



Lifetimes of partial charge transfer exciplexes of 9-cyanophenanthrene and 9-cyanoanthracene

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Abstract

The fluorescence decays of several exciplexes with partial charge transfer have been investigated in solvents of various polarity. The measured lifetimes are found to be in reasonable agreement with the activation enthalpy and entropy of exciplex decay obtained earlier from the temperature dependence of the exciplex emission quantum yields. For exciplexes with 9-cyanophenanthrene substantial contribution of the higher local excited state into the exciplex electronic structure is found and borrowed intensity effect enhances the exciplex emission rate constants.

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1. Introduction

Exciplexes with partial charge transfer are formed in non-polar as well as in polar solvents when the driving force of excited-state electron transfer (ET) is small ($\Delta G_{\text{ET}}^* > -0.5$ eV) [1–10]. An important feature of these exciplexes is a variable degree of charge transfer (z) which depends on both ΔG_{ET}^* and medium polarity [11–14] and reflects the change of the contribution of charge transfer state (CT, A^-D^+) into the exciplex wavefunction $\Psi(A^{-z}D^{+z}) = c_1\Psi_1(\text{LE}) + c_2\Psi_2(\text{CT})$. Here $\Psi_1(\text{LE})$ and $\Psi_2(\text{CT})$ are the wavefunctions of the locally excited (LE, *AD) and charge transfer states, re-

spectively, $c_1^2 + c_2^2 = 1$, and $z = c_2^2$. The variation of z causes variations of emission (k'_F) and intersystem crossing (k'_{ISC}) rate constants [1,2,15] and a non-linear dependence of the exciplex emission frequency on the medium polarity [11–14,16–19]. These effects allow to evaluate z from experimental dependence the of the exciplex emission frequency on solvent polarity [11–14,16,17] or from the values of $k'_F = (\varphi_0/\tau'_0)(\varphi'/\varphi)/(\varphi_0/\varphi - 1)$ (where φ' and φ are the fluorescence quantum yields of the exciplex and parent excited molecules in the presence of the quencher, respectively, φ_0 is the fluorescence quantum yield of the parent excited molecules in the absence of quencher; τ'_0 is the exciplex lifetime) [1,2,11].

In this work, we have measured the lifetimes τ'_0 of several exciplexes composed of 9-cyanoanthracene

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(CA) and 9-cyanophenanthrene (CP) with electron donors – methoxybenzenes and 1,8-dimethylnaphthalene ($-0.1 < \Delta G_{\text{ET}}^* < 0.1$ eV) whose emission quantum yields in the temperature range 200–380 K have been investigated earlier [16,17].

Experimental measurements of exciplex emission kinetics, which is biexponential, and determination of rise-time τ_{R} and decay-time τ_{D} are rather simple and deconvolution procedure can be used to improve the accuracy of these measurements. But extraction of exciplex lifetime τ_0' and rate constants of its formation k_1 from these data are complicated by intricate dependence of τ_{R} and τ_{D} on k_1 and τ_0' as well as on the quencher concentration in the case when exciplexes are in equilibrium with the parent excited molecules (when $k_1\tau_0' > 1$ or $\Delta G_{\text{ET}}^* > -0.5$ eV).

Once obtained, the τ_0' values provide a possibility to determine the emission rate constants k_{F}' for these exciplexes in various solvents and to analyse the relationship between k_{F}' and the electronic structure of the exciplexes (z).

2. Experimental

2.1. Time-resolved fluorescence

The fluorescence lifetime measurements were performed with two different systems depending on the excitation wavelength. The fluorescence lifetime of the exciplexes with CA ($\tau_0 > 13$ ns, $0.5 < \tau_0' < 35$ ns) was measured using the time-correlated single photon counting (TCSPC) technique [20]. Excitation at 395 nm was achieved using a laser diode (Picoquant model LDH-P-C-400B) operating at 10 MHz. The pulse duration was of the order of 50 ps and the average power of 0.5 mW. The detection was achieved with a photomultiplier tube (Hamamatsu, H5783-P-01). The detector output was connected to a TCSPC computer board module (Becker and Hickl. SPC-300-12). The full-width at half maximum of the response function was around 200 ps.

In another system [21], used for the exciplexes with CP ($\tau_0 > 14$ ns, $\tau_0' > 7$ ns), the sample was excited by the third harmonic output at 355 nm of an active/passive mode-locked Nd:YAG laser

(Continuum PY61-10). The pulse duration was around 30 ps and the excitation intensity was less than 1 mJ cm^{-2} . Electron acceptor and exciplex fluorescence were selected using bandpass and cutoff filters, respectively. The detection was achieved by a fast pin photodiode (Motorola MRD500) connected to a 500 MHz, 2 GS s^{-1} digital oscilloscope (Tektronik TDS-620A). The full-width at half maximum of the response function of this system was less than 1 ns.

2.2. Samples

9-Cyanoanthracene ($E(\text{A}/\text{A}^-) = -1.7$ V, $E^* = 3.7$ eV) (Aldrich, 98%), 9-cyanophenanthrene ($E(\text{A}/\text{A}^-) = -1.91$ V, $E^* = 3.42$ eV) (Aldrich, 98%) and 1,3,5-trimethoxybenzene (135TMB, $E(\text{D}^+/\text{D}) = -1.49$ V) (Aldrich, 99%) were used as received; 1,8-dimethylnaphthalene (18DMN, $E(\text{D}^+/\text{D}) = -1.3$ V) (Merck, 98%) was purified by sublimation; 1,2-dimethoxybenzene (12DMB, veratrol, $E(\text{D}^+/\text{D}) = 1.45$ V) (Aldrich, 98%) was distilled. The solvents (Fluka) were of the best commercially available quality and were used without further purification. The concentration of the absorber was adjusted to achieve an absorbance of 0.1 on 1 cm at the excitation wavelength. Before measuring, the samples were purged with high purity argon for 20 min. No sample degradation was observed after the measurements.

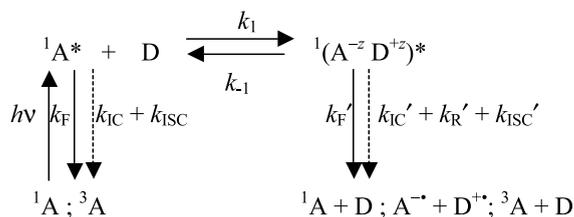
The value of ΔG_{ET}^* in acetonitrile was calculated as the difference of the redox (polarographic) potentials of the electron donor and the electron acceptor in acetonitrile and the excited-state energy of the acceptor ($E^* = h\nu_{00}$, where ν_{00} is the frequency of 0–0 transition of the acceptor):

$$\Delta G_{\text{ET}}^*/F = E(\text{D}^+/\text{D}) - E(\text{A}/\text{A}^-) - E^*, \quad (1)$$

where F is the Faraday constant.

3. Results

According to the conventional kinetic scheme of exciplex formation [22,23] the fluorescence of both parent excited molecule $^1\text{A}^*$, $I(t)$, and exciplex $^1(\text{A}^{-z}\text{D}^{+z})^*$, $I'(t)$, can be described by two-exponential functions [24,25] (Scheme 1)



Scheme 1.

$$I(t) = \alpha \exp(-t/\tau_R) + \exp(-t/\tau_D), \quad (2)$$

$$I'(t) = \exp(-t/\tau_D) - \exp(-t/\tau_R), \quad (3)$$

where

$$1/\tau_R = (1/\tau_0 + k_1[D] + 1/\tau'_0 + k_{-1})/2 + \{(1/\tau_0 + k_1[D] - 1/\tau'_0 - k_{-1})^2/4 + k_1 k_{-1}[D]\}^{1/2}, \quad (4)$$

$$1/\tau_D = (1/\tau_0 + k_1[D] + 1/\tau'_0 + k_{-1})/2 - \{(1/\tau_0 + k_1[D] - 1/\tau'_0 - k_{-1})^2/4 + k_1 k_{-1}[D]\}^{1/2}, \quad (5)$$

$$\alpha = (1/\tau_0 + k_1[D] - 1/\tau_R) / \{1/\tau_D - (1/\tau_0 + k_1[D])\}. \quad (6)$$

Here k_1 and k_{-1} are the rate constants of exciplex formation and dissociation into parent reactants. $1/\tau_0 = k_F + k_{IC} + k_{ISC}$; $1/\tau'_0 = k'_F + k'_{IC} + k'_{ISC} + k'_R$, where k_F , k'_F , k_{IC} , k'_{IC} , k_{ISC} , and k'_{ISC} are the emission, internal conversion and intersystem crossing rate constants for $^1A^*$ and exciplex, respectively; k'_R is the rate constant for exciplex dissociation into radical ions.

The Stern–Volmer quenching constant is:

$$K_{SV} = (\varphi_0/\varphi - 1)/[D] = k_1\tau_0/(1 + k_{-1}\tau'_0). \quad (7)$$

The fluorescence decays of CA and CP in various solvents in the absence of electron donors are monoexponential. The measured values of τ_0 are presented in Table 1. Figs. 1 and 2 show typical fluorescence time profiles measured with exciplexes with CP and CA. For exciplexes with CP decay-time τ_D and rise-time τ_R can be obtained very easily by standard procedure from emission kinetics in both the CP emission band and the exciplex emission band since the overlap of CP and

CP–12DMB and CP–135TMB exciplexes emission spectra is negligible. For CA in the presence of 18DMN, the experimental decay of CA fluorescence is biexponential (curve 1) but the rise of the exciplex emission (curve 2) cannot be followed accurately due to substantial overlap of the exciplex and CA emission spectra. The slow exponential decay component of CA emission can be seen very clear. It coincides with the decay of the exciplex emission at longer times. For CA in the presence of 135TMB, only the slow component (τ_D) was observed in both electron acceptor and exciplex fluorescence decays. This is caused by the very short lifetime and the small amplitude, α , of the fast component (τ_R) (see below in the discussion). The overlap of exciplex and electron acceptor emission spectra does not complicate the determination of τ_R (in the electron acceptor emission band) and τ_D (in both emission bands) since Eqs. (2) and (3) contain the sum and difference of the same exponents, but hinders the determination of the amplitude α . The measured values of τ_R and τ_D are presented in Table 1.

3.1. Determination of τ'_0

The determination of τ'_0 from the observed fluorescence decay for exciplexes with $\Delta G_{ET}^* > -0.5$ eV at reasonable quencher concentrations is complicated because of the small conversion of the parent excited electron acceptor into the exciplex and because of the existence of an equilibrium between them ($K_{Ex} \approx 1$ to 100 M⁻¹). The observed values of τ_R and τ_D depend on the quencher concentration (see Eqs. (4) and (5)). With increasing $[D]$, $1/\tau_R$ increases approximately linearly and $1/\tau_D$ decreases (when $\tau'_0 > \tau_0$) or increases (when $\tau'_0 < \tau_0$) towards $1/\tau'_0$ [25]. Only when $1/\tau'_0 \gg k_{-1}$ and $1/\tau'_0 < (1/\tau_0 + k_1[D])$ the observed decay time τ_D coincides with τ'_0 . In all other cases the calculation of τ'_0 from the measured fluorescence decay time τ_D needs additional information, either on the value of τ_R or on the concentration dependence of τ_D . We have calculated τ'_0 by several methods, depending on the experimental possibility to measure τ_R and τ_D : (a) when both τ_R and τ_D were available, the values of τ'_0 , k_1 and k_{-1} were found by solving of the system of Eqs. (4), (5) and (7);

Table 1

Lifetimes of electron acceptor excited states τ_0 (ns), Stern–Volmer quenching constants K_{SV} (M^{-1}) (293 K), rate constants k_1 ($M^{-1} s^{-1}$) and k_{-1} (s^{-1}), quencher concentrations $[D]$ (M), degree of quenching ($\phi_0/\phi - 1$), rise-time τ_R (ns) and decay-time τ_D (ns), evaluated (Eq. (6)) relative amplitude of the fast component of excited acceptor decay (α), exciplex lifetime τ'_0 (ns), degree of charge transfer in the exciplex (z) [13,14], ratio of emission rate constants k'_F/k_F and ratio of radiative transition dipole moments of exciplex and parent electron acceptor (M^2/M_1^2)

Exciplex (ΔG_{ET}^*) (eV)	Solvent	τ_0	K_{SV}	k_1	k_{-1}	[D]	$(\phi_0/\phi - 1)$	τ_R	τ_D	α	τ'_0	z	k'_F/k_F	M^2/M_1^2
CP–12DMB (–0.06)	PrCN	20.8	154	1×10^{10}	3.8×10^7	0.05	7.7	1.7	7.6	7.5	8	0.96	0.18	0.4
	CH ₂ Cl ₂	14.5	32	1.2×10^{10}	1.5×10^8	0.11	3.5	1.5	27	11	11	0.94	0.49	1.0
	AcOBu	26.7	28	6.5×10^9	1.4×10^8	0.036	1	6.1	29	2.5	36	0.93	0.44	0.8
CP–135TMB (–0.02)	PhCH ₃	27.4	1.5	2.2×10^9	8.5×10^8	0.24	6.7	1.2	36	15				
	PrCN	20.8	25	4×10^9	1.6×10^8	0.1	2.5	2.3	32	0.6	46	0.89	0.65	1.1
	AcOBu	26.7	3.4	1.6×10^9	3.8×10^8	0.24	0.8	3.9	29	1.3	32	0.89	0.94	1.5
CA–18DMN (–0.1)	MeCN	16.6	143	1.8×10^{10}	8.5×10^7	0.1	14.3	0.5	13	21	13	0.55	0.26	0.43
	PrCN	15.4	55	9.3×10^9	4.7×10^7	0.05	2.5	2	31	11	34	0.52	0.12	0.33
	CH ₂ Cl ₂	14	42	1.1×10^{10}	9×10^7	0.3	12.9	0.3	29	38	29	0.47	0.28	0.46
CA–135TMB (0.09)	PhCH ₃	13	13	7.3×10^9	2.7×10^8	0.32	4.1	0.4	21	8.5	23	0.37	0.37	0.57
	MeCN	16.6	94	1.2×10^{10}	1×10^9	0.14	13		1.8	0.7	1.1	0.76	0.16	0.34
						0.2	19		1.6	1.2				
	PrCN	15.4	46	4.5×10^9	6.3×10^8	0.2	9		1.9	0.3	0.8	0.7	0.38	0.53
						0.29	13		1.4	0.4				
	CH ₂ Cl ₂	14	32	6.2×10^9	2.4×10^9	0.1	3		3.8	0.1	0.7	0.5	0.33	0.53
						0.3	9.5		1.7	0.3				
	AcOBu	14.7	30	3.6×10^9	8×10^8	0.2	6		2.3	0.2	0.8	0.37	0.51	0.54
						0.3	9		1.8	0.3				
	PhCH ₃	13	19	3.2×10^9	1×10^9	0.2	3.8		3.3	0.2	1.2	0.28	0.23	0.22
						0.3	5.7		2.6	0.4				

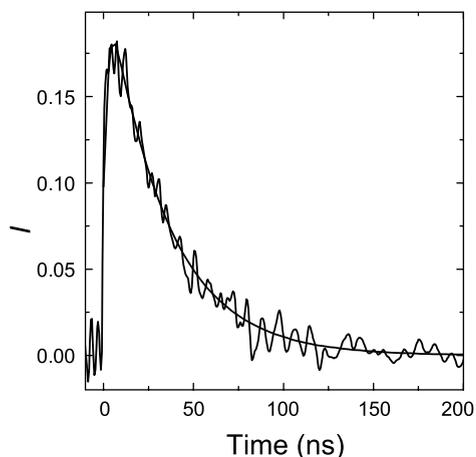


Fig. 1. Experimental time profile of exciplex fluorescence measured with solutions of CP and 0.2 M 12DMB in PhCH₃ and curve simulated by two-exponential function (Eq. (3)) ($\tau_R = 2.3$ and $\tau_D = 32$ ns).

(b) when τ_D were available at two different values of [D] we have used the system of Eqs. (5) and (7); (c) when τ_D were available at one value of [D] we have used the system of Eqs. (5) and (7) and a value of diffusion rate constant in the respective solvent [16,17] instead of k_1 . For all calculation, we used previously measured values of K_{SV} [16,17]. When it was possible to calculate τ'_0 by all the three ways obtained values of τ'_0 coincided with each other. That confirms the validity of the measurements and calculations.

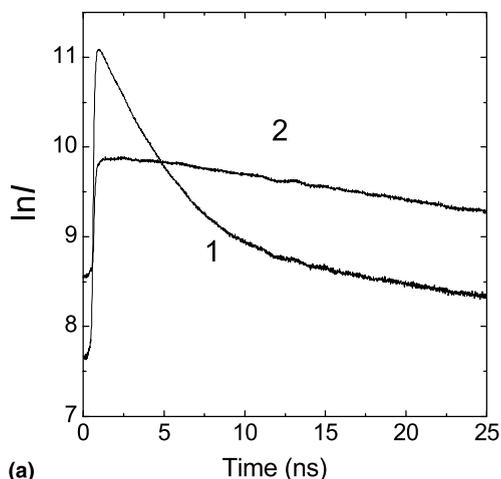
The calculated values of τ'_0 , k_1 , k_{-1} and α are shown in Table 1. Obtained values of α and k_1 confirm the reasons why fast exponent was not observed in CA decay kinetics in the presence of 135TMB.

3.2. Exciplex emission rate constants k'_F

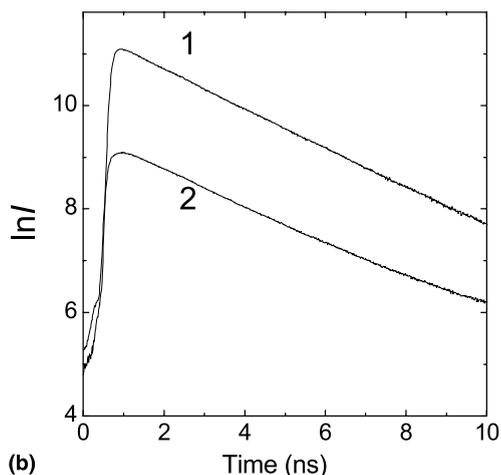
The ratio of emission rate constants of exciplex and parent electron acceptor A* was calculated from the ratio of their lifetimes and relative emission quantum yields (ϕ'/ϕ) [11–13]:

$$(k'_F/k_F) = (\tau_0/\tau'_0)(\phi'/\phi)/(\phi_0/\phi - 1). \quad (8)$$

The so-obtained values of (k'_F/k_F) are listed in Table 1. The dependence of the emission rate constants on the degree of charge transfer in the



(a)



(b)

Fig. 2. Time profiles of the electron acceptor (1) and exciplex (2) fluorescence measured with solutions of: (a) CA and 0.05 M 18DMN in PrCN, (b) CA and 0.3 M 135TMB in PhCH₃.

exciplexes z was discussed by several authors in terms of intensity borrowing by the exciplex CT transition from the transition to the ground state from lower LE state of the fluorescer [26–28]. Gould et al. [2] have taken into account the orthogonality of vectors of radiative transition dipole moments from the LE (M_1) and CT (M_2) states, and have given a simple expression for the relationship between (k'_F/k_F) and z :

$$\begin{aligned} (k'_F/k_F)/(v'_{Av}/v_{Av})^3 &= [(1-z)M_1^2 + zM_2^2]/M_1^2 \\ &= 1 - z(1 - M_2^2/M_1^2), \end{aligned} \quad (9)$$

where ν'_{Av} and ν_{Av} are the average emission frequencies of exciplex and electron acceptor [15,16]. A ratio M_2^2/M_1^2 of ca. 0.1 ($M_2 = 2.8$ to 2.9 D) was found for exciplexes with 9,10-dicyanoanthracene (DCA) and 2,6,9,10-tetracyanoanthracene (TCA) with methylbenzenes [2].

Fig. 3 presents plots of $(k'_F/k_F)/(v'_{Av}/v_{Av})^3$ vs. z for exciplexes with CA and CP in various solvents. The z values were found from the dependence of the exciplex emission spectral shift relative to that of the parent electron acceptor $h\Delta\nu$ in our previous works [13,14]. For exciplexes with CA, one can see an approximately linear decrease of $(k'_F/k_F)/(v'_{Av}/v_{Av})^3$ with increasing z . The intercept at $z = 0$ is close to 1, in accordance to Eq. (9), and the intercept at $z = 1$ gives a ratio $M_2^2/M_1^2 \approx 0.05$.

For exciplexes with CP, the value of $(k'_F/k_F)/(v'_{Av}/v_{Av})^3$ exceeds 1 already at z close to 1 and extrapolation to $z = 0$ gives a value of ca. 10 in contrast to Eq. (9). Such a high value of the ratio M^2/M_1^2 for exciplexes with CP can be accounted for the effect of intensity borrowing from higher LE state. The peculiarity of CP is the presence of the transition to higher excited state with much higher (ca. 10 times; $\log(\epsilon_{\max}/M^{-1} \text{ cm}^{-1}) = 4.2$ and

3.1, respectively) intensity relative to $S_0 \rightarrow S_1$ transition and small energy gap between them (ca. 0.5 eV). Thus, both these states can provide some contribution into the exciplex wavefunction $\Psi(A^{-z}D^{+z}) = c_1\Psi_1(LE_1) + c_3\Psi_3(LE_n) + c_2\Psi_2(CT)$. For CA and other cyanoanthracenes, the gap between $S_0 \rightarrow S_1$ band and near more intense band ($\log(\epsilon_{\max}/M^{-1} \text{ cm}^{-1}) = 3.8$ and 5.3 , respectively) is much larger (ca. 1.6 eV). This difference in energy gaps results in a much greater contribution of the S_n state, c_3 , and a much greater effect of intensity borrowing from $S_0 \rightarrow S_n$ transition in the exciplexes with CP relative to those with CA. To account for this effect, we should substitute M_1^2 in the numerator of Eq. (9) by the $S_n \rightarrow S_0$ transition dipole moment, M_3^2 :

$$\begin{aligned} (k'_F/k_F)/(v'_{Av}/v_{Av})^3 &= [(1-z)M_3^2 + zM_2^2]/M_1^2 \\ &= M_3^2/M_1^2 - z(M_3^2/M_1^2 - M_2^2/M_1^2). \end{aligned} \quad (10)$$

The intercepts at $z = 0$ (ca. 10) and $z = 1$ (ca. 0.2) are equal to M_3^2/M_1^2 and M_2^2/M_1^2 , respectively.

De Schryver et al. [26] and Gould et al. [2] have already discussed the problem of intensity borrowed from upper states. Gould et al. came to the conclusion that this effect was negligible for cyanoanthracenes. Our results show that the borrowed intensity effect becomes important for exciplexes with CP in contrast to exciplexes with CA. We can compare the relative values of M_2^2 for various exciplexes using the radiative rate constants of the corresponding electron acceptors. The relative magnitude of k_F for CA, DCA, TCA, and CP ($37:28:25:12 \mu\text{s}^{-1}$) is close to that of the (M_1^2/M_2^2) ratio for their exciplexes (20:10:10:5) that indicate similar values of M_2^2 for radiative transitions from their CT states.

Therefore, when a fluorescer has an electronic transition close to $S_0 \rightarrow S_1$ transition with energy gap ca. 0.5, a substantial contribution of this state into the exciplex wavefunction can be expected. This effect should be taken into account in the consideration of spectral and chemical properties of exciplexes, including the evaluation of (k'_F/k_F) and (τ'_0/τ_0) from the ratio of exciplex and fluorescer emission quantum yield.

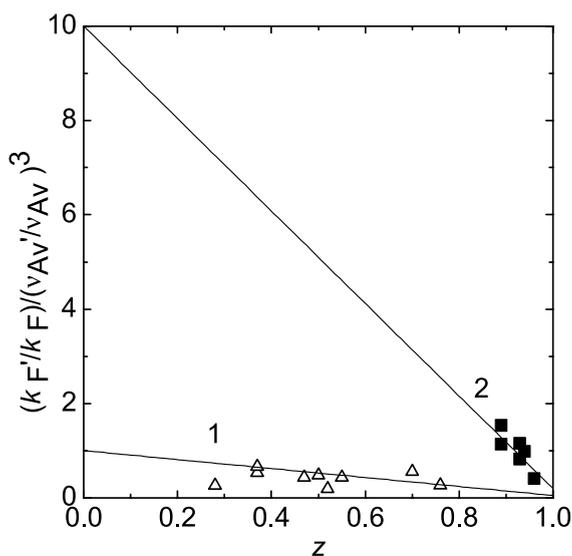


Fig. 3. Plot of the relative rate constants of exciplex emission $(k'_F/k_F)/(v'_{Av}/v_{Av})^3$ vs. the degree of charge transfer z for exciplexes with CA (1) and CP (2).

Acknowledgements

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