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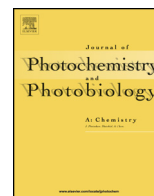


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Photoinduced electron transfer from silyl end-capped sexithiophene to benzoquinone derivatives studied by laser photolysis



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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,

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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

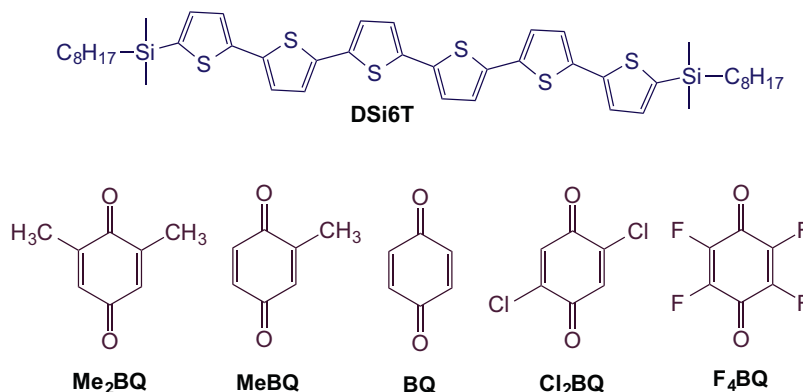


Fig. 1. Molecular structures of the examined DSi6T and BQs.

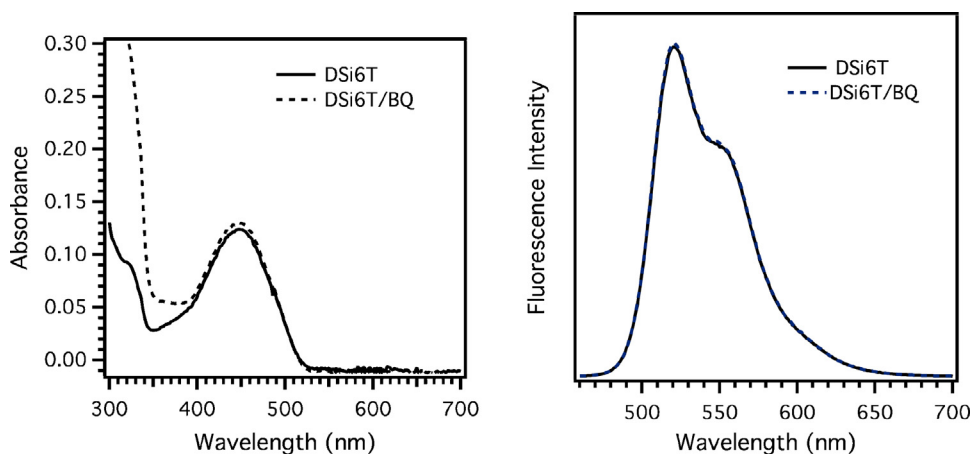


Fig. 2. Steady-state absorption (left) and fluorescence (right) spectra of DSi6T and DSi6T/BQ mixture in benzonitrile.

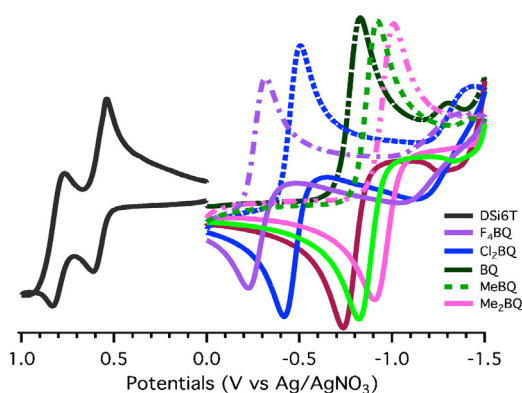


Fig. 3. Cyclic voltammograms of DSi6T and BQs in deaerated benzonitrile. Scan rate = 20 mV/s.

and second oxidation potentials (E_{ox}) of the electron donating DSi6T at 605 and 828 mV vs. Ag/AgNO₃, as shown in Fig. 3. On the other hand, the first reduction potential (E_{red}) of the BQ was located at -468 mV vs. Ag/AgNO₃. The E_{red} was negatively shifted by

substitution of the BQ with the electron accepting units (DSi6T/ $Cl_2BQ = -448$ mV and DSi6T/ $F_4BQ = -260$ mV). In contrary, the E_{red} of BQ was cathodically shifted when substituted with electron donating groups (DSi6T/ $MeQ = -870$ mV and DSi6T/ $Me_2BQ = -950$ mV). This trend is quite consistent with the reported values of *p*-benzoquinone derivatives in benzonitrile [45].

3.3. Photoinduced electron transfer from DSi6T to BQs

The femtosecond transient absorption spectra of DSi6T obtained by 390 nm laser excitation in deaerated benzonitrile exhibited absorption band (770 nm) at 20 ps which is assigned to the singlet-singlet DSi6T. With the decay of the singlet state DSi6T, the new absorption band was recorded at 710 nm which is assigned to the triplet state of Si6T. From the decay of the singlet DSi6T or the formation of the triplet DSi6T, the rate of the intersystem crossing process was determined to be 2.0×10^9 s⁻¹. Similar features were observed in the spectra of DSi6T/ F_4BQ mixture systems in deaerated benzonitrile (Fig. 4). The absence of the characteristic absorption bands of the electron-transfer products (DSi6T^{•+}/BQ^{•-}) indicates that the interaction between the singlet DSi6T and BQ derivatives is not feasible

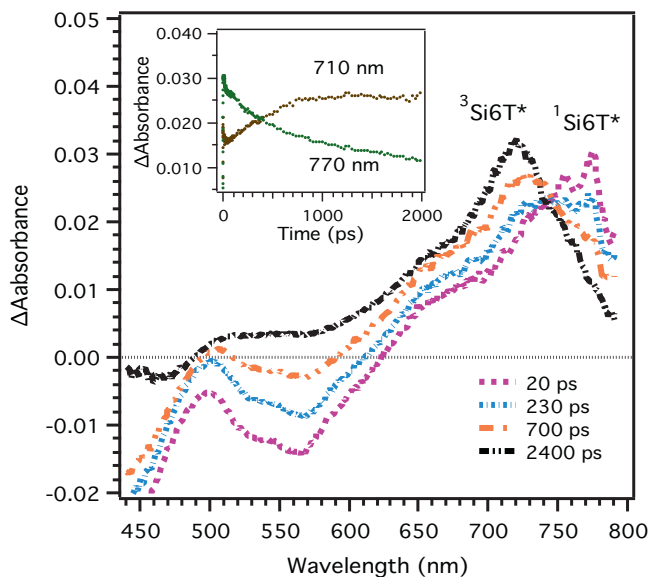


Fig. 4. Femtosecond transient absorption spectra obtained by 390 nm laser photolysis of DSi6T in deaerated PhCN. Inset: decay of the singlet DSi6T at 770 nm and the rise of the triplet DSi6T at 710 nm.

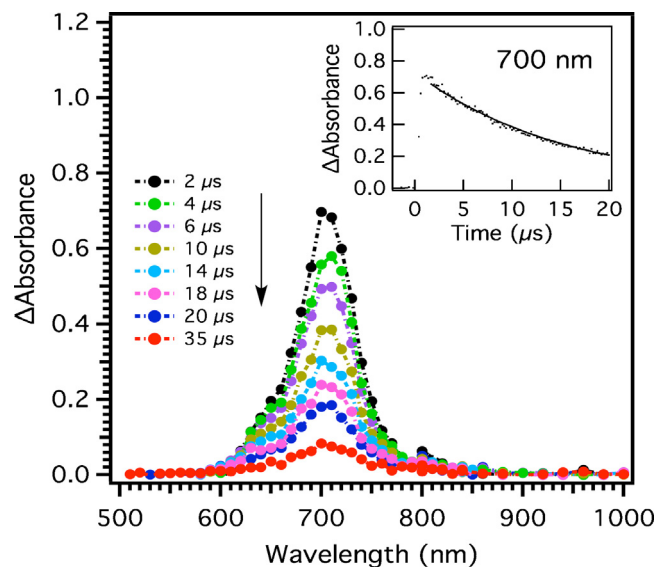


Fig. 5. Nanosecond transient absorption spectra obtained by 440 nm laser excitation light of DSi6T in benzonitrile.

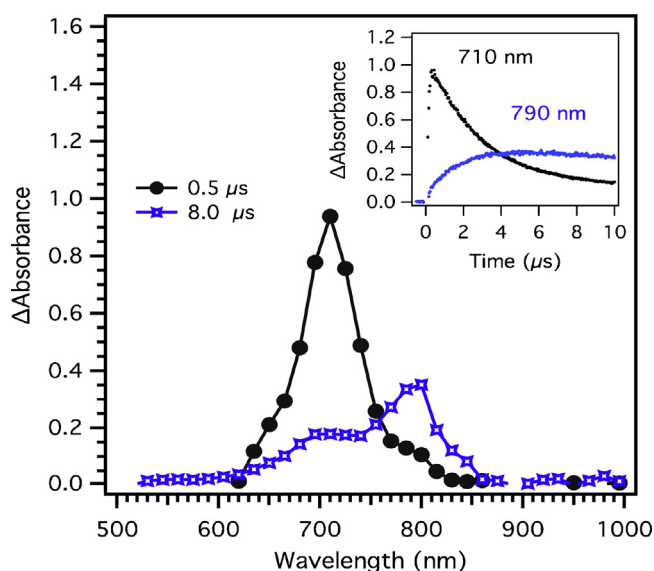
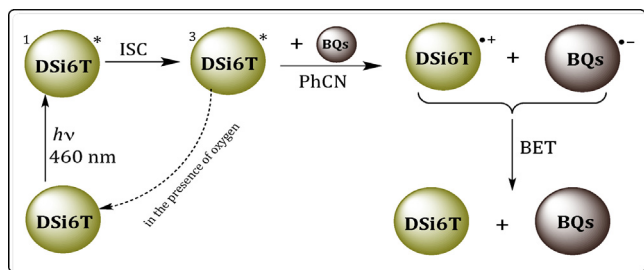


Fig. 6. Nanosecond transient absorption spectra obtained by 440 nm laser excitation light of DSi6T in the presence of BQ in benzonitrile.



Scheme 1. Schematic diagram showing the electron transfer process of DSi6T/BQs mixture systems in benzonitrile.

because of the fast intersystem crossing process from the singlet to the triplet DSi6T.

By photoexcitation of DSi6T (0.05 mM) in benzonitrile using 440 nm laser photolysis, the nanosecond transient absorption spectrum immediately after the laser pulse exhibited only an absorption band at 710 nm, which assigned to the triplet-excited state of Si6T ($^3\text{DSi6T}^*$) (Fig. 5). The decay rate of the triplet DSi6T was determined to be $6.50 \times 10^4 \text{ s}^{-1}$. By photo-excitation of DSi6T (0.05 mM) in the presence of BQs (0.05–0.30 mM) in Ar-saturated benzonitrile using 440 nm laser photolysis, the transient spectra exhibit the characteristic band of $^3\text{DSi6T}^*$ at 710 nm (Fig. 6). With

the decay of $^3\text{DSi6T}^*$, the concomitant rise of the DSi6T radical cation ($\text{DSi6T}^{\bullet+}$) was observed at 795 nm. The absorption band in the visible region at 795 nm was assigned to the one-electron oxidized species $\text{DSi6T}^{\bullet+}$ by comparison with the spectrum obtained in the one-electron oxidation reaction of DSi6T with FeCl_3 (Fig. S7). The assignment of the one-electron oxidized species $\text{DSi6T}^{\bullet+}$ in the visible region at 326, 363, and 795 nm was confirmed by comparison with the spectrum obtained in the one-electron oxidation reaction of DSi6T with FeCl_3 . The absorption band of $\text{DSi6T}^{\bullet+}$ at 795 nm was found to decrease in intensity with increasing the concentrations of FeCl_3 . It was interesting to record the formation of the DSi6T dimer radical cation at 1040 nm accompanied with the decrease of $\text{DSi6T}^{\bullet+}$ at 795 nm. The BQ radical anion $\text{BQ}^{\bullet-}$ was not recorded in the spectra because of its low extinction coefficient. These observations show clear evidence of the electron-transfer reaction from the triplet-excited state of DSi6T to BQ as shown in Scheme 1. Similar spectral features were observed when DSi6T mixed with other BQs (Figs. S4–S6). In oxygen-saturated solutions, an intermolecular energy transfer from $^3\text{DSi6T}^*$ to oxygen emerges, suppressing the electron-transfer process.

A more detailed picture of the kinetic is shown in Fig. 7 (left), where the rate constants of the electron-transfer process (k_{et}) were evaluated by monitoring the decay of the triplet excited states of DSi6T and the formation of $\text{DSi6T}^{\bullet+}$ as function of the concentrations of BQs. The rates of electron transfer from the triplet excited states of DSi6T to the BQs obeyed pseudo-first-order kinetics. A typical example is shown in Fig. 7. The pseudo-first-order rate constant increased linearly with increasing concentration of MeBQ, as shown in Fig. 7 (right). From the slope of the linear plot, the second order rate constant (k_{et}) of intermolecular electron transfer from to MeBQ was determined to be $1.85 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Similarly, the k_{et} values of electron transfer from the triplet-excited state of DSi6T to the examined BQs were determined as listed in Table 1.

The feasibility of the electron-transfer process via the triplet-excited state of DSi6T is controlled by the free-energy change ($\Delta G_{\text{et}}^{\text{T}}$), which can be expressed by the Rehm–Weller relation [46], in which e is the elemental charge.

$$\Delta G_{\text{et}}^{\text{T}} = e(E_{\text{ox}} - E_{\text{red}}) - E_{\text{T}} + E_{\text{c}}$$

where E_{ox} is the first oxidation potential of the DSi6T, E_{red} is the first reduction potential of quinone derivatives, E_{T} is the triplet energy of DSi6T (1.78 eV) as obtained from the phosphorescence measurements (see Supporting information, Fig. S1), and E_{c} is the Coulomb energy term (approximately 0.06 eV in the polar benzonitrile). The free energy change ($\Delta G_{\text{et}}^{\text{T}}$) values via the triplet-excited state of DSi6T was determined to be -0.28 eV (DSi6T/Me₂BQ), -0.36 eV

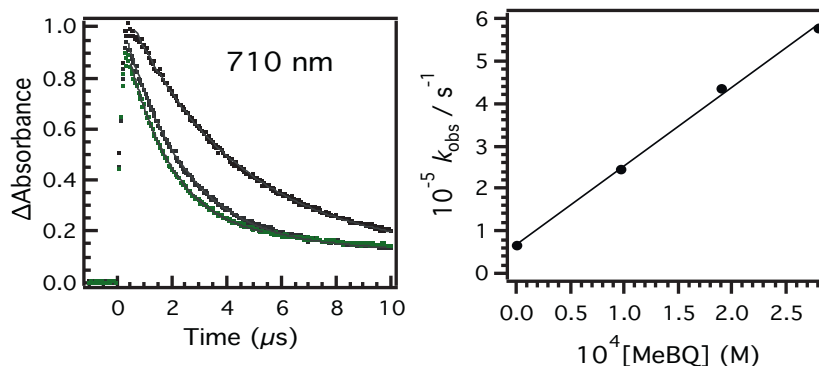


Fig. 7. (Left) Decay time profiles at 710 nm of the triplet DSi6T (0.05 mM) in the presence of MeBQ in deaerated benzonitrile at 298 K. (Right) Plot of the pseudo-first-order rate constant (k_{obs}) versus MeBQ concentrations.

Table 1

One-electron reduction potentials (E_{red}) of BQs, driving forces for electron transfer (ΔG_{et}), and rate constants for electron transfer (k_{et}) via the triplet DSi6T in benzonitrile at 298 K.

Electron acceptor	$E_{\text{red}}^{\text{a}}$ (mV vs. Ag/AgNO ₃)	$-\Delta G_{\text{et}}^{\text{b}}$ (eV)	k_{et} (M ⁻¹ s ⁻¹)	$\log k_{\text{et}}$
Me ₂ BQ	-950	0.285	6.18×10^8	8.79
MeBQ	-870	0.365	1.80×10^9	9.26
BQ	-776	0.457	2.71×10^9	9.43
Cl ₂ BQ	-448	0.787	4.10×10^9	9.61
F ₄ BQ	-260	0.975	4.20×10^9	9.62

^a Determined from cyclic voltammetry in PhCN containing TBAPF₆(0.1 M) at 298 K.

^b E_{T} of DSi6T = 1.78 eV.

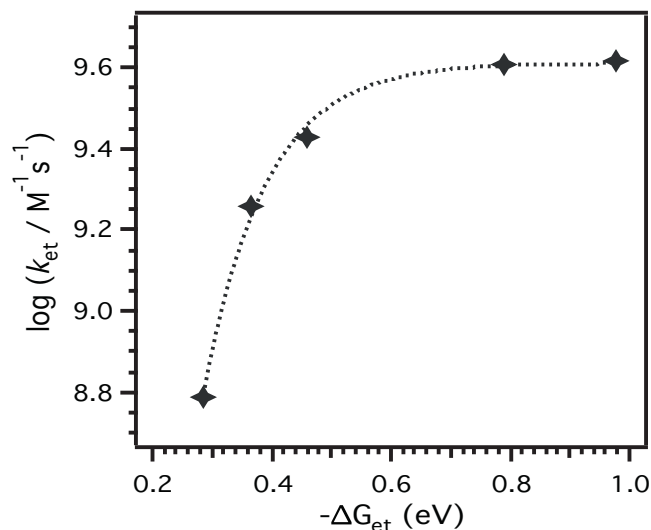


Fig. 8. Dependence of $\log k_{\text{et}}$ on $-\Delta G_{\text{et}}$ for electron transfer from the triplet DSi6T to BQ derivatives in benzonitrile at 298 K.

(DSi6T/MeBQ), -0.46 eV (DSi6T/BQ), -0.79 eV (DSi6T/Cl₂BQ) and -0.98 eV (DSi6T/F₄BQ). The negative $\Delta G_{\text{et}}^{\text{T}}$ value suggests that the electron-transfer process should be close to the diffusion-controlled limit (k_{diff}) (Fig. 8). Plots of $\log k_{\text{et}}$ via the triplet-excited state of DSi6T (1.78 eV) and the concentrations of BQs are shown in

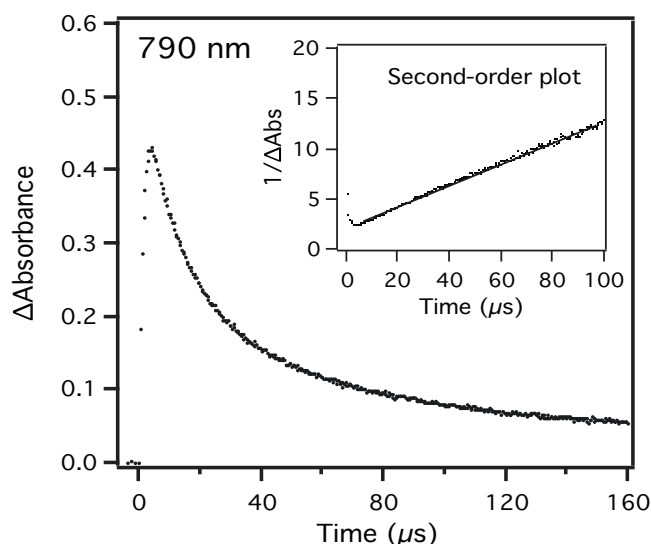


Fig. 9. Decay of DSi6T^{•+} on long time scale produced under the same conditions as described in Fig. 6. Inset: second-order plot.

Fig. 7, from where the rate of electron transfer (k_{et}) of DSi6T/BQs were estimated.

In long time-scale (200 μs), the DSi6T^{•+} and BQs^{•-} begin to decay slowly after reaching the maximal absorbance (Fig. 9). The decay time profile of DSi6T^{•+} was fitted with second-order kinetics, suggesting the bimolecular back electron-transfer process between DSi6T^{•+} and BQs^{•-}. The rate-constant of the back electron-transfer (k_{bet}) was estimated as $2.59 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ from the slope of the second-order plot in the form of k_{bet}/ϵ where ϵ refers to the molar extinction coefficient of DSi6T^{•+} ($\epsilon = 2.47 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ at 790 nm). The obtained k_{bet} for DSi6T^{•+} and BQs^{•-} is close to the diffusion-controlled limit in benzonitrile ($5.60 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$) [47].

4. Conclusion

Bis(dimethyl-*n*-octylsilyl)sexithiophene (DSi6T) with its high electron mobility is a promising material in the organic thin film transistor application. To explore its electronic properties in these applications, we have examined photoinduced electron-transfer reactions from the electron-donating bis(dimethyl-*n*-octylsilyl)sexithiophene (DSi6T) to the electron-accepting benzoquinone derivatives with wide varieties of reduction potentials by utilizing the laser flash photolysis techniques and other complementary techniques. The electron-transfer reactions from the singlet-excited state of DSi6T to BQs were not observed in the picosecond time region because of the fast intersystem crossing from the singlet to the triplet DSi6T ($2.00 \times 10^9 \text{ s}^{-1}$). By utilizing the nanosecond laser flash photolysis, the electron-transfer properties from the triplet DSi6T to BQs were confirmed in benzonitrile by recording the clear absorption bands of DSi6T radical cation (DSi6T^{•+}) at 790 nm. The absorption band of BQ radical anion was not recorded due to the low extinction coefficients. Dependence of the rates of electron transfer from the triplet DSi6T to BQs on the driving forces was confirmed in this study. The observed higher electron donating of DSi6T when combined with the electron deficient BQs render its ability as promising electro-active species in the photovoltaic solar cells and thin film transistor applications.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.jphotochem.2015.01.003>.

References

- [1] Anoxygenic Photosynthetic Bacteria, in: R.E. Blankenship, M.T. Madigan, C.E. Bauer (Eds.), Kluwer Academic Publishers, Dordrecht, 1995.
- [2] G.T. Babcock, Proc. Natl. Acad. Sci. 96 (1999) 12971.
- [3] V. Balzani (Ed.), Electron Transfer in Chemistry, vols. 1–5, Wiley-VCH, Weinheim, 2001.
- [4] Photoinduced Electron Transfer, in: M.A. Fox, M. Chanon (Eds.), Elsevier, Amsterdam, 1988.
- [5] S. Fukuzumi, K. Ohkubo, Coord. Chem. Rev. 254 (2010) 372.
- [6] S. Fukuzumi, Phys. Chem. Chem. Phys. 10 (2008) 2283.
- [7] G.J. Kavarnos, N.J. Turro, Chem. Rev. 86 (1986) 401.
- [8] S.V. Rosokha, J.K. Kochi, Acc. Chem. Res. 41 (2008) 641.
- [9] D. Gust, T.A. Moore, A.L. Moore, Acc. Chem. Res. 42 (2009) 1890.
- [10] M.E. El-Khouly, Y. Chen, X. Zhuang, S. Fukuzumi, J. Am. Chem. Soc. 131 (2009) 6370.
- [11] M.E. El-Khouly, D.K. Ju, K.-Y. Kay, F. D'souza, S. Fukuzumi, Chem. Eur. J. 16 (2010) 6193.
- [12] M.E. El-Khouly, S. Fukuzumi, F. D'souza, ChemPhysChem 15 (2014) 30.

- [13] M.E. El-Khouly, C.A. Wijesinghe, V.N. Nesterov, M.E. Zandler, S. Fukuzumi, F. D'souza, *Chem. Eur. J.* 18 (2012) 13844.
- [14] M.E. El-Khouly, A.N. Amin, M.E. Zandler, S. Fukuzumi, F. D'souza, *Chem. Eur. J.* 18 (2012) 5239.
- [15] M.E. El-Khouly, J.-H. Kim, J.-H. Kim, K.-Y. Kay, S. Fukuzumi, *J. Phys. Chem. C* 116 (2012) 19709.
- [16] M.E. El-Khouly, O. Ito, P.M. Smith, F. D'souza, *J. Photochem. Photobiol. C* 5 (2004) 79.
- [17] M.E. El-Khouly, M. Fujitsuka, O. Ito, M. El-Kemary, *J. Photochem. Photobiol. A* 141 (2001) 1.
- [18] M.E. El-Khouly, S. Fukuzumi, *J. Porphyrins Phthalocyanines* 15 (2011) 111.
- [19] M.E. El-Khouly, Y. Araki, M. Fujitsuka, O. Ito, *Phys. Chem. Chem. Phys.* 4 (2002) 3322.
- [20] T. Nojiri, M.M. Alam, H. Konami, A. Watanabe, O. Ito, *J. Phys. Chem.* 101 (1997) 7943.
- [21] M.E. El-Khouly, M. Fujitsuka, O. Ito, *J. Porphyrins Phthalocyanines* 4 (2000) 591.
- [22] M.E. El-Khouly, S.D.-M. Islam, M. Fujitsuka, O. Ito, *J. Porphyrins Phthalocyanines* 4 (2000) 713.
- [23] B. Fu, J. Baltazar, Z. Hu, A.-T. Chien, S. Kumar, C.L. Henerson, D.M. Collard, E. Reichmanis, *Chem. Mater.* 24 (2012) 4123.
- [24] *Electronic Materials: The Oligomer Approach*, in: K. Müllen, G. Wegner (Eds.), Wiley-VCH, Weinheim, Germany, 1998.
- [25] *Handbook of Oligo- and Polythiophenes*, in: D. Fichou (Ed.), Wiley-VCH, Weinheim, Germany, 1999.
- [26] A. Mishra, C.-Q. Ma, P. Bäuerle, *Chem. Rev.* 109 (2009) 1141.
- [27] Z. Ma, W. Sun, S. Himmelberger, K. Vandewal, Z. Tang, J. Bergqvist, A. Salleo, J.W. Andreasen, O. Inganäs, M.R. Andersson, C. Müller, F. Zhang, E. Wang, *Energy Environ. Sci.* 7 (2014) 361.
- [28] N. Noma, T. Suzuki, Y. Shirota, *Adv. Mater.* 7 (1995) 647.
- [29] C. Vidélot, A. El Kassmi, D. Fichou, *Solar Energy Mater. Solar Cells* 63 (2000) 69.
- [30] P. Liu, Q. Li, M. Huang, W. Pan, W. Deng, *Appl. Phys. Lett.* 89 (2006) 213501.
- [31] J.A. Kong, E. Lim, K.K. Lee, S. Lee, S.H. Kim, *Solar Energy Mater. Solar Cells* 94 (2010) 2057.
- [32] J. Sakai, T. Taima, K. Saito, *Org. Electron.* 9 (2008) 582.
- [33] J.H. Choi, M.E. El-Khouly, T. Kim, Y.-S. Kim, U.C. Yoon, S. Fukuzumi, K. Kim, *Int. J. Photoenergy* (2013) 1.
- [34] *Functions of Quinones in Energy Conserving Systems*, in: B.I. Trumpower (Ed.), Academic Press, New York, 1986.
- [35] M.Y. Okamura, G.A. Feher, *Rev. Biochem.* 61 (1992) 861.
- [36] R. Calvo, E.C. Abresch, R. Bittl, G. Feher, W. Hofbauer, R.A. Isaacson, W. Lubitz, M.Y. Okamura, M.L. Paddock, *J. Am. Chem. Soc.* 122 (2000) 7327.
- [37] G. Feher, J.P. Allen, M.Y. Okamura, D.C. Rees, *Nature* 339 (1989) 111.
- [38] R.A. Isaacson, E.C. Abresch, F. Lendzian, C. Boullais, M.L. Paddock, C. Mioskowski, W. Lubitz, M.-E. Feher, *The Reaction Center of Photosynthetic Bacteria: Structure and Dynamics*, in: M.-E. Michel-Beyerle (Ed.), Springer, Berlin, 1996, pp. 353–367.
- [39] B.G. Malmström, *Acc. Chem. Res.* 26 (1993) 332.
- [40] S. Ferguson-Miller, G.T. Babcock, *Chem. Rev.* 96 (1996) 2889.
- [41] C.W. Hoganson, G.T. Babcock, *Science* 277 (1997) 1953.
- [42] Y. Amao, I. Okura, *J. Mol. Catal. B Enzym.* 17 (2002) 9.
- [43] Y. Amao, K. Asai, T. Miyashita, I. Okura, *Polym. Adv. Technol.* 11 (2000) 705.
- [44] J.H. Choi, D.W. Cho, H.J. Park, S.-H. Jin, S. Jung, M. Yi, C.K. Song, U.C. Yoon, *Synth. Met.* 159 (2009) 1589.
- [45] M. Kanematsu, P. Naumov, T. Kojima, S. Fukuzumi, *Chem. Eur. J.* 17 (2011) 12372.
- [46] D. Rehm, A. Weller, *Ber. Bunsenges. Phys. Chem.* 73 (1969) 834.
- [47] *Handbook of Photochemistry*, in: S.I. Murov (Ed.), Marcel Dekker, New York, 1985.