated system have attracted attention, because the conjugated materials exhibit interesting properties such as electric conductivity, electrochromism, optical nonlinearity and so on [1–11]. Various properties of polythiophenes and oligothiophenes have been extensively investigated both experimentally and theoretically [12–31]. One of the well-known properties of oligothiophenes is that the electronic structures largely depend on their number of the repeating unit, showing a tendency to saturate with increase in the units [13–20]. The HOMO–LUMO gap of the oligothiophenes becomes small as increase of the thiophene unit, which also changes oxidation potentials, energies of the excited states [13–20]. By steady-state absorption and fluorescence spectra measurements, Janssen et al. reported that oligothiophenes have considerable rigid planer structures in the lowest excited singlet state (S_1 state) [21]. The dynamics for the excitation and relaxation processes of oligothiophenes were investigated by several groups with fluorescence up-conversion technique and pump-probe methods on combining with theoretical approaches [22–31]. According to the reports by Lanzani et al., the planarization occurs after excitation, and the kinetics of this process are controlled by excess energy redistribution via vibrational and/or torsional coupling

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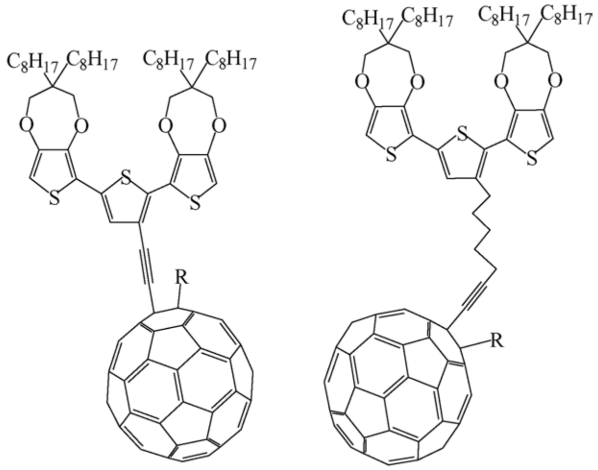
3T-br1-C_{60}-R 3T-br2-C_{60}-R

R = -Me or -CN

Fig. 1. Molecular structures of 3T-br1-C_{60}-R and 3T-br2-C_{60}-R.

of oligothiophenes [23]. The torsional energy redistribution is caused by a steric hindrance of substituents [23]. With employing pump-probe technique, Rentsch and co-workers revealed that the fast singlet–triplet intersystem crossing occurs within about 2 ps in the excited singlet state of terthiophene (^{1}3T*) [27]. They also reported a conformation dependence of the rate constants for the radical cation formation in a hybrid polymer matrix [29]. Kobayashi and co-workers reported the fluorescence anisotropy and solvent reorientation times during the excitation and relaxation of terthiophene (3T), tetrathiophene (4T) and pentathiophene (5T) in CH_2Cl_2 [30,31]; in the case of 3T, the solvent reorientation time was estimated to be 18 ± 4 ps in CH_2Cl_2 [31].

Meanwhile, the basic physical properties on fullerene (C_{60}) were explored [32–37], and many groups utilized C_{60} as an electron acceptor in the donor–acceptor linked systems because of its small reduction potential [38–44]. In the present study, the CS and CR processes were investigated using femtosecond time-resolved fluorescence up-conversion technique and transient absorption measured using pump-probe method in terthiophene-acetylene bridge-C_{60}-R dyads (3T-br1-C_{60}-R), where R is the subtituent linked with C_{60} (R = CN and Me), and pentamethyl chain inserted type (3T-br2-C_{60}-R) (Fig. 1). In the case of 3T-br1-C_{60}-R, it is expected to exhibit π-conjugation between 3T and acetylene, whereas such conjugation is not expected for 3T-br2-C_{60}-R by the insertion of the methylene chain. Changing subtituent (R) of C_{60} may cause the variation of the reduction potential; therefore, the driving force can be change.

2. Experimental

2.1. Materials

3T-br*n*-C_{60}-R were synthesized according to the similar method described in the literature [45,46]. Other chemicals such as solvents (benzonitrile (PhCN) and toluene) were of the best commercial grade available.

2.2. Experimental set-up

Steady-state absorption spectra were measured on a JASCO V-530 UV–vis spectrophotometer. Steady-state fluorescence spectra were measured on a Shimadzu RF-5300 PC spectrofluorophotometer.

Ultrafast fluorescence dynamics of the ^{1}3T* moiety were measured using the fluorescence up-conversion method. The light source was a mode-locked Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S, FWHM 100 fs) pumped with a diode-pumped solid state laser (Spectra-Physics, Millennia VIs, 6.0 W). The oscillator produced an 82 MHz pulse train with 1.0 W average power in a fixed range of 800 nm. The fundamental pulse ($\lambda = 800$ nm) was used for a gate pulse in up-conversion process. The second-harmonic pulse ($\lambda = 400$ nm) was generated in a 0.4 mm-thick LiB_3O_5 (LBO) crystal, which was used for a pump beam for photoexcitation. To avoid polarization effect, the angle between the polarizations of the excitation and gate beams was set to the magic angle by a $\lambda/2$ plate. The fluorescence emitted from a sample was collected and focused into a 0.4 mm-thick β-BaB_2O_4 (BBO) crystal, which was mixed with the gate pulse. The gate beam and fluorescence interacted nonlinearly in a BBO crystal and the up-converted signal was generated at the phase-matching angle. The signal was separated by a monochromator and detected by a photomultiplier (Hamamatsu, R-4220P) with a photon counter (Stanford Research System, SR400). The time resolution of measurements was estimated as 150 fs from the full width at half maximum of the cross-correlation trace between the pump and gate pulses. A typical spectral window of fluorescence for up-conversion was 420–640 nm. The up-converted signal was accumulated for 10 s for each time-delay step.

The fluorescence lifetimes of the $^{1}C_{60}$* moiety in the 600–800 nm region were measured by a conventional single-photon counting method with a streak scope (Hamamatsu Photonics, C4334-01) using the second harmonic generation (SHG, 400 nm) of a Ti:sapphire laser (Spectra-Physics, Tsunami 3950-L2S, FWHM 100 fs) as an excitation source.

The femtosecond transient absorption spectra were measured by the pump and probe method using a Ti:sapphire regenerative amplifier seeded by the SHG of an Er-doped fiber laser (Clark-MXR CPA-2001 plus, 1 kHz, FWHM 150 fs). A white continuum pulse used as a monitoring light was generated by focusing the fundamental of the amplifier on a rotating H_2O cell. The samples were excited by the SHG (388 nm) of fundamental. The monitoring light transmitted through the sample in a rotating cell was detected with a dual MOS detector (Hamamatsu Photonics, C6140) equipped with a polychromator for the visible region or an InGaAs linear image sensor (Hamamatsu Photonics, C5890-128) for the near-IR region. A typical time resolution of the system is 200 fs.

2.3. Molecular orbital calculation

Optimized structures were calculated with the Gaussian package.