Exciplex Emission of Carbazole–Terephthalate Cyclophane and Its Application as a Fluorescent Probe for Local Polarity of Solvents

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Photophysical properties of carbazole–terephthalate cyclophane (Cz–TP) were studied. The absorption spectra of Cz–TP in various solvents were slightly broadened due to the distortion of the carbazole (Cz) moiety and became similar to that of a reference compound of carbazole–benzene cyclophane (Cz–Bz). The absorption spectrum and the peak wavelengths of Cz–TP were insensitive to the solvent polarity. These findings show that there is transannular π–π electronic interaction between the Cz and TP moieties but that the charge transfer interaction from the Cz to TP moieties is small in the ground state. On the other hand, the emission spectrum was broad, structureless, and red-shifted compared with that of the reference compound. The peak wavelength of the emission was shifted to a longer wavelength with increases in the dielectric constant of solvents. The peak shift was quantitatively explained by the Lippert–Mataga formula. Therefore, we conclude that the broad emission is due to the intramolecular exciplex in Cz–TP. The dielectric constant of 2-methyl tetrahydrofuran was evaluated from the exciplex emission of Cz–TP ranging from 77 to 292 K, indicating that the Cz–TP molecule is an excellent polarity probe not only in a liquid phase but also in a solid phase over a wide temperature range.

Since the first report on an exciplex of perylene–*N*,*N*-dimethylaniline in non-polar solvents,[1] much attention has been focused on the electronic state and geometrical structures of exciplexes. Intramolecular donor (D) and acceptor (A) systems provide much information about the dynamics of exciplex formation as well as about the electronic state and geometrical requirements. In particular, the intramolecular exciplex of D–$(CH_2)_n$–A systems where D and A are linked by a flexible polymethylene bridge has been extensively investigated.[2–5] A twisted intramolecular charge transfer (TICT) state is observed for the D–A ($n = 0$) system.[6,7] On the other hand, a face-to-face sandwich structure is formed in the D–$(CH_2)_n$–A molecules with longer methylene chains. Even in these bridged systems, the attainable exciplex conformation depends on a polarity, viscosity, and temperature of media, and also on the structure and flexibility of the bridge itself.[8–11] Conformational changes in the flexibly bridged D–$(CH_2)_n$–A systems inevitably lead to uncertainty of the geometrical structure of the exciplex. Rigid systems with well-defined geometries of D and A are desirable to avoid these conformational complexities of a flexible bridge.

Paracyclophanes have a unique structure in which two aromatic rings are aligned in parallel face-to-face orientations by the para bridging with methylene groups. In particular, [2.2]paracyclophane[12,13] is so rigid that there is no conformational change in the ground and excited states over wide viscosity and temperature ranges. Owing to these characteristics, various [2.2]paracyclophanes such as paracyclophane, naphthalenophane,[14] anthracenophane, pyrenophane,[15] and phenanthrenophane[16] have been used as model compounds for studying electronic interactions in the ground and excited states. Most of them have the same two aromatic moieties and are used as a model for excimers. On the other hand, although there are fewer reports on mixed cyclophanes containing D and A moieties, various interesting compounds have been prepared.[17–19] They are suitable model compounds for studying the photophysical properties of charge transfer (CT) complexes and exciplexes, based on the separation and orientation of D and A moieties.

Here we studied the exciplex properties of carbazole–terephthalate cyclophane (Cz–TP)[20] whose geometrical alignments are clearly defined: Cz–TP has a structure with a symmetrical face-to-face conformation. The photophysical properties of Cz–TP were compared with those of an intermolecular system of *N*-ethylcarbazole and dimethyl terephthalate (EtCz/DMTP) and intramolecular systems of Cz–$(CH_2)_n$–TP.[21–23] We also demonstrate the functionality of Cz–TP as a fluorescence polarity probe: local polarity of a solvent was quantitatively evaluated over a wide temperature range by using the polarity probe of the Cz–TP molecule.

Experimental

1. Materials. Cyclophanes and Reference Compounds: Carbazole–terephthalate cyclophane (Cz–TP)[20] and carbazole–benzene cyclophane (Cz–Bz)[24] were synthesized by photodeselenation of the corresponding selenacarbazolophanes. Details of the synthesis have been described elsewhere.[20,24] *N*-Ethyl-3,6-dimethylcarbazole (DMeCz) was synthesized by the reduction of 3,6-bis(bromomethyl)-*N*-ethylcarbazole with $NaBH_4$. 3-(*N*-Carba-

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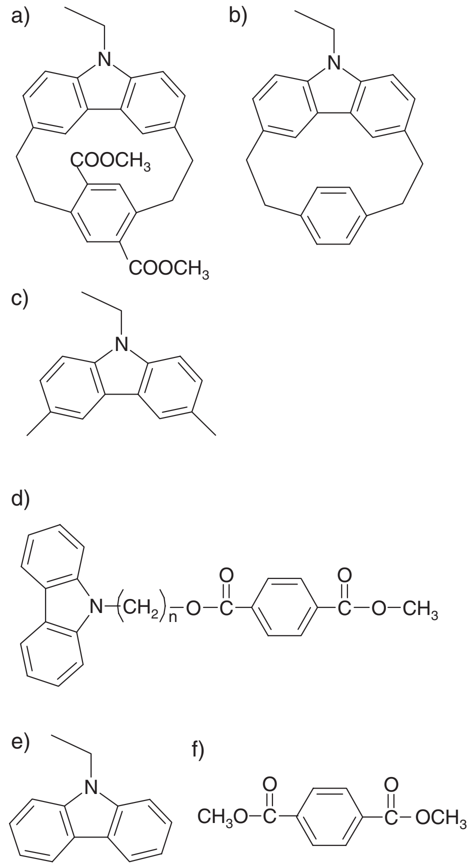

Fig. 1. Chemical structures of intra- and intermolecular exciplex systems used in this study: a) carbazole–terephthalate cyclophane (Cz–TP); b) carbazole–benzene cyclophane (Cz–Bz); c) *N*-ethyl-3,6-dimethylcarbazole (DMeCz); d) flexibly-linked intramolecular compounds (Cz–$(CH_2)_n$–TP); e) *N*-ethylcarbazole (EtCz); f) dimethyl terephthalate (DMTP).

zolyl)propyl methyl terephthalate (Cz–$(CH_2)_3$–TP) and 5-(*N*-carbazolyl)pentyl methyl terephthalate (Cz–$(CH_2)_5$–TP) were used as an intramolecular exciplex system where Cz and TP are flexibly linked by the propane or pentane chain. Details of the syntheses have been described elsewhere.[21–23] *N*-Ethylcarbazole (EtCz, Wako) and dimethyl terephthalate (DMTP, Wako) were purified by repeated recrystallization from hexane and from methanol, respectively. The chemical structures of these compounds are shown in Fig. 1.

Solvents: The following solvents were used for the measurements: hexane (Nacalai Tesque, spectroscopic grade), cyclohexane (Nacalai Tesque, spectroscopic grade), 1,4-dioxane (Wako, spectroscopic grade), dibutyl ether (Wako, spectroscopic grade), dipropyl ether (Wako, guaranteed grade), diethyl ether (Nacalai Tesque, spectroscopic grade), butyl acetate (Nacalai Tesque, spectroscopic grade), ethyl acetate (Nacalai Tesque, spectroscopic grade), tetrahydrofuran (THF, Nacalai Tesque, spectroscopic grade), ethyl methyl ketone (Nacalai Tesque, spectroscopic grade), acetone (Nacalai Tesque, spectroscopic grade), *N*,*N*-dimethylformamide (DMF, Wako, spectroscopic grade), and acetonitrile (Nacalai Tesque, spectroscopic grade). 2-Methyltetrahydrofuran (MTHF, Tokyo Kasei) was dried with solid KOH, passed through freshly activated alumina, and then distilled from CaH_2 with 2,6-di-*t*-butyl-*p*-cresol before use. All other solvents were used without further purification.

2. Measurements. The concentration of chromophores was adjusted to the order of 10^{-4} mol L^{-1} to prevent intermolecular processes. For EtCz/DMTP intermolecular system, the concentration was adjusted to the order of 10^{-4} mol L^{-1} for EtCz and 10^{-2} mol L^{-1} for DMTP. Sample solutions were degassed in 1-cm quartz cells by several freeze–pump–thaw cycles or by Ar bubbling for 30 min. Measurements of the solution samples at low temperatures were carried out by immersing the sample cell into isopentane precooled by liquid nitrogen in a quartz Dewar equipped with a thermocouple. Absorption and emission spectra were measured with a spectrophotometer (Hitachi, U-3500) and a calibrated fluorescence spectrophotometer (Hitachi, F-4500), respectively. For steady state fluorescence measurements, samples were excited at 295 nm for DMeCz, at 310 nm for Cz–Bz, and at 310 or 350 nm for Cz–TP. Fluorescence decay was measured by the time-correlated single-photon-counting method. Excitation of samples was carried out using the generated third-harmonic pulses (295 nm) of an Ar^+–Ti:sapphire laser. Details have been described elsewhere.[25]

Results and Discussion

Absorption and Fluorescence Spectra. Figure 2 shows the absorption spectra of Cz–TP and reference compounds of DMeCz and Cz–Bz in a THF solution at room temperature. The absorption bands of Cz–TP around 310 and 350 nm were assigned to the $^1L_a \leftarrow {}^1A$ and $^1L_b \leftarrow {}^1A$ transitions of the Cz moiety, respectively, compared with those of DMeCz. Both bands were broadened and the ^1L_a band was red-shifted. These spectral changes were also observed for Cz–Bz, which has a Bz moiety in place of the TP moiety. In both cyclophanes, the Cz ring is bent owing to [2.2]linkage while TP and Bz ring maintain the planarity.[20,24] Thus, the broadening and red-shift are considered to be mainly due to the distortion of Cz moiety by tight cyclic conformation and transannular π–π electronic interaction between Cz and the other aromatic ring.[20,24]

Figure 3 shows absorption spectra of Cz–TP in various sol-

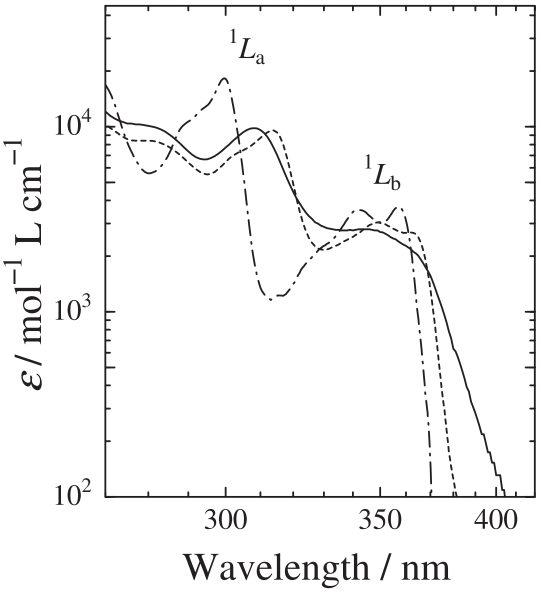

Fig. 2. Absorption spectra of Cz–TP (solid line), Cz–Bz (broken line), and DMeCz (dashed–dotted line) in a THF solution at room temperature.

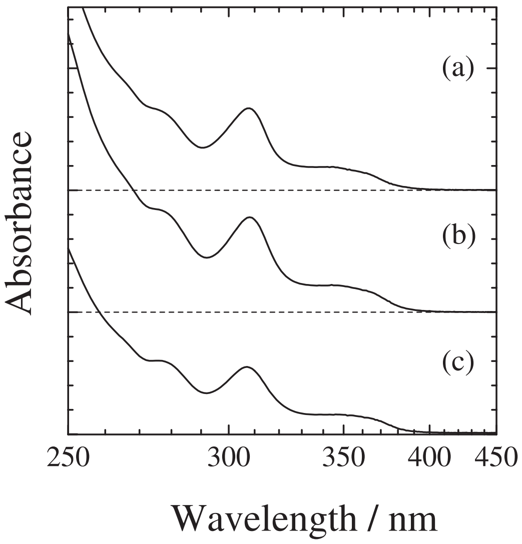

Fig. 3. Absorption spectra of Cz–TP in various solvents with different polarities at room temperature. (a) hexane $\mathcal{E}_S = 1.89$, (b) THF $\mathcal{E}_S = 7.58$, (c) acetonitrile $\mathcal{E}_S = 37.5$. Absorbance was normalized.

vents with different polarity: hexane ($\mathcal{E}_S = 1.89$), THF ($\mathcal{E}_S = 7.58$), and acetonitrile ($\mathcal{E}_S = 37.5$). Absorption spectra of Cz–TP were insensitive to the solvent polarity. This indicates that CT interaction in the ground state is small even in the Cz–TP molecule, where the electron donor Cz moiety and the electron acceptor TP moiety are arranged in a face-to-face conformation. The EtCz/DMTP intermolecular system also shows little interaction between EtCz and DMTP in the ground state.[21] The stabilization of a CT complex depends on the ionization potential of the donor (I_D) and the electronic affinity of the acceptor (E_A), which are linearly related to the oxidation potential of the donor $E_D{}^{ox}$ and reduction potential of the acceptor $E_A{}^{red}$, respectively.[26] In other words, CT complexes are more stable as the difference between $E_D{}^{ox}$ and $E_A{}^{red}$ decreases. The representative value of $E_D{}^{ox} - E_A{}^{red}$ is at most 2.5 V for intermolecular CT complexes formed in aromatic D and A pairs.[26–28] In contrast, the $E_D{}^{ox} - E_A{}^{red}$ of EtCz and DMTP pair is as large as 2.87 V: $E_D{}^{ox}$ of EtCz is 1.12 V[29] and $E_A{}^{red}$ of DMTP is -1.75 V.[21] Owing to the large difference of $E_D{}^{ox} - E_A{}^{red}$, EtCz and DMTP cannot form a stable CT complex in the ground state intermolecularly. Consequently, it can be safely said that the small CT nature of Cz–TP is also due to the large difference of $E_D{}^{ox} - E_A{}^{red}$.

On the other hand, as shown in Fig. 4, the emission spectra were broad, structureless, and red-shifted compared with those of the references of DMeCz and Cz–Bz. The excitation spectrum for the broad emission was identical with the absorption spectrum of Cz–TP. Figure 5 shows emission spectra of Cz–TP in various solvents at room temperature. The peak wavelength of the broad emission band was shifted to longer wavelengths with increases in the dielectric constant of solvents. This red-shift of the peak wavelength is due to the stabilization of the polar excited state by solvent–solute dipole–dipole interactions. In polar solvents, the emission intensity decreased with increasing solvent polarity. Fluorescence quantum yields of Cz–TP in solvents are summarized in Table 1. Fluorescence

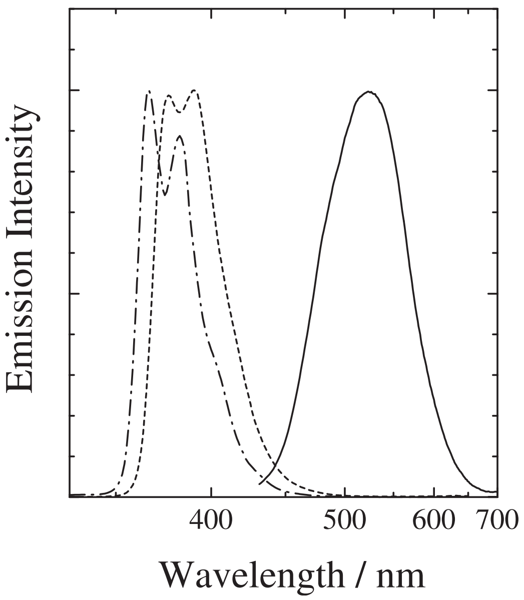

Fig. 4. Emission spectra of Cz–TP (solid line), Cz–Bz (broken line), and DMeCz (dashed–dotted line) in a THF solution at room temperature. Emission intensity was normalized.

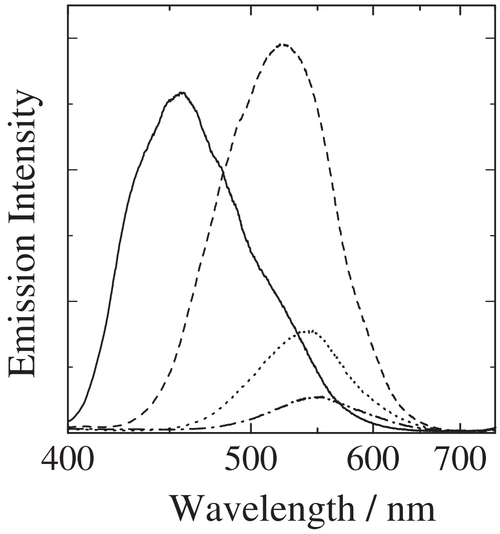

Fig. 5. Exciplex emissions of Cz–TP in various solvents with different polarities: cyclohexane (solid line); THF (broken line); acetone (dotted line); acetonitrile (dashed–dotted line), at room temperature.

Table 1. Fluorescence Quantum Yields of Cz–TP Exciplex Emission in Various Solvents with Different Polarities: Cyclohexane ($\mathcal{E}_S = 2.02$), THF ($\mathcal{E}_S = 7.58$), Acetone ($\mathcal{E}_S = 20.7$), and Acetonitrile ($\mathcal{E}_S = 37.5$) at Room Temperature

	Cyclohexane	THF	Acetone	Acetonitrile
Φ_f[a)]	0.018	0.024	0.0050	0.0016

a) Solutions were prepared through Ar bubbling for 30 min.

Table 2. Peak Wavelength $\lambda_{\max}$ and Peak Shift $\Delta\tilde{\nu}$ of Exciplex Fluorescence from EtCz/DMTP, Cz–$(CH_2)_n$–TP ($n = 3, 5$), and Cz–TP Measured in a THF Solution at Room Temperature and Dipole Moments in the Excited State μ_e

	EtCz/DMTP	Cz–$(CH_2)_n$–TP		Cz–TP
		$n = 3$	$n = 5$	
$\lambda_{\max}$/nm	510[a)]	503[a)]	510[a)]	524
$\Delta\tilde{\nu}$/cm^{-1}	9290[b)]	9110[b)]	9380[b)]	9900[b)]
μ_e/D	16.4	16.1	16.1	13.6

a) Taken from Ref. 21. b) $\Delta\tilde{\nu} = \tilde{\nu}_{abs} - \tilde{\nu}_e$ where $\tilde{\nu}_{abs}$ is peak wavenumber of the ^1L_b bands of EtCz (28900 cm^{-1}), Cz–$(CH_2)_n$–TP (28990 cm^{-1}), and Cz–TP (29070 cm^{-1}).

Table 3. Lifetime τ of the Exciplex Emission in a MTHF Solvent at Room Temperature

	EtCz/DMTP	Cz–$(CH_2)_n$–TP				Cz–TP
		$n = 1$	$n = 2$	$n = 3$	$n = 5$	
τ/ns[a)]	24.4	9.8[b)]	21.3[b)]	31.4	37.4	35.1

a) Excitation wavelength was 295 nm for all samples except for $n = 1$ and $n = 2$. Monitor wavelengths were 520 nm for EtCz/DMTP, 510 nm for $n = 3$, 520 nm for $n = 5$, and 515 nm for Cz–TP. b) Taken from Ref. 22.

quantum yields decreased with increasing solvent polarity. This is due to the energy gap between the fluorescent excited state and the ground state being smaller in more polar solvents, which leads to the increase in the rate of the internal conversion from the excited state to the ground state. These results show that the Cz–TP molecule has a large dipole moment in the excited state. As shown in Table 2, the peak wavelength $\lambda_{\max}$ and the peak shift $\Delta\tilde{\nu}$ of the Cz–TP emission in a THF solution at room temperature were in good agreement with those of the intermolecular exciplex of EtCz/DMTP as well as intramolecular exciplex of Cz–$(CH_2)_n$–TP ($n = 3, 5$).[21] The broad emission of Cz–TP was observed even in such a dilute concentration that the intermolecular exciplex of EtCz/DMTP could not be observed. Therefore, we conclude the broad emission band of Cz–TP should be ascribed to the intramolecular exciplex formed between the Cz and TP moieties in the cyclophane.

The solvent polarity dependence can be quantitatively described by the Lippert–Mataga[30–33] formula (Eq. 1) where $\tilde{\nu}_e$ is the wavenumber of emission maximum, $\tilde{\nu}_0$ corresponds to the emission maximum in the gas phase, ε_0 is the vacuum permittivity, h is the Planck constant, c is the velocity of the light, ρ is the radius of a spherical solute, μ_e is the dipole moment of the solute in the excited state, ε_S is the dielectric constant of the solvent, and n is the refractive index of the solvent.

$$\begin{aligned} \tilde{\nu}_e &= \tilde{\nu}_0 - \frac{1}{4\pi\varepsilon_0}\frac{2}{hc\rho^3}\mu_e^2 f(\varepsilon_S, n) \\ f(\varepsilon_S, n) &= \left(\frac{\varepsilon_S - 1}{2\varepsilon_S + 1} - \frac{1}{2}\frac{n^2 - 1}{2n^2 + 1}\right) \end{aligned} \tag{1}$$

As shown in Fig. 6a, the Lippert–Mataga plots of exciplex emission for the Cz–TP molecule agreed well with the line calculated by Eq. 1 over a wide solvent polarity range. In some cases, the solvent-induced change of electronic states and geometrical structure of the exciplex have been reported.[11,19,34] However, those solvent-induced changes should be negligible for our cyclophane owing to the rigid structure that prevents large conformational changes in the ground and excited states. From the Lippert–Mataga plots, the dipole moment μ_e of Cz–TP in the excited state was evaluated to be 13.6 D with a radius of 5 Å; this was estimated from the molecular structure determined by X-ray analysis.[20,24] These findings show that the exciplex of Cz–TP maintains a polar electronic structure even in nonpolar solvents.

Figures 6b, 6c, and 6d show the Lippert–Mataga plots for the intermolecular exciplex of EtCz/DMTP[21] and the intramolecular exciplexes of Cz–$(CH_2)_n$–TP ($n = 3, 5$).[21] The excited state dipole moments μ_e obtained from the Lippert–Mataga analysis are summarized in Table 2. The radius ρ was assumed to be 5 Å, which is the same value as that of Cz–TP. The dipole moments in the excited state were evaluated to be about 16 D for both the intermolecular exciplex of EtCz/DMTP and the intramolecular exciplexes of Cz–$(CH_2)_n$–TP ($n = 3, 5$). For both inter- and intramolecular systems, the data were fitted to the Lippert–Mataga plots by Eq. 1 over a wide solvent polarity range. This indicates that the solvent-induced change is also negligible for the exciplex of EtCz/DMTP. The dipole moment of Cz–TP in the excited state is slightly smaller than those of the inter- and intramolecular systems. This difference is probably because geometrical alignment of the Cz and TP rings in Cz–TP slightly deviates from a parallel conformation and because the distance between the Cz and TP rings is short owing to the [2.2]linkage. Exciplexes formed in the inter- and intramolecular systems might have a more stable structure owing to lack of restrictions.

It is noteworthy that a large red-shift was observed for the emission spectra of Cz–TP in 1,4-dioxane. As shown in Fig. 6, solid circles deviate from the straight line calculated

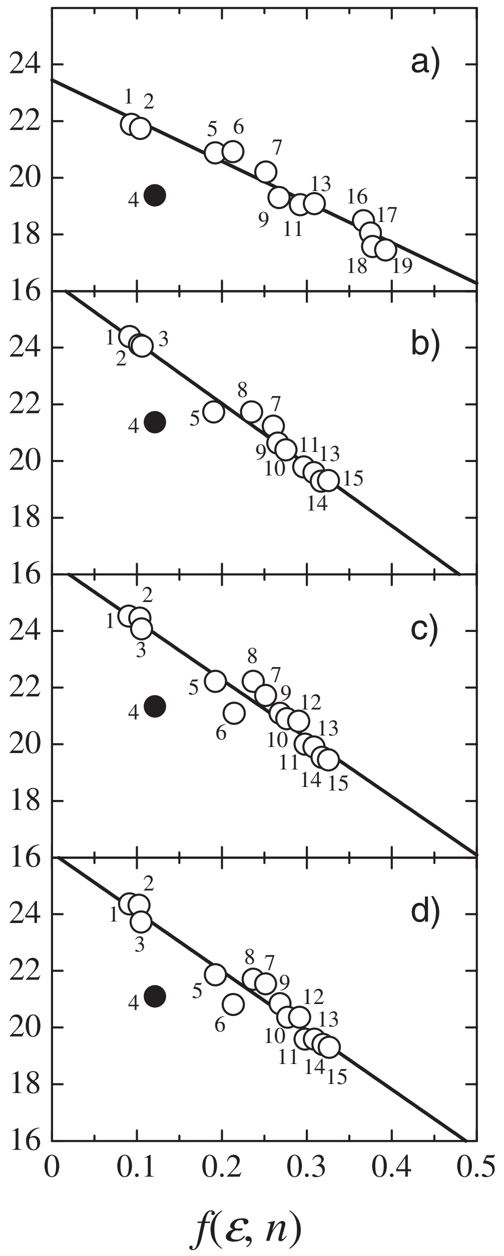

Fig. 6. Lippert–Mataga plots of exciplex emissions from each compound at room temperature: a) Cz–TP, b) intermolecular system of EtCz/DMTP, c) intramolecular system of Cz–$(CH_2)_3$–TP, d) Cz–$(CH_2)_5$–TP. Solid lines are fitted to the data with Eq. 1 by the least-squares method. The data for a 1,4-dioxane (solid circles) were excluded from this analysis. Solvents: (1) hexane, (2) cyclohexane, (3) decahydronaphthalene, (4) 1,4-dioxane, (5) dibutyl ether, (6) dipropyl ether, (7) diethyl ether, (8) diisopropyl ether, (9) butyl acetate, (10) tetrahydropyrane, (11) ethyl acetate, (12) MTHF, (13) THF, (14) dichloromethane, (15) 1,2-dichloroethane, (16) ethyl methyl ketone, (17) acetone, (18) DMF, (19) acetonitrile.

from Eq. 1. This deviation reflects the fact that the microscopic polarity in 1,4-dioxane is larger than a macroscopic dielectric constant of $\varepsilon_S = 2.2$. It has been reported that these polar exciplexes interact with a large dipole moment of the C–O–C unit in a 1,4-dioxane molecule, although the total dipole moment is canceled out by the symmetrical two C–O–C units in the same ring.[35,36] This finding proves that our cyclophane is also sensitive to microscopic polarity.

Fluorescence Decay Measurements. To examine the electronic state of the exciplex, we measured the fluorescence decay of EtCz/DMTP intermolecular and Cz–$(CH_2)_n$–TP, Cz–TP intramolecular exciplex in a MTHF solution. No fluorescence rise was observed for either Cz–TP or Cz–$(CH_2)_3$–TP and the rise was negligible for Cz–$(CH_2)_5$–TP within the excitation laser pulse (an instrument response function of ca. 780 ps).[25] On the other hand, time evolution of exciplex emission from EtCz/DMTP intermolecular system showed a rise during several nanoseconds after laser excitation. These results indicate that the exciplex emissions of the Cz–TP and Cz–$(CH_2)_n$–TP are due to not intermolecular but to intramolecular exciplex formation. The fluorescence lifetime of Cz–TP observed at 515 nm was 35.1 ns; this was compared with the lifetimes of exciplex systems as listed in Table 3. The lifetime of the Cz–TP exciplex was similar to those of the intermolecular exciplex of EtCz/DMTP and the intramolecular exciplex of Cz–$(CH_2)_n$–TP ($n = 3$, 5), but it is longer than that of Cz–$(CH_2)_n$–TP ($n = 1$, 2).[22] The long lifetime of the Cz–TP exciplex shows a large CT nature in the excited state, which causes the decrease in the transition dipole moment of the Cz–TP exciplex. The large CT interaction in the excited state is probably due to the compact structure of Cz–TP, where Cz and TP are aligned in a sandwich conformation. The long lifetimes of the inter- and intramolecular systems also suggest that these exciplexes take a face-to-face sandwich structure, similar to that of Cz–TP. On the other hand, the shorter lifetime of the intramolecular Cz–$(CH_2)_n$–TP ($n = 1$, 2) system indicates that the CT nature in the excited state is smaller than that in other systems because Cz–$(CH_2)_n$–TP ($n = 1$, 2) are unlikely to take a sandwich-like compact conformation in the excited state owing to geometrical restriction by short methylene chains.

Evaluation of Dielectric Constant of MTHF over a Wide Temperature Range. Exciplex fluorescence of Cz–TP in MTHF was measured from 140 to 292 K where MTHF is a fluid and at 77 K where MTHF is a glassy solid. As shown in Fig. 7, the peak wavelength of the exciplex emission shifted from 547 to 516 nm with increasing temperature. From Fig. 5 or 6, this continuous blue-shift of exciplex emission indicates that polarity of MTHF decreases continuously with increasing temperature. The dielectric constant ε_S of MTHF was evaluated from the peak shift of exciplex emission by using the Lippert–Mataga relation at room temperature. In this evaluation, the refractive index n of MTHF is assumed to be constant ($n = 1.406$) for the whole temperature range measured. As shown in Fig. 8, the evaluated ε_S was in good agreement with the results of dielectric relaxation measurement[37] in the temperature range from 140 to 292 K. Furthermore, it is noteworthy that the agreement was also seen even at 77 K, where MTHF is frozen. In a glassy solid, polar solvents behave as nonpolar solvents because solvent dipole reorientation is highly restricted. An abrupt decrease in the ε_S at a low temperature is due to a glass transition of MTHF from a liquid to a glassy solid. On the contrary, the flexibly bridged Cz–$(CH_2)_3$–TP was useless as a polarity probe at 77 K, where no exciplex emission was ob-

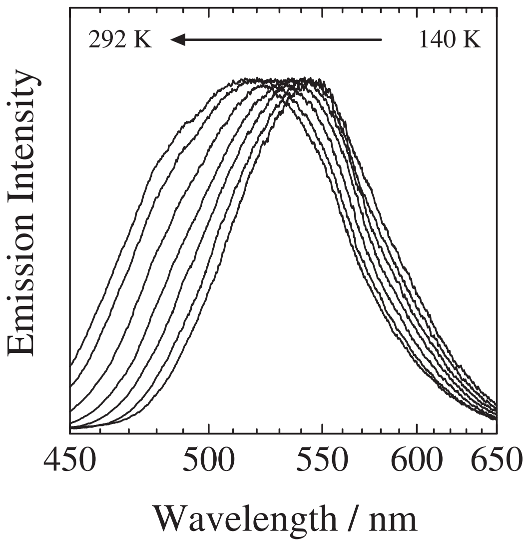

Fig. 7. Exciplex emissions of Cz–TP in MTHF at temperatures from 140 to 290 K. Emission intensity was normalized.

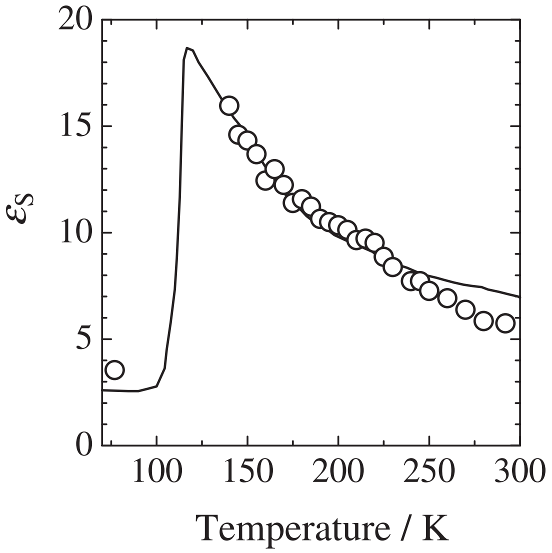

Fig. 8. Dependence of the static dielectric constant ε_S on the temperature for the solvent MTHF. Open circles represent the ε_S evaluated from the exciplex emission of the Cz–TP molecule from 77 to 290 K. Solid line represents the ε_S measured by the dielectric relaxation measurement at a frequency of 1 kHz.[37]

served, because the dynamical formation of the intramolecular exciplex in Cz–$(CH_2)_3$–TP is inhibited in the MTHF glassy solid. These good agreements prove that the exciplex emission of Cz–TP depends on solvent polarity rather than on temperature and that the dielectric constant of solvents can be quantitatively evaluated not only in a liquid phase but also in a solid phase over a wide temperature range. While most polarity probes are limited to only a narrow temperature range owing to their conformational changes with temperature, the Cz–TP molecule is useful as a polarity probe for a wide temperature range.

Conclusions

We synthesized a novel cyclophane compound having an electron donor (Cz) and an electron acceptor (TP). The well-defined geometrical arrangement of the paired donor–acceptor moiety in both the ground and excited states allowed us to discuss the photophysical characteristics, in terms of the ability as a polarity probe for a variety of the surrounding medium. Our conclusions are as follows.

1. The Cz–TP molecule forms an exciplex in the excited state while CT interaction is very small in the ground state.
2. The polarity dependence of the exciplex emission is well described by the Lippert–Mataga relation over wide polarity and temperature ranges.
3. The Cz–TP molecule has a long lifetime of 35.1 ns in the excited state; this is due to the CT nature in the excited state.
4. The Cz–TP molecule is useful as a polarity probe for the evaluation of local dielectric constants of solvents not only in a liquid phase but also in a solid phase over a wide temperature range, owing to the rigid structure of [2.2]-cyclophane framework.

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