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Photoinduced electron transfer from silyl end-capped sexithiophene to benzoquinone derivatives studied by laser photolysis

Mohamed E. El-Khouly^{a,*}, Maged A. El-Kemary^a, Shunichi Fukuzumi^{b,**}^a Department of Chemistry, Faculty of Science, Kafrelsheikh University, Kafr El-Sheikh 33516, Egypt^b Department of Material and Life Science, Graduate School of Engineering, Osaka University, AICA, Japan Science and Technology Agency (JST), Suita, Osaka 565-0871, Japan

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ABSTRACT

Photoinduced electron transfer from the electron-donating bis(dimethyl-*n*-octylsilyl)sexithiophene, (DSi6T), to the electron-accepting benzoquinone derivatives, BQs, in polar benzonitrile has been investigated with laser photolysis method. The employed benzoquinone derivatives include 1,4-benzoquinone (BQ), 2,5-dichloro-1,4-benzoquinone (Cl₂BQ), 2,6-dimethyl-1,4-benzoquinone (Me₂BQ), tetrafluoro-1,4-benzoquinone (F₄BQ) and 2-methyl-1,4-benzoquinone (MeBQ). The electrochemical measurements showed pronounced effect of the substituted groups on the reduction potentials of BQs, and consequently on the driving forces of the electron transfer of the DSi6T/BQs mixture systems. Such effect of the driving forces for electron-transfer reactions of DSi6T/BQs mixture systems have been examined by utilizing the femtosecond and nanosecond laser flash photolysis, in addition to the complementary steady state absorption and fluorescence techniques. Upon excitation of DSi6T with 440 nm laser light, the electron-transfer reactions from the triplet excited state of DSi6T to BQs were confirmed by observing the transient absorption bands of DSi6T radical cation in the visible region. The excellent electron donating properties of DSi6T suggests its potential to be a photoactive unit in the bulk heterojunction solar cells.

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1. Introduction

Electron-transfer processes play important roles in chemistry and biology [1–15]. Photoinduced electron transfer from the electron-donating species (D) to the electron-accepting species (A) produced the radical cation of the donor (D^{•+}) and the radical anion of the acceptor (A^{•-}), when D or A is photoexcited [16–22]. If these charged species (D^{•+} and A^{•-}) are utilized as electrons and holes to drive electrical current or promote chemical reactions before back electron transfer leading to the initial states of the reactants occurs, the light energy is effectively converted into electrical or chemical energy. A critical factor in electron transfer lies in the successful matching of donor and acceptor with suitable electrochemical and photophysical properties for the occurrence of such an exothermic electron transfer.

Among organic materials, oligothiophenes have received much attention as electron-donating materials in designing an efficient

organic photovoltaic cells (OPVs) because of their high hole mobility, easy multi-gram synthesis, high purity and simple chemical modification [23–26]. Some studies on oligothiophene-based solar cells have already been reported using bilayer heterojunction solar cells [27–31]. By controlling the film morphology using co-evaporation of excess fullerene (C₆₀), bulk heterojunction organic photovoltaic cells consisting sexithiophene (6T) as a donor and C₆₀ as an acceptor showed good photovoltaic properties [32].

Bis(dimethyl-*n*-octylsilyl)sexithiophene (DSi6T) with its high field-effect mobility in the organic thin film transistor is a promising material for solar energy conversion systems. Recently, we fabricated solution-processed organic photovoltaic cells (OPVs) using DSi6T, as electron donor, and [6,6]-phenyl-C₆₁-butyric acid methyl ester (PCBM) as an electron acceptor [33]. Solution-processed OPVs using DSi6T/PCBM showed good photovoltaic properties in spite of their poor solubility. The best performance was observed on DSi6T:PCBM 1:5 (w/w) blend cell with a open circuit voltage (V_{oc}) of 0.63 V, short circuit current density (J_{sc}) of 1.34 mA/cm², fill factor (FF) of 55% and power conversion efficiency of 0.44% under AM 1.5G illumination (see Supporting information, Fig. S1). Despite the excellent electron-donor properties of DSi6T as a promising material for solar energy conversion systems,

* Corresponding author. Tel.: +81 668797370.

** Corresponding author.

E-mail addresses: mohamedelkhouly@yahoo.com (M.E. El-Khouly), fukuzumi@chem.eng.osaka-u.ac.jp (S. Fukuzumi).

fundamental photoinduced electron-transfer properties of DSi6T have yet to be reported.

We report herein a systematic study on the dynamics of intermolecular photoinduced electron-transfer reactions of bis(dimethyl-*n*-octylsilyl)sexithiophene (DSi6T), as an electron donor, with benzoquinone derivatives (BQs), as excellent electron acceptors (Fig. 1). Benzoquinones are ubiquitous to living systems, providing important cofactors for electron transfer in energy conserving systems, photosynthesis and respiration [34–41], generating photocurrent and hydrogen evolution [42,43]. The employed benzoquinone derivatives in this study are 1,4-benzoquinone (BQ), 2,5-dichloro-1,4-benzoquinone (Cl₂BQ), 2,6-dimethyl-1,4-benzoquinone (Me₂BQ), tetrafluoro-1,4-benzoquinone (F₄BQ) and 2-methyl-1,4-benzoquinone (MeBQ). As seen from Fig. 1, the substituted groups in the used BQs have pronounced effect on the reduction potentials, and consequently on the driving forces of the electron transfer of the DSi6T/BQs mixture systems. The effects of the driving forces for electron transfer have been also examined by utilizing the femtosecond and nanosecond laser flash photolysis, in addition the complementary cyclic voltammetry and steady state absorption and fluorescence techniques.

2. Experimental

2.1. Materials

Bis(dimethyl-*n*-octylsilyl)sexithiophene (DSi6T) was prepared according to the literature [44]. 1,4-Benzoquinone (BQ), 2,5-dichloro-1,4-benzoquinone (Cl₂BQ), 2,6-dimethyl-1,4-benzoquinone (Me₂BQ), tetrafluoro-1,4-benzoquinone (F₄BQ) and 2-methyl-1,4-benzoquinone (MeBQ) (Aldrich; >99.9%) were purchased as reagent grade and used without further purification.

2.2. Methods

Steady-state absorption spectra were recorded on a Shimadzu UV-3100PC spectrometer or a Hewlett Packard 8453 diode array spectrophotometer at room temperature. Steady-state fluorescence spectra were measured on a Shimadzu RF-5300 PC spectrofluorophotometer equipped with a photomultiplier tube having high sensitivity in the 700–800 nm region. Phosphorescence spectra were obtained by a SPEX fluorolog τ 3 spectrophotometer. Emission spectra in the NIR region were detected by using a Hamamatsu Photonics R5509-72 photomultiplier. An argon-saturated 2-methyltetrahydrofuran (2-MeTHF) solution containing DSi6T at 77 K was excited at the indicated wavelengths.

Cyclic voltammograms were carried on a BAS CV-50W Voltammetric Analyzer. A platinum disk electrode was used as a working electrode, while a platinum wire served as a counter electrode. Ag/AgNO₃ electrode was used as a reference electrode. All measurements were carried out in benzonitrile containing tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆; 0.10 M) as a supporting electrolyte. The scan rate = 20 mV/s.

The DSi6T was excited by a Panther OPO pumped by Nd:YAG laser (Continuum, SLII-10, 4–6 ns fwhm) at $\lambda = 440$ nm with the energies of 1.5 and 3.0 mJ per pulse. The transient absorption measurements were performed using a continuous xenon lamp (150 W) and an InGaAs-PIN photodiode (Hamamatsu 2949) as a probe light and a detector, respectively. The output from the photodiodes and a photomultiplier tube was recorded with a digitizing oscilloscope (Tektronix, TDS3032, 300 MHz). All measurements were conducted at 298 K. The transient spectra were recorded using fresh solutions in each laser excitation.

3. Results and discussion

3.1. Steady-state absorption and fluorescence measurements

The absorption spectra of the examined compounds were measured in benzonitrile (Fig. 2). The absorption spectrum of DSi6T exhibited absorption bands at 445 and 322 nm. Similar absorption spectra were recorded of DSi6T/BQ mixture, the only difference is the higher absorption intensity at ~ 300 nm that arise from the absorption of BQ entity. The spectral features of the mixture of Si6T and BQ closely resemble the sum of their spectrum in benzonitrile, suggesting that the interaction between both entities in the ground state is negligibly weak.

Upon photoexcitation of DSi6T using 450 nm excitation light, the fluorescence spectrum exhibited emission bands at 521 and 552 nm, from which the energy of the singlet-excited state is determined as 2.38 eV. Upon mixing DSi6T with BQ, the spectra showed no quenching of the singlet DSi6T indicating the absence of electron transfer/energy transfer interactions between BQ and the singlet DSi6T.

3.2. Electrochemical studies

Knowledge of the excited state energies of the chromophores and the redox potentials of donor and acceptor is thus an essential requirement for investigating the electron-transfer reactions. In order to determine the driving forces of electron transfer via the triplet-excited state of DSi6T ($-\Delta G_{et}^T$), the redox potentials have been studied using cyclic voltammetry (CV) and differential pulse voltammetry (DPV) techniques. Both techniques showed the first

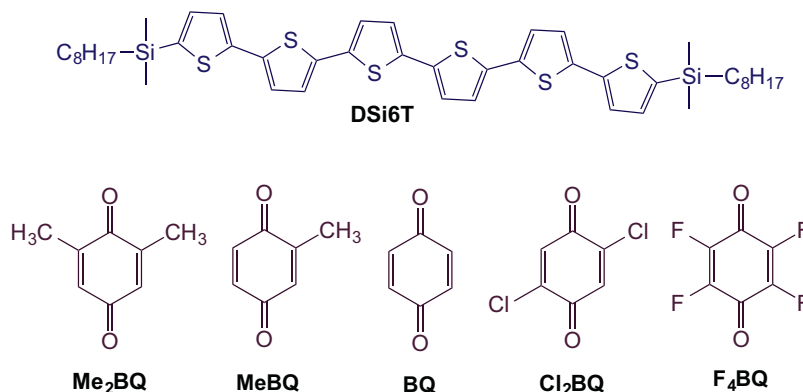


Fig. 1. Molecular structures of the examined DSi6T and BQs.

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