Photoinduced electron transfer of carbazole–acceptor dyads in solution and in a polymer solid

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Received 10th February 2004, Accepted 28th May 2004 First published as an Advance Article on the web 14th June 2004

Photoinduced charge separation (CS) of carbazole–acceptor dyads (Cz–S–A) in solutions and in a polymer solid was examined by the measurement of fluorescence decay. For the discussion of CS from the viewpoint of thermal fluctuations in a solution and in a polymer solid, the separation distance between the Cz donor moiety and acceptor moiety was fixed with a rigid spacer. The photoinduced CS was observed for various solutions with different dielectric constants ranging from 3.06 to 37.5 at room temperature. The rate constant k_{CS} increased with an increase in the free energy gap of $-\Delta G_{CS}$, indicating that CS is in the normal region of the Marcus theory. The temperature dependence of CS in a solution from 183 to 296 K was quantitatively explained by an electron transfer (ET) formula where solvent motions are treated as a classical mode and vibrational motions of the reactant are treated as a quantum mode. On the other hand, the photoinduced CS was also observed for a polymer solid with polar cyano groups over a wide temperature range from 100 to 400 K, although most motions are highly restricted compared with those in a solution with dielectric constants measured at a high frequency. Below T_g , CS was independent of temperature, indicating that CS is caused by nuclear tunneling at low temperatures.

1. Introduction

The first-order rate constant for electron transfer (ET) k_{ET} between two molecules with very weak electronic coupling is simply expressed by eqn. (1):¹⁻⁶

$$k_{\rm ET} = \frac{2\pi}{\hbar} |V|^2 (\rm FC) \tag{1}$$

where V is the electronic coupling matrix element and FC is the Franck-Condon factor. The former term, V, decreases exponentially with an increase in the separation distance between the reactants. The latter term, FC, is the probability of the fulfilment of the Franck-Condon conditions: the Franck-Condon principle and energy conservation, which is given by a sum of products of overlap integrals of the wavefunctions of the reactants with those of the products, weighted by Boltzmann factors. Thus, ET will occur only when the total energy of the reactants and surrounding medium is equal to that of the products and surrounding medium. In a solution, the energy matching takes place by thermal fluctuations in the orientational coordinates of solvent molecules and in the vibrational coordinates of the reactants. In other words, ET requires not only a spatial approach of the reactants but also the energy matching caused by thermal fluctuations.

In a polymer solid, molecular motions are highly restricted compared with those in a solution. Above the glass transition temperature (T_g) , segments in the main chains are freely mobile. Below the T_g , on the other hand, the free rotational motions of the main chain are frozen but local motions such as rotational motions of side chains and librational motions of a few segments in the main chain are still allowed. The relaxation time of these local motions shows a wide distribution, which is heavily dependent on temperature in general. In other words, the orientational fluctuations of polar groups in a polymer solid are different from those in a solution. Thus, ET in a polymer solid should be different from that in a solution. A few researchers have discussed ET in glassy solids from a theoretical standpoint.^{7–11} However, there are few experimental reports on intramolecular ET in polymer solids.^{12–14}

Here we investigated photoinduced charge separation (CS) of intramolecularly linked donor (D) and acceptor (A) compounds in a polymer solid and in various solvents. The D–A molecules have a carbazole and an A moiety whose separation distance is fixed by a rigid cyclohexane spacer. In other words, the electronic coupling V is considered to be constant in our system. We focus on the latter term, FC, in eqn. (1) to discuss intramolecular photoinduced ET in a polymer solid where the orientational motions of polar group are partially restricted and have various relaxation modes.

2. Experimental

2.1. Materials

A series of nine carbazole (Cz; Donor) cyclohexane (S; Spacer) acceptor (A; Acceptor) molecules (Cz-S-A) were synthesized as described below. The synthetic scheme of the Cz-S-A molecules is summarized in Scheme 1. N-Ethylcarbazole (EtCz) was synthesized by N-alkylation of carbazole and was purified by silica-gel column chromatography and recrystallization. 1,12-Di(9-carbazolyl)dodecane (Cz-12-Cz) was synthesized by the reaction of carbazole with 1,12-dibromododecane and purified by recrystallization and silica-gel column chromatography. Either EtCz or Cz-12-Cz was used as a reference. Solvents used here were hexane (Hex; Nacalai Tesque, spectroscopic grade), dibutyl ether (DBE; Nacalai Tesque), 2-methyltetrahydrofuran (MTHF; Nacalai Tesque), and acetonitrile (MeCN; Nacalai Tesque, spectroscopic grade). Before use, DBE was purified by distillation under reduced pressure and MTHF was dried with solid KOH, passed through freshly activated alumina, and then distilled from CaH₂ with 2,6-ditert-butyl-p-cresol. Other solvents of spectroscopic grade were





Scheme 1 Synthetic scheme of a series of nine carbazole (Donor)–cyclohexane (Spacer)–acceptor (Acceptor) molecules (Cz–S–A): $A = CF_3$ (1), 5F (2), Cin (3), 2CF₃ (4), TP (5), CN (6), DEF (7), NO₂ (8), and 2NO₂ (9).

used without further purification. The polymer used here was cyanoethylated *O*-(2-hydroxypropyl)cellulose (CN-HPC), which was kindly provided by Professor Takeaki Miyamoto and Associate Professor Yoshinobu Tsujii.

Synthesis of *trans*-1,4-cyclohexylenedimethylene diacetate. A solution of acetic anhydride (160 g) was added dropwise to a mixture of *cis*- and *trans*-cyclohexanedimethanol (100 g) stirred at 140–165 °C, with the evolution of acetic acid. After the removal of acetic acid, the solution was heated at 200 °C to remove the residual acetic anhydride and cooled to room temperature. The resulting white crystals were collected and dried to afford a mixture of *cis*- and *trans*-1,4-cyclohexylene-dimethylene diacetate. The mixture was heated at 35 °C to

remove the melt of *cis*-1,4-cyclohexylenedimethylene diacetate. The residue was recrystallized from acetone and from methanol to give *trans*-1,4-cyclohexylenedimethylene diacetate: yield 82.5 g (52.1%); mp 69.0–72.5 °C; IR (KBr) 2950, 2875 (ν_{CH_3}), 2925, 2850 (ν_{CH_2}), 1750 ($\nu_{C=O}$), 1240 ($\nu_{C-C-O-C}$), 1040 (ν_{C-O}) cm⁻¹.

Synthesis of *trans***-1,4-cyclohexanedimethanol.** The *trans*-diacetate (82.5 g) was added to 10 wt.% aqueous NaOH (825 g), and refluxed for 10 h. After cooling to room temperature, the reaction mixture was neutralized with aqueous HCl. The reaction product was extracted into chloroform and the solvent was evaporated. The residual powder was recrystallized from ether to give *trans*-1,4-cyclohexanedimethanol: yield 24.1 g

(46.3%); mp 62.0–64.0 °C; IR (KBr) 3300 (ν_{OH}), 2920 (ν_{CH_2}), 2850 (ν_{CH_2}), 1040 (ν_{C-O}) cm⁻¹.

Synthesis of *trans*-1,4-cyclohexanedimethanol monotosylate. The dimethanol (30 g) was dissolved in a mixture solution of chloroform (150 mL) and pyridine (150 mL) at 0 °C. To the solution was added dropwise a mixture solution of chloroform (100 mL) and pyridine (150 mL) with p-toluenesulfonyl chloride (39.6 g). After stirring for 4 h, the solvent was evaporated below 35 °C. The reaction product was dissolved in excess chloroform solution, washed with dilute aqueous H₂SO₄, aqueous NaHCO3, and water. After the chloroform layer was dried over anhydrous Na₂SO₄, the solvent was evaporated. The residue was dissolved in methanol solution, cooled at 0 °C, filtrated, and evaporated to afford yellow oil of trans-1,4cyclohexanedimethanol monotosylate: yield 34.2 g (55.1%); ¹H NMR (CDCl₃, 90 MHz) δ 0.80–1.80 (m, 10H, cyclohexane ring), 2.40 (s, 3H, CH₃), 3.40 (t, 2H, CH₂), 3.80 (d, 2H, CH₂), 7.30 (d, J = 6.0 Hz, 2H, ArH), 7.72 (d, J = 6.0 Hz, 2H, ArH); IR (KBr) 3550, 3375 (ν_{OH}), 2920, 2850 (ν_{CH_2}), 1750 ($\nu_{C=O}$), 1240 ($\nu_{C-C-O-C}$), 1040 (ν_{C-O}) cm⁻¹.

Synthesis of trans-4-(carbazole-9-yl)methylcyclohexylmethanol. Carbazole (6.9 g) was dissolved in a solution of N,Ndimethylformamide (DMF, 50 mL). To the solution was added sodium hydride (2.0 g) with stirring at 60 °C for 1 h. To the solution cooled to room temperature, a DMF solution (20 mL) of trans-1,4-cyclohexanedimethanol monotosylate (12.3 g) was added dropwise and stirred for 2 h. The reaction solvent was changed to dichloromethane from DMF. The mixture was washed with water three times. After the dichloromethane layer was dried over CaCl₂, the solvent was evaporated. The residue was recrystallized from benzene-hexane solution to give trans-4-(carbazole-9-yl)methylcyclohexylmethanol: yield 2.5 g (20.7%); ¹H NMR (CDCl₃, 90 MHz) δ 0.64–1.84 (m, 10H, cyclohexane ring), 3.20 (d, J = 4.0 Hz, 2H, CH₂), 4.12 (d, J = 4.0 Hz, 2H, CH₂), 7.12–7.44 (m, 6H, ArH), 8.10 (d, J = 4.8 Hz, 2H, ArH); IR (KBr) 3375 (v_{OH}), 2920, 2850 (v_{CH₂}), 1450 (Ar skeleton vibration), 750 (δ_{Ar-H}) cm⁻¹.

Synthesis of Cz–S–A (Cz–S–DEF excluded). Eight of the nine Cz–S–A molecules (Cz–S–DEF excluded) were synthesized by the esterification reaction of *trans*-4-(carbazole-9-yl)methylcyclohexylmethanol with acyl chloride having an acceptor moiety. To an acetone solution of *trans*-4-(carbazole-9-yl)methylcyclohexylmethanol and one molar equivalent of pyridine was added one molar equivalent of acyl chloride having an acceptor moiety and refluxed for 2 h. The reaction solvent was changed to dichloromethane from acetone. The mixture was washed with dilute aqueous HCl three times and water two times. After the dichloromethane layer was dried over CaCl₂, the solvent was evaporated. The product was purified by silica-gel column chromatography and recrystallization from a dichloromethane–hexane solution.

Cz–S–CF₃ (1). ¹H NMR (CDCl₃, 90 MHz) δ 0.94–1.88 (m, 10H, cyclohexane ring), 4.10–4.20 (m, 4H, CH₂), 7.13–7.46 (m, 8H, ArH), 7.68 (d, J = 6.0 Hz, 2H, ArH), 8.10 (d, 4H, ArH); IR (KBr) 2920, 2850 (v_{CH_2}), 1720 ($v_{C=0}$), 1460 (Ar skeleton vibration), 1320 (v_{C-0}), 750 (δ_{Ar-H}) cm⁻¹; elemental anal. calcd: C, 72.24; H, 5.63; N, 3.01; F, 12.25; found: C, 72.49; H, 5.39; N, 2.90; F, 12.28%.

Cz–S–5F (2). ¹H NMR (CDCl₃, 90 MHz) δ 1.02–1.88 (m, 10H, cyclohexane ring), 4.18 (d, 4H, CH₂), 7.16–7.48 (m, 6H, ArH), 8.10 (d, J = 4.8 Hz, 2H, ArH); IR (KBr) 2925, 2850 (ν_{CH_2}), 1740 ($\nu_{C=0}$), 1500 (Ar skeleton vibration), 1320 (ν_{C-0}), 1240 (ν_{C-F}), 750 (δ_{Ar-H}) cm⁻¹; elemental anal. calcd: C, 66.52;

H, 4.55; N, 2.87; F, 19.49; found: C, 66.78; H, 4.33; N, 2.86; F, 19.51%.

Cz–S–Cin (3). ¹H NMR (CDCl₃, 90 MHz) δ 0.90–1.88 (m, 10H, cyclohexane ring), 4.00 (d, J = 4.0 Hz, 2H, CH₂), 4.16 (d, J = 4.0 Hz, 2H, CH₂), 6.32 (s, 1H, ring) 4.00 (d, J = 4.0 Hz, 2H, CH₂), 4.16 (d, J = 4.0 Hz, 2H, CH₂), 6.32 (s, 1H, -CH=), 6.50 (s, 1H, =-CH-), 7.16–7.60 (m, 10H, ArH), 7.76 (s, 1H, ArH), 8.10 (d, J = 4.8 Hz, 2H, ArH); IR (KBr) 2925, 2850 (v_{CH_2}), 1710 ($v_{C=O}$), 1640 ($v_{C=C}$), 1330 (v_{C-C-O}), 1200 (v_{C-O}), 750 (δ_{Ar-H}) cm⁻¹; elemental anal. calcd: C, 82.24; H, 6.90; N, 3.31; O, 7.56; found: C, 82.36; H, 6.99; N, 3.35; O, 7.42%.

Cz–S–2CF₃ (4). ¹H NMR (CDCl₃, 90 MHz) δ 0.82–1.86 (m, 10H, cyclohexane ring), 4.13 (d, 4H, CH₂), 7.08–7.52 (m, 8H, ArH), 8.10 (d, J = 4.8 Hz, 2H, ArH), 8.42 (s, 1H, ArH); IR (KBr) 2925, 2850 (v_{CH_2}), 1740 ($v_{C=0}$), 1280 (v_{C-O-}), 1250 (v_{C-O}), 1240 (v_{C-O-C}), 1150 (v_{CF_3}), 750 (δ_{Ar-H}) cm⁻¹; elemental anal. calcd: C, 65.28; H, 4.72; N, 2.63; F, 21.37; found: C, 65.39; H, 4.66; N, 2.59; F, 21.18%.

Cz–S–TP (5). ¹H NMR (CDCl₃, 90 MHz) δ 0.92–1.90 (m, 10H, cyclohexane ring), 3.90 (s, 3H, CH₃), 4.12 (m, 4H, CH₂), 7.12–7.28 (m, 6H, ArH), 8.04–8.12 (m, 6H, ArH); IR (KBr) 2925, 2850 (v_{CH_2}), 1720 ($v_{C=0}$), 1450 (v_{OCH_3}), 1270 (v_{C-C-0}), 1120 (v_{C-0}), 750 (δ_{Ar-H}) cm⁻¹; elemental anal. calcd: C, 76.46; H, 6.42; N, 3.08; O, 14.05; found: C, 76.43; H, 6.41; N, 3.05; O, 14.17%.

Cz–S–CN (6). ¹H NMR (CDCl₃, 90 MHz) δ 0.93–1.90 (m, 10H, cyclohexane ring), 4.13–4.24 (m, 4H, CH₂), 7.16–7.50 (m, 6H, ArH), 7.72 (d, J = 6.0 Hz, 2H, ArH), 8.10 (d, 4H, ArH); IR (KBr) 2925, 2850 (v_{CH_2}), 1720 ($v_{C=0}$), 1280 (v_{C-C-0}), 750 (δ_{Ar-H}) cm⁻¹; elemental anal. calcd: C, 79.59; H, 6.20; N, 6.63; O, 7.57; found: C, 79.77; H, 6.08; N, 6.48; O, 7.40%.

Cz–S–NO₂ (8). ¹H NMR (CDCl₃, 90 MHz) δ 0.92–1.90 (m, 10H, cyclohexane ring), 4.16 (d, 4H, CH₂), 7.12–7.48 (m, 6H, ArH), 8.08–8.32 (m, 6H, ArH); IR (KBr) 2930, 2850 (ν_{CH_2}), 1720 ($\nu_{C=O}$), 1525 (ν_{NO_2}), 1340 (ν_{NO_2}), 1260 (ν_{C-C-O}), 750 (δ_{Ar-H}) cm⁻¹; elemental anal. calcd: C, 73.28; H, 5.92; N, 6.33; O, 14.46; found: C, 73.15; H, 5.78; N, 6.30; O, 14.57%.

Cz–S–2NO₂ (9). ¹H NMR (CDCl₃, 90 MHz) δ 0.92–1.90 (m, 10H, cyclohexane ring), 4.16–4.30 (m, 4H, CH₂), 7.16–7.50 (m, 6H, ArH), 8.10 (d, *J* = 4.8 Hz, 2H, ArH), 9.10–9.20 (m, 3H, ArH); IR (KBr) 2930, 2850 (v_{CH_2}), 1720 ($v_{C=O}$), 1525 (v_{NO_2}), 1340 (v_{NO_2}), 1260 (v_{C-C-O}), 750 (δ_{Ar-H}) cm⁻¹; elemental anal. calcd: C, 66.52; H, 5.17; N, 8.62; O, 19.69; found: C, 66.24; H, 5.03; N, 8.64; O, 19.42%.

Synthesis of Cz–S–DEF. To a solution of carbon tetrachloride with *trans*-4-(carbazole-9-yl)methylcyclohexylmethanol (1.2 g) and fumaryl chloride (2.5 g) was added AlCl₃ (0.84 g). After the solution was refluxed with stirring for 30 min, ethanol (0.6 g) was added to the solution and the reflux was further continued for 30 min. The product was purified by silica-gel column chromatography and recrystallization from hexane.

Cz–S–DEF (7). ¹H NMR (CDCl₃, 90 MHz) δ 0.84–1.90 (m, 13H, cyclohexane ring, CH₃), 3.92–4.32 (m, 6H, CH₂), 6.80 (s, 2H, CH=CH), 7.12–7.44 (m, 6H, ArH), 8.08 (d, *J* = 4.8 Hz, 2H, ArH); IR (KBr) 2920, 2850 (ν_{CH_2}), 1725 ($\nu_{C=O}$), 1300 ($\nu_{= CH}$, $\nu_{C-C-O-C}$), 750 (δ_{Ar-H}) cm⁻¹; elemental anal. calcd: C, 74.44; H, 6.97; N, 3.34; O, 15.26; found: C, 74.06; H, 6.98; N, 3.40; F, 14.00%.

Table 1 Potential difference between oxidation of Cz and reduction of A moieties

A moieties	CF ₃	5F	Cin	2CF ₃	TP	CN	DEF	NO ₂	$2NO_2$
$E_{\rm ox}{}^{\rm D} - E_{\rm red}{}^{\rm A}/{\rm eV}$	3.05	2.99	2.97	2.89	2.84	2.80	2.59	2.04	1.89

2.2. Sample preparation

Samples dissolved in solvents were degassed by the freezepump-thaw method and sealed in a 1 cm quartz cell. The concentration of Cz compounds in the solutions was kept in the order of 10^{-5} mol L⁻¹ to prevent intermolecular interaction. Polymer films of CN-HPC doped with carbazole compounds were prepared by the solvent-casting method. The Cz compounds were dissolved in MeCN with the CN-HPC so that the concentration of Cz compounds in the final polymer films was in the order of 10^{-3} mol L⁻¹. The polymer solution was dropped onto a quartz plate ($15 \times 15 \times 1$ mm³), dried for 2 days under atmospheric pressure and for 1 week in a desiccator under reduced pressure at room temperature. The polymer films had a thickness of about 15 µm.

2.3. Absorption and fluorescence measurements

Steady-state absorption and emission spectra were measured at room temperature in a 1 cm quartz cell with a spectrophotometer (Hitachi, U-3500) and a fluorescence spectrophotometer (Hitachi, 850 or F-4500), respectively. Fluorescence decay was measured by the time-correlated single-photoncounting method. The excitation light source was third harmonic pulses (295 nm) generated from a mode-locked Ti:sapphire laser (Spectra-Physics, Tsunami 3950) that was pumped by an Ar⁺ laser (Spectra-Physics, BeamLok 2060). The fluorescence emission was collected at 90° relative to the incident excitation laser light pathway and detected by a photomultiplier tube (PMT; Hamamatsu Photonics, R3234) through a monochromator (Ritsu, MC-10N) or by a microchannel plate-photomultipiler tube (MCP-PMT; Hamamatsu Photonics, R3809), with a polarizer set at a magic angle of 54.75° to the vertically polarized excitation light and a cut-off filter (UV-360 or UV-34) for the excitation light. The details of this apparatus have been described elsewhere.¹⁵ The total instrument response function has an FWHM of ca. 750 ps for the PMT system and ca. 60 ps for the MCP-PMT system. The decay data were fitted with the sums of a function that were convoluted with the instrument response function by the nonlinear least-squares method.

The temperature of samples sealed in a 1 cm quartz cell was controlled in a heat bath of isopentane or water and measured with a thermocouple. For the measurement below 0 °C, the quartz cell was dipped in a Dewar cell filled with isopentane precooled by liquid nitrogen and the spontaneous heating rate was slow enough to measure within a temperature precision of ± 1 °C. For the measurement above 0 °C, the quartz cell was dipped in a Dewar cell filled with water equipped with a heater to control the temperature. Temperature of film samples cast on a quartz plate was controlled in a cryostat (Iwatani Plantech Corp., CRT510) with PID temperature control unit (Scientific Instruments, Model 9650).

2.4. Electrochemical measurements

The standard potential of the one electron oxidation E_{ox}^{D} of EtCz and reduction E_{red}^{A} of all the Cz–S–A compounds used here were determined by the cyclic voltammetry and polarography techniques, respectively. The cyclic voltammogram was measured in MeCN containing 0.1 mol L⁻¹ of tetra-*n*-butyl-ammonium perchlorate as the supporting electrolyte. Reference electrode was Ag in MeCN containing 0.01 mol L⁻¹ of

Ag⁺. Scan rate was 100 mV s⁻¹. Direct-current polarogram was obtained by a Yanagimoto model p-8 polarograph. Height of the mercury reservoir of the dropping mercury electrode was 60 cm. An electrode of Ag/Ag⁺ (0.1 mol L⁻¹) was used as the reference electrode, which has the potential 0.36 V *versus* SCE in the solution of 0.1 mol L⁻¹ of tetra-*n*-butylammonium iodide in MeCN. Polarographic measurements were all carried out in MeCN containing 0.1 mol L⁻¹ of tetra-*n*-butylammonium iodide. Temperature of the electrolytic cell was maintained at 25 °C. The oxygen dissolved in the electrolytic solution was removed by bubbling pure nitrogen gas through the solution. The differences between E_{ox}^{D} and E_{red}^{A} are summarized in Table 1.

3. Results and discussion

3.1. Fluorescence spectra of Cz-S-A dyads in solutions

Fig. 1 shows the fluorescence spectra of EtCz and Cz-S-A molecules in MeCN at room temperature. The fluorescence spectra of Cz-S-A molecules were the same as that of the reference compound EtCz and were almost mirror images of absorption spectrum of EtCz. This proves that there are no intra- and intermolecular interactions between Cz and A moieties in the ground state. From the absorption and fluorescence spectra, the energy level of the lowest excited singlet state of EtCz $E(S_1)$ was evaluated to be 3.56 eV. The fluorescence intensity of Cz-S-A was weak in comparison with that of EtCz. This fluorescence quenching was ascribed not to energy transfer but to electron transfer from the excited Cz moiety to the A moieties, because there is no spectral overlap between fluorescence of the Cz donor and absorption of the A moieties: there is no absorption of the A moieties in the wavelength range of >300 nm where absorption spectra of Cz-S-A are essentially the same as that of EtCz shown in Fig. 1.

As shown in Fig. 2, the fluorescence of Cz–S–A decayed rapidly compared with that of EtCz. The fluorescence decay I(t) of Cz–S–A in solution was well fitted with a single or double exponential function: $I(t) = \Sigma A_i \exp(-t/\tau_i)$. The lifetime of the minor component is ascribable to a Cz molecule having no A moiety, because it was similar to that of EtCz. The minor fraction was less than 5%. Thus, the CS rate constant $k_{\rm CS}$ was calculated by $k_{\rm CS} = \tau^{-1} - \tau_0^{-1}$ where τ_0 is the fluorescence



Fig. 1 Fluorescence spectra of EtCz and Cz–S–A in MeCN at room temperature: thick lines EtCz; thin lines Cz–S– CF_3 (1), Cz–S–Cin (3), Cz–S–TP (5), and Cz–S–DEF (7) from top to bottom (solid lines). Absorption spectra of EtCz in MeCN at room temperature (broken line).



Fig. 2 Fluorescence decay curves of EtCz (open circles) and Cz–S–TP (5) (closed circles) in MeCN at room temperature. Excitation wavelength was 295 nm. Monitor wavelength was 368 nm. Broken line shows an excitation laser pulse: instrumental response function with an FWHM of 750 ps.

lifetime of EtCz and τ the major component of the fluorescence lifetime of Cz–S–A. The fluorescence lifetimes and k_{CS} are summarized in Table 2. On the other hand, the fluorescence spectra of Cz–S–A molecules in a polymer film were also the same as that of Cz–12–Cz and the intensity was quenched compared with that of Cz–12–Cz, indicating that intramolecular CS from the excited Cz to the A moieties also occurred even in a polymer film.

3.2. Solvent polarity effects of photoinduced CS in solutions

First, we investigated the intramolecular CS of D–S–A molecules in various solvents. Fig. 3 shows the free energy gap $(-\Delta G_{\rm CS})$ dependences of the $k_{\rm CS}$ for D–S–A molecules in various solvents. Solid and broken curves in the figure represent the theoretical prediction of the following ET formula. In a classical ET formula of the Marcus theory,^{1,2} the Franck– Condon factor FC_{CC} can be expressed by eqn. (2), where both orientational motions of solvents and vibrational motions of the reactants are treated as a classical mode. In a single quantum mode formula in the Jortner theory,^{16,17} the Franck–Condon factor FC_{CQ} can be expressed by eqn. (3), where the orientational motion of solvents is treated as a classical mode and the vibrational motion of reactants is treated as a quantum one.

$$k_{\rm CC} = \frac{2\pi}{\hbar} |V|^2 FC_{\rm CC}$$

$$FC_{\rm CC} = \frac{1}{\sqrt{4\pi(\lambda_{\rm S} + \lambda_{\rm V})k_{\rm B}T}} \exp\left[-\frac{(\lambda_{\rm S} + \lambda_{\rm V} + \Delta G_{\rm CS})^2}{4(\lambda_{\rm S} + \lambda_{\rm V})k_{\rm B}T}\right]$$
(2)

$$k_{\rm CQ} = \frac{2\pi}{\hbar} |V|^2 FC_{\rm CQ}$$

$$FC_{\rm CQ} = \frac{1}{\sqrt{4\pi\lambda_{\rm S}k_{\rm B}T}}$$

$$\times \sum_{m} \left\{ \frac{S^m \exp(-S)}{m!} \exp\left[-\frac{(\lambda_{\rm S} + m\hbar\omega + \Delta G_{\rm CS})^2}{4\lambda_{\rm S}k_{\rm B}T}\right] \right\}$$
(3)



Fig. 3 Free energy gap dependence of the charge separation rate $k_{\rm CS}$ of a series of nine Cz–S–A molecules in various solvents: square DBE; triangle MTHF; circle MeCN. Solid lines is the theoretical prediction calculated by using eqn. (3) with the following parameters: $\lambda_{\rm V} = 0.56 \text{ eV}$, $V = 5.8 \text{ cm}^{-1}$, $\hbar\omega = 1300 \text{ cm}^{-1}$. Broken line is the theoretical prediction of the rate $k_{\rm CS}$ in DBE calculated by using eqn. (2) with the same parameters.

The free energy gap for the photoinduced CS $(-\Delta G_{\rm CS})$ and reorganization energy for solvent $(\lambda_{\rm S})$ were calculated by eqn. (4) and (5), respectively,

$$-\Delta G_{\rm CS} = E(S_1) - (E_{\rm ox}^{\rm ox} - E_{\rm red}^{\rm A}) + \frac{e^2}{4\pi\varepsilon_0} \left\{ \frac{1}{\varepsilon_{\rm S} r_{\rm DA}} + \frac{1}{2} \left(\frac{1}{r_{\rm D}} + \frac{1}{r_{\rm A}} \right) \left(\frac{1}{37.5} - \frac{1}{\varepsilon_{\rm S}} \right) \right\}$$
(4)
$$\lambda_{\rm S} = \frac{e^2}{4\pi\varepsilon_0} \left(\frac{1}{2r_{\rm D}} + \frac{1}{2r_{\rm A}} - \frac{1}{r_{\rm DA}} \right) \left(\frac{1}{\varepsilon_{\infty}} - \frac{1}{\varepsilon_{\rm S}} \right)$$
(5)

where e is the elementary charge, ε_0 the vacuum permittivity, ε_S dielectric constant of the matrix, r_{DA} separation distance between donor (Cz) and acceptor (A) (12.2 Å), $r_{\rm D}$ and $r_{\rm A}$ spherical radii of donor and acceptor moieties (4.5 and 3.7 Å), respectively, and ε_{∞} optical dielectric constant of the matrix, which is equal to the square of the refractive index of the matrix n^2 . In the ε_s range from 3.06 (DBE) to 37.5 (MeCN), as shown in Fig. 3, $k_{\rm CS}$ increased with increasing $-\Delta G_{\rm CS}$, indicating that CS is in the normal region of the Marcus theory. In a non-polar solvent such as Hex, CS was not observed except for DEF, NO₂, and 2NO₂ with large $-\Delta G_{CS}$. This finding indicates that CS in solutions is promoted by the orientational fluctuations of polar solvents. The Marcus plots of k_{CS} of Cz–S–A in various solvents were well explained by eqn. (3) rather than eqn. (2) with the following parameters: the electronic coupling matrix element $V = 5.8 \text{ cm}^{-1}$, the reorganization energy for intramolecular vibration of Cz–S–A molecules $\lambda_V = 0.56 \text{ eV}$, and the vibrational energy $\hbar\omega = 1300 \text{ cm}^{-1.18-21}$ Thus, we conclude that intramolecular CS in solutions results from vibrational motion of Cz-S-A molecules as well as classical solvent motions.

3.3. Temperature dependence of photoinduced CS in MTHF

The CS rate depends on both dielectric constant $\varepsilon_{\rm S}$ of the matrix and temperature. As shown by eqn. (4) and (5), both $\lambda_{\rm S}$ and $-\Delta G_{\rm CS}$ decrease with the decrease in $\varepsilon_{\rm S}$, but $\lambda_{\rm S} + \Delta G_{\rm CS}$ is independent of $\varepsilon_{\rm S}$. Thus, $k_{\rm CS}$ should decrease with the decrease

Table 2 Fluorescence lifetime and CS rate constant of Cz-S-A molecules in MeCN at room temperature

A moieties	EtCz	CF_3	5F	Cin	$2CF_3$	TP	CN	DEF	NO_2	$2NO_2$
τ/ns	15.0	12.3	14.0	9.0	8.6	6.0^{a}	4.2^{a}	2.4 ^{<i>a</i>}	0.26 ^a	0.20^{a}
$\log k_{CS}^{b}$		7.2	6.7	7.6	7.7	8.0	8.2	8.6	9.6	9.7



Fig. 4 Upper: temperature dependence of dielectric constant $\varepsilon_{\rm S}$ of MTHF.²² Bottom: $k_{\rm CS}$ of Cz–S–Cin (3) (closed circles) and Cz–S–CN (6) (open circles) in MTHF. Temperature range of the measurements was from 183 to 296 K. Broken and solid curves are the theoretical prediction calculated by using eqn. (2) and (3), respectively, with the following parameters: $\lambda_{\rm V} = 0.56$ eV, V = 5.8 cm⁻¹, $\hbar\omega = 1300$ cm⁻¹.

in ε_{S} at a temperature. On the other hand, k_{CS} should increase with increasing temperature at a fixed dielectric constant. In the temperature range from 183 to 296 K, as shown in Fig. 4, k_{CS} of Cz-S-Cin and Cz-S-CN in MTHF gradually increased with increasing temperature while dielectric constant ε_S of MTHF decreased with increasing temperature.²² This shows that thermal activation of the intramolecular $k_{\rm CS}$ in a solution is governed by temperature rather than ε_{S} of solvents. Broken and solid lines in the figure are the theoretical prediction calculated by eqn. (2) and (3), respectively. The temperature dependence of $k_{\rm CS}$ was well reproduced by eqn. (3) but not by the classical ET theory (eqn. (2)). These findings shows that the intramolecular CS of Cz-S-A in a solution is thermally activated mainly by orientational motions of a polar solvent but intramolecular vibrational motions of the reactants also contribute to the activation.

3.4. Free energy gap dependence of photoinduced CS in a polymer solid

Next, we investigated the intramolecular CS in a polymer solid where orientational fluctuations of polar groups are highly restricted compared with those in a solution. Owing to inhomogeneity of polymer solids, the fluorescence decay I(t) of Cz-S-A in a polymer solid was well fitted with a sum of three exponential functions: $I(t) = \sum A_i \exp(t/-\tau_i)$. Since lifetime of the minor component (less than 5%) is ascribable to a Cz molecule having no A molety, the CS rate constant $k_{\rm CS}$ was calculated by $k_{\rm CS} = \langle \tau \rangle^{-1} - \tau_0^{-1}$ where τ_0 is the fluorescence lifetime of EtCz and $\langle \tau \rangle$ the average of major two components in the fluorescence lifetime of Cz-S-A. Fig. 5 shows Marcus plots of a series of five Cz-S-A molecules in CN-HPC films at room temperature. As in a solution system, k_{CS} increased with increasing $-\Delta G_{\rm CS}$. Although the free energy dependence of $k_{\rm CS}$ was roughly explained by eqn. (3) with the same parameters as those for a solution system, it was reproduced better with $V = 3.5 \text{ cm}^{-1}$ smaller than that for a solution system (5.8 cm^{-1}). This is probably because the mean separation distance between Cz and A moieties in a solution is shorter than that in a polymer solid because the conformational change in a solution is so rapid that the mean separation distance effectively decreases in the time scale of the photoinduced CS. The CN-HPC polymer has a polar cyano group at the end of the side chain and has a glass transition temperature (T_g) of 248 K. Thus, there exist rotational motions of polar



Fig. 5 Free energy gap dependence of the charge separation rate $k_{\rm CS}$ of a series of five Cz–S–A molecules in CN-HPC films at room temperature: Cz–S–Cin (3), Cz–S–2CF₃ (4), Cz–S–TP (5), Cz–S–CN (6), and Cz–S–2NO₂ (9). The solid curve is the theoretical prediction calculated by using eqn. (3) with the following parameters: $\lambda_{\rm V} = 0.56$ eV, V = 3.5 cm⁻¹, $\hbar\omega = 1300$ cm⁻¹. Dielectric constant of CN-HPC was measured at 1 MHz.

groups at room temperature above the T_g sufficient to fluctuate the energy of the D–S–A system, which leads to ET.

3.5. Temperature dependence of photoinduced CS in a polymer solid

As mentioned in the previous section, the fluorescence decay of Cz–S–A in a polymer solid was well fitted with a three exponential function. Fig. 6 shows the temperature dependence of the lifetime τ_i of each fraction of Cz–S–CN over a temperature range from 100 to 400 K. One of them (open circles) was independent of temperature and the lifetime was similar to that of Cz–12–Cz. This fraction represented less than 5% of the whole. Thus, this minor component was ascribed to a Cz molecule having no A moiety. The lifetime of the other two components decreased above T_g . A similar tendency was observed for the other Cz–S–A dyads. Here we calculated the averaged lifetime $\langle \tau \rangle$ of Cz–S–A from the major two components.

The relaxation time of rotational motions of polar groups in polymer solids varies widely. Consequently, it is difficult to evaluate ε_S of polymer solids: the dielectric constant of polymer solids significantly depends on the measuring frequency. Fig. 7 shows the temperature dependence of dielectric constant ε evaluated by dielectric relaxation measurement. The value of



Fig. 6 Temperature dependence of the lifetime τ_i of each fraction in the decay analysis for Cz–S–CN (6). Open circles are the minor fraction in the three decay components, being less than 5%. This fraction was neglected in the lifetime evaluation: see text.



Fig. 7 Top: temperature dependence of the dielectric constant ε of CN–HPC films over the temperature range from 77 to 380 K. Broken and solid lines are the dielectric constants ε measured by dielectric relaxation measurement at a frequency of 20 Hz (broken) and 1 MHz (solid). Bottom: temperature dependence of the charge separation rate $k_{\rm CS}$ of Cz–S–2CF₃ in CN-HPC films over the temperature range from 100 to 400 K. Broken and solid lines are the theoretical prediction of $k_{\rm CS}$ calculated by using eqn. (3) with dielectric constants ε evaluated by dielectric relaxation measurement at a frequency of 20 Hz (broken) and 1 MHz (solid). Thick line is calculated by eqn. (6) with following parameters: $S_{\rm L}\hbar\omega_{\rm L} = 0.31$ eV, $S_{\rm H}\hbar\omega_{\rm H} = 0.56$ eV, V = 3.5 cm⁻¹, $\hbar\omega_{\rm H} = 1300$ cm⁻¹, $\hbar\omega_{\rm L} = 500$ cm⁻¹, $\varepsilon = 3.11$.

 ε was nearly constant from 100 to 248 K and steeply increased at 248 K, which corresponds to the $T_{\rm g}$. As mentioned above, ε depends on the measuring frequency: ε measured at 20 Hz was larger than that at 1 MHz.

Broken and solid lines in Fig. 7 show the theoretical prediction of $k_{\rm CS}$ calculated by eqn. (3) with the ε measured at 20 Hz and 1 MHz, respectively. Above the $T_{\rm g}$, temperature dependence of $k_{\rm CS}$ was well reproduced by the solid line (1 MHz) rather than the broken line (20 Hz). This is because CS occurred in the time domain from sub-nanoseconds to a hundred nanoseconds, which corresponds to 10 to 100 MHz in the frequency domain. In other words, the slow motion of a polar group in a polymer solid does not contribute to ET but the fast motion of a polar group effectively causes ET. This finding shows that a variety of motions of polar groups in polymer solids allow ET although most of the motions are restricted compared with those in a solution.

Below the T_{g} , k_{CS} was nearly constant and independent of temperature whereas the theoretical prediction by eqn. (3) monotonously decreased with decreasing temperature. The single-mode formula of eqn. (3) treats orientational motions of polar groups as a classical mode and vibrational motions of the reactant molecule as a quantum one. The classical mode results in temperature dependence of the Arrhenius type. Thus, this deviation shows that the classical mode has no contribution any more to intramolecular CS in a polymer solid. In fact, ε was nearly constant below the $T_{\rm g}$, indicating that most orientational motions of polar cyano groups are frozen. It is worthwhile to note that ET still occurs even below T_g where orientational motions of polar groups are highly restricted. This tendency is similar to ET in the photosynthetic bacterium Chromatium.^{23,24} In the low temperature range, ET is probably caused by a high-frequency quantum mode such as vibrational motions of the reactant molecule or the polar cyano groups of the polymer matrix. These high-frequency motions cause ET by nuclear tunneling, which is independent of temperature.^{16,17} The thick line in Fig. 7 is calculated by eqn. (6) with a dielectric constant of 3.11.

$$k_{QQ} = \frac{2\pi}{\hbar} |V|^2 FC_{QQ}$$

$$FC_{QQ} = \frac{\exp[-S_L(2n_L+1) - S_H(2n_H+1)]}{\hbar\omega_L}$$

$$\times \sum_m \left(\frac{n_L+1}{n_L}\right)^{\frac{p(m)}{2}} I_{|p(m)|} \left\{ 2S_L \sqrt{n_L(n_L+1)} \right\}$$

$$\times \left(\frac{n_H+1}{n_H}\right)^{\frac{m}{2}} I_{|m|} \left\{ 2S_H \sqrt{n_H(n_H+1)} \right\}$$

$$n_L = \left[\exp\left(\frac{\hbar\omega_L}{k_BT}\right) - 1 \right]^{-1}, n_H = \left[\exp\left(\frac{\hbar\omega_H}{k_BT}\right) - 1 \right]^{-1},$$

$$p(m) = -\frac{\Delta G_{CS} + m\hbar\omega_H}{\hbar\omega_L}$$
(6)

The theoretical line well reproduced temperature independent of $k_{\rm CS}$ observed below T_g . Another possibility is that ET may be no longer in thermal equilibrium at low temperatures, because the relaxation time of most orientational motions of polar groups is longer than the lifetime of D–S–A molecules in the excited state. The non-thermal equilibrium ET also could result in temperature independent ET at low temperatures.^{10,11} Although both situations are possible for ET in a polymer solid, the former is probably the major cause of the temperature independence of $k_{\rm CS}$ because there are some polar groups with motions fast enough to cause ET even in a polymer solid, which are probably in the thermal equilibrium.

4. Conclusions

Photoinduced CS of carbazole-acceptor dyads (Cz-S-A) in solutions is caused by not only classical solvent motions but also vibrational motions of the reactant. The temperature dependence of CS in solutions results from mainly classical solvent motions but also the quantum vibrational motions over a wide temperature range. These results could be quantitatively explained by a single quantum mode ET formula. As for the photoinduced ET in a polymer solid, the CS of Cz-S-A was also observed over a wide temperature range although most motions are highly restricted compared with those in a solution. Above T_g , CS was explained with dielectric constants at a high frequency by the same ET formula as that in a solution. Below T_{g} , CS was independent of temperature, indicating that ET is caused by nuclear tunneling. We conclude that these features of ET in a polymer solid are due to the presence of a variety of motions over a wide time domain.

Acknowledgements

This work was supported by the Murata Science Foundation and the Takeda Science Foundation. We would like to thank Professor Takeaki Miyamoto and Associate Professor Yoshinobu Tsujii for provision of CN-HPC and DSC measurement of CN-HPC and Dr Yasuo Kita for dielectric relaxation measurement of CN-HPC.

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