Cationic Exciplexes: Role of Hydrogen Bonding in Deactivation and Electronic Coupling

Joseph P. Dinnocenzo* and Samir Farid*

Department of Chemistry, University of Rochester, Rochester, NY 14627-0216

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Emissive properties for the cationic exciplex (A^{+}*/D → $A^{\bullet}D^{\bullet+}$) of an isoquinolinium cation tethered to a substituted arene (**1**$^{+}$) are strongly affected by hydrogen bonding solvents. At equal dielectric constant (ε), the ground-to-excited state energy gaps (ΔG) and solvent reorganization energies (λ_s) decrease from nitriles to aliphatic alcohols. The corresponding decreases from aliphatic alcohols to high hydrogen bond acidity solvents is ~3 times larger. The exciplex decay (k_{Ex}) – largely determined by unfolding of the exciplex to a stretched conformer – changes in a complex way depending on the strength of the hydrogen bond ability of these solvents. In contrast, the electronic couplings between the exciplex ground, excited, and charge transfer states do not show a solvent functionality dependence.

1. Introduction

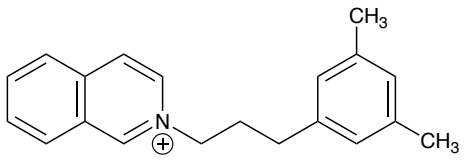
Cationic exciplexes are a new class of organic exciplexes in which the electron acceptor is a cation.[1-3] The excited state electron transfer to form these exciplexes represent charge shift reactions, eq 1, unlike those from the extensively investigated, conventional exciplexes,[4] which are charge formation reactions, eq 2.

$$A^{+} + D \xrightarrow{h\nu} A^{+*}D \leftrightarrow A^{\bullet}D^{\bullet+} \quad (1)$$

$$A + D \xrightarrow{h\nu} A^{*}D \leftrightarrow A^{\bullet-}D^{\bullet+} \quad (2)$$

Cationic exciplexes expand the scope and potential applications of exciplexes, such as probing processes in highly polar solvents, including water.[2] We recently

described solvents effect on the intramolecular cationic exciplex fluorescence of $\mathbf{1}^+$, which has a high degree of charge transfer character.[3] The spectral shift of the charge shift reaction for the cationic exciplex was much less sensitive than for conventional exciplexes to changes in solvent polarity as measured by dielectric constant (ε). Interestingly, the spectral shifts for series of homologous nitriles and alcohols of varying solvent polarity separately correlated linearly with ε. The difference between the nitriles and alcohols was attributed to hydrogen bonding in the protic solvents, a hypothesis supported by deviation of the emission spectra for aliphatic alcohols in more strongly hydrogen-bonding solvents.[3]



$\mathbf{1}^+$ PF_6^-

In the current paper we describe additional differences between nitriles, alcohols, and strong hydrogen bonding solvents, and also address whether these differences affect the electronic coupling matrix elements for the exciplex of $\mathbf{1}^+$.

Experimental

Materials

In general, solvents were fractionally distilled before use. Following an earlier procedure used to purify acetonitrile,[5] octanenitrile was treated by heating with $AlCl_3$ (100°, 1 h), decanted, and distilled. The distilled material was further heated with $KMnO_4/LiCO_3$ (100°, 1 h) and then fractionally distilled. $\mathbf{1}^+$ PF_6^- was prepared as previously described.[2]

Fluorescence Measurements

Fluorescence spectra were measured using a Fluorolog-3 spectrofluorometer (Jobin Yvon, Horiba) at room temperature, and corrected for the efficiency of the monochromator and the spectral response of the photomultiplier tube using the Calibration Kit *Spectral Fluorescence Standards* BAM-F001–BAM-F005 (Sigma–Aldrich). Measurements were performed in argon-saturated solutions containing a low concentration of perchloric acid (0.01 M) for alcohol solvents and trifluoroacetic acid (0.005 M) for nitrile solvents, which eliminated the formation of minor emissive impurities, presumably by protonating trace basic impurities in the solvents. Neither acid was added when formic acid was used as solvent. To decrease the noise, 12-15 runs were averaged to generate the final spectra. There was no discernible difference between the spectra for the individual runs, indicating no degradation or any product formation. The optical densities of solutions typically varied between ~0.05-0.25 depending on the excitation wavelength.

To determine the exciplex quantum yields, fluorescence spectra were measured at different excitation wavelengths and corrected for different fractions of absorbed light by dividing the fluorescence intensity by $(1-10^{-OD})$. *N*-Methylisoquinolinium emission in air-saturated acetonitrile ($\phi_f = 0.50$)[1] was used as actinometer.

Time-Correlated Single Photon Counting

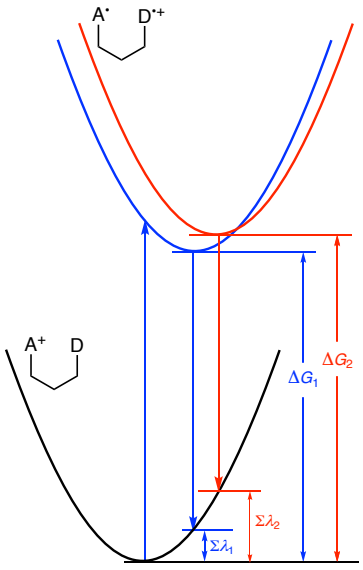
Fluorescence lifetime measurements were made using the time-correlated single photon counting (TCSPC) method. The output of a tunable (680-1080 nm), 80 MHz femtosecond titanium-sapphire (Ti:S) laser was serially passed through a pulse selector and a harmonic generator. The repetition rate was varied between 1.6 and 5 MHz to ensure sufficient decay of excited states between laser pulses. The excitation wavelength (340 or 360 nm) from the second harmonic of the Ti:S wavelength was passed through a Glan-Taylor polarizer to ensure clean vertical polarization and could be attenuated with a

rotating neutral filter of variable optical density. The excitation beam entered a FluoTime200 fluorescence lifetime spectrometer equipped with a PicoHarp300 TCSPC module (PicoQuant) and a Hamamatsu R3809U-50 MCP-PMT. The emission beam was passed through a polarizer set at the magic angle. Dilute Ludox solutions were used to collect the instrument response function (IRF) at the excitation wavelength, which had a full width at half maximum (fwhm) of ~50 ps. Emission decays were monitored between 370 and 560 nm. The fluorescence decays were analyzed using the FluoFit, version 4.6.0.0 (PicoQuant) software package.

2. Results and Discussion

2.1. Solvent effect on ΔG

As mentioned in the Introduction, we have shown that hydrogen bonding affects the emission spectra for the cationic exciplex of $\mathbf{1}^{+}$. Several related electron transfer parameters affect the position and shape of the exciplex spectra, the energy gap between the exciplex excited state and ground state (ΔG), and reorganization energies, λ_s and λ_v, for low (mostly solvent) and high frequencies, respectively, where $\Sigma\lambda = \lambda_s + \lambda_v$ (Scheme 1).



Scheme 1. Free energy curves for the ground state and the exciplex of $\mathbf{1}^+$ as a function of solvent polarity. Black, normalized ground state; blue, less polar solvent; red, more polar solvent.

The electron transfer parameters were determined by fitting the exciplex spectra using the model described in detail previously.[1] Typical exciplex spectra and the best fits to them are shown in Figure 1 for three different solvents with similar dielectric constants: butyronitrile, ethanol, and 2,2,2-trifluoroethanol (top panel). Additional comparisons are shown for octanenitrile and 3-pentanol (bottom panel), which also have similar dielectric constants. As can be seen, the fits to all of the experimental spectra are excellent. The fitted parameters for all solvents will be discussed in detail below.

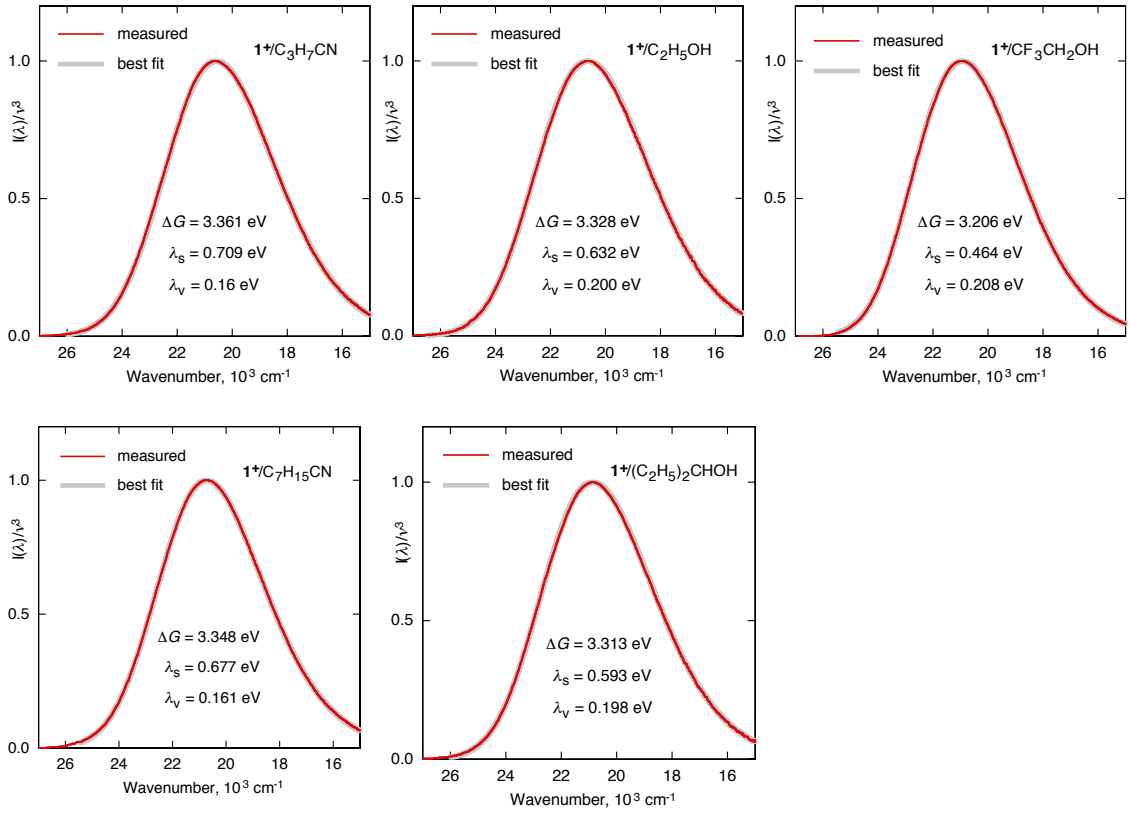


Figure 1. Exciplex spectra in butyronitrile, ethanol, 2,2,2-trifluoroethanol, octanenitrile, and 3-pentanol (red lines), best fit to spectra (gray lines), and fitted parameters (ΔG, λ_s, and λ_v).

In conventional exciplexes, where the ground state is neutral and the excited state is zwitterionic, ΔG *decreases* with increasing solvent polarity, primarily due to changes in the energy of the charge-separated exciplex with changes in the polarity of the medium. For cationic exciplexes, the ground state and the excited state are both cationic and, therefore, the energies of both states are expected to be affected by changes in solvent polarity. If both states were equally solvent-stabilized, ΔG would be expected to be solvent-polarity independent. In the case of the exciplex of $\mathbf{1}^+$, the ground state is somewhat more solvent-stabilized than the excited state.[3] As a result ΔG *increases* with increasing solvent polarity for this exciplex, as indicated in Scheme 1.

For homologous series of alcohols and nitriles, ΔG increases linearly and nearly equally with increasing ε, although the two solvent classes fall on separate lines (Figure 2 and Table 1). As previously proposed,[3] the difference between these two solvent classes can be attributed to hydrogen bonding. Consistent with this explanation, the stronger hydrogen bonding acidity solvents 2,2,2-trifluoroethanol (TFE) and formic acid (FA) fall well below the line for the aliphatic alcohols (Figure 2). Interestingly, the data point for water also falls well below the line for the alcohols and, to a lesser extent, the data point for ethylene glycol (EG). Although the strong deviation for water may seem surprising, it is consistent with several measures of hydrogen-bond acidity (HBA) for solvents,[6-9] which indicate that the HBA for water is significantly greater than for aliphatic alcohols and can even exceed that for TFE. The smaller deviation for EG can be similarly explained by its slightly greater HBA than that for aliphatic alcohols.[6,8] The combined results in Figure 2 make a strong case for hydrogen bonding playing a dominant role in explaining the difference between the dependence of ΔG on ε for nitriles versus solvents capable of hydrogen bonding.

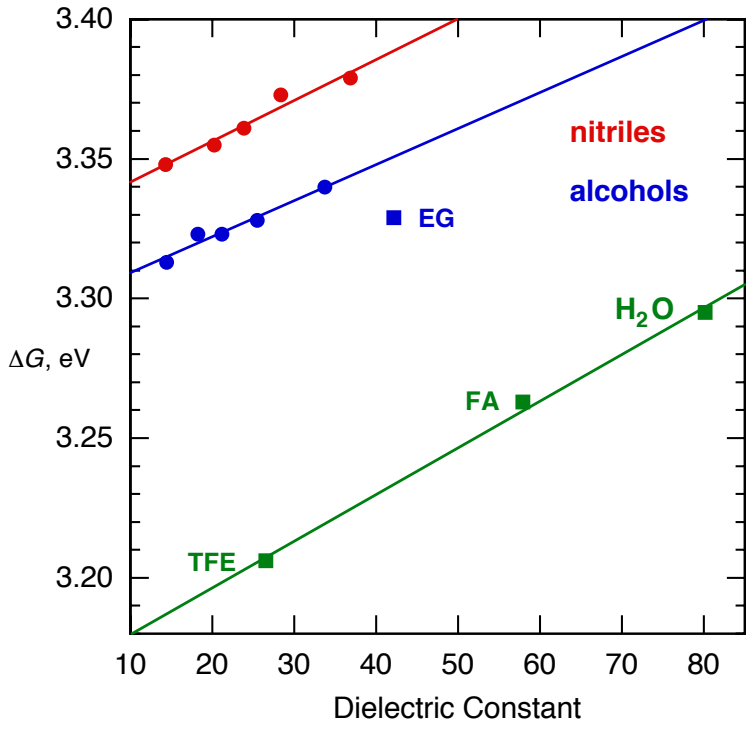


Figure 2. Dependence of the ground-to-excited state energy gap (ΔG) on the solvent dielectric constant and functionality

As mentioned above, the exciplex of $\mathbf{1}^+$ has a high degree of charge transfer character. To a first approximation the exciplex can be considered to consist of covalently linked isoquinolinyl radical and arene radical cation moieties. Hydrogen bonding solvents can reasonably be expected to stabilize the isoquinolinyl radical fragment by hydrogen bonding to the nitrogen atom (see **2** below). This interaction will stabilize the exciplex relative to the ground state and lower ΔG.

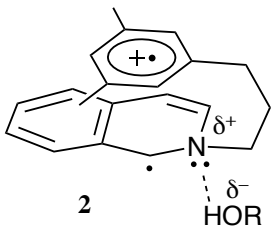


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Table 1. Exciplex of $\mathbf{1}^+$ in different solvents.

solvent	ε^a	ΔG^b (eV)	$\lambda_s{}^c$ (eV)	$\tau_{Ex}{}^d$ (ns)	$k_{Ex}{}^e$ (10^7 s^{-1})
CH_3CN	36.80	3.379	0.749	17.0	5.88
C_2H_5CN	28.32	3.373	0.723	21.2	4.72
C_3H_7CN	23.82	3.361	0.709	27.3	3.66
C_4H_9CN	20.18	3.355	0.692	25.4	3.94
$C_7H_{15}CN$	14.23	3.348	0.677	37.8	2.65
$HOCH_2CH_2OH$	42.14	3.329	0.665	32.4	3.09
CH_3OH	33.71	3.34	0.658	11.0_4	9.06
C_2H_5OH	25.41	3.328	0.632	15.4	6.49
C_3H_7OH	21.10	3.323	0.616	18.8	5.32
C_4H_9OH	18.16	3.323	0.611	20.9	4.78
$(C_2H_5)_2CHOH$	14.35	3.313	0.593	31.8	3.14
H_2O	80.16	3.295	0.660	16.8	5.95
HCO_2H	57.9	3.263	0.564	34.2	2.92
CF_3CH_2OH	26.53	3.206	0.464	55.0	1.82

[a]Dielectric constant at 20 °C (reference 10). [b]Energy gap between the exciplex excited state and ground state. [c]Low frequency (mostly solvent) reorganization energy. [d]Exciplex lifetime. [e]Rate constant for exciplex decay ($1/\tau_{Ex}$).

As indicated in **2**, hydrogen bonding to the isoquinolinyl radical moiety in the exciplex should impart some partial positive charge to this fragment and, correspondingly, some partial negative charge to the hydrogen bond donor fragment. The negative charge on the donor fragment might be expected to be diffused to some extent due to the network of hydrogen bonds with other solvent molecules. If the positive charge on the isoquinolinyl radical is comparatively more localized, this could result in a

partial orientation of the solvent dipoles around the isoquinolinyl fragment that somewhat resembles the solvent arrangement in the ground state isoquinolinium cation. To the extent this is the case, one might expect a decrease in λ_s for protic solvents. As shown in Figure 3, this expectation is borne out when comparing solvents of comparable ε. As expected, EG shows a slightly smaller λ_s than the aliphatic alcohols and the high HBA solvents much larger deviations.

Interestingly, in the plots of ΔG and λ_s versus s ε (Figures 2 and 3), the data points for TFE, FA, and water all fall nearly equally below the lines for the aliphatic alcohols. Literature estimates of the relative HBA of these three solvents depend on the methodology used to estimate HBA, which is not surprising. The data in Figures 2 and 3 are consistent with relatively similar HBAs for TFE, FA, and water as judged by their hydrogen bonding interactions with the exciplex of $\mathbf{1}^+$.

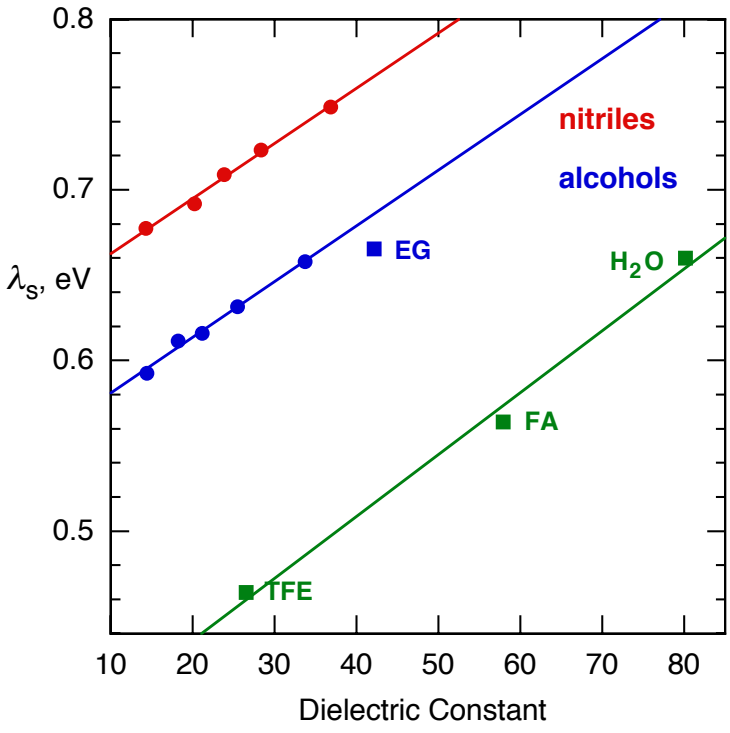
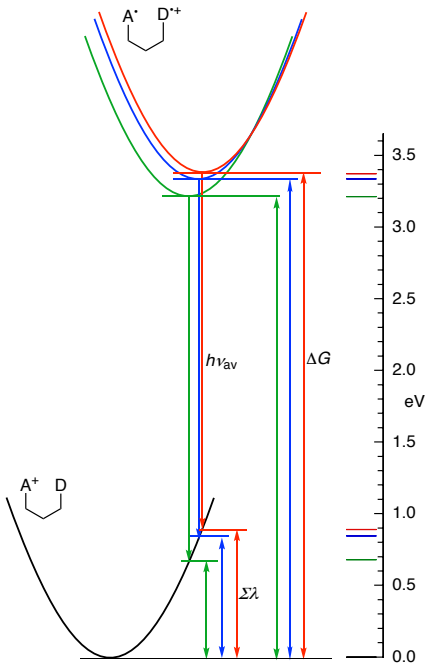


Figure 3. Dependence of the solvent reorganization energy (λ_s) on the solvent dielectric constant and functionality.

As shown in Figure 1, hydrogen bonding leads to opposite effects on λ_s and λ_v. Hydrogen bonding to the exciplex of $\mathbf{1}^+$, as indicated in **2**, might reasonably be expected to increase λ_v due to additional vibrational contributions from hydrogen bonding. As described previously,[3] within the sets of nitrile and aliphatic alcohol solvents λ_v is nearly constant and approximately independent of the solvent dielectric constant. Figure 1 shows that alcohols have larger λ_v values than nitriles, as does TFE, consistent with an additional contribution from hydrogen bonding in these solvents.

A graphical summary of the solvent effects on the energetic parameters for the exciplex of $\mathbf{1}^+$ at constant ε are shown in Scheme 2. Relative to nitriles, aliphatic alcohols lead to small decreases in both ΔG and λ_s, with a negligible effect on average emission frequency ($h\nu_{av}$), as discussed below. High HBA solvents lead to larger decreases in ΔG and λ_s, and a modest increase in $h\nu_{av}$.



Scheme 2. Free energy curves for the ground and charge transfer states of the exciplex of $\mathbf{1}^+$ in different solvent types at $\varepsilon = 30$. Black, normalized ground state; red, nitriles; blue, aliphatic alcohols; green, high hydrogen bond acidity (HBA) solvents.

2.2. Solvent effect on exciplex lifetimes

The reciprocal of the exciplex lifetime, $1/\tau_{Ex}$, is the sum of all deactivation rate constants for the exciplex (k_{Ex}). Three reactions contribute to the deactivation: fluorescence (k_f), non-radiative return electron transfer to the ground state (k_{-et}), and, for the exciplex of $\mathbf{1}^+$, solvent insertion leading to a stretched conformer (k_{solv}), followed by fast return electron transfer (eq 3). Return electron transfer from the stretched conformer is equivalent to that from a solvent separated radical ion pair, which for reactions deep into the Marcus inverted region are much faster than those from the contact pair, analogous to the folded conformer in case of an intramolecular exciplex.[11-12] As described previously,[2] the return electron transfer rate constant (k_{-et}) is expected to be much smaller than k_{solv}. In addition, with increasing solvent polarity, k_f decreases whereas k_{-et} increases. Thus, the change in k_{Ex} with solvent is largely due to change in k_{solv}.

$$1/\tau_{Ex} = k_{Ex} = k_f + k_{-et} + k_{solv} \quad (3)$$

For the homologous series of alcohols and nitriles, k_{Ex} linearly correlates with ε (Figure 4). The general trends for these solvents can be correlated with the relative energies of the exciplex versus the unfolded state from which rapid return electron transfer occurs. As shown in Scheme 3, the unfolded state is expected to be more strongly stabilized with increasing solvent polarity relative to the folded exciplex due to the greater solvent accessibility of the unfolded state. The greater driving force for unfolding with increasing solvent polarity should lead to an increase in the rate constant

for unfolding (k_{unfold}) and, consequently, a greater k_{Ex}. That the aliphatic alcohols have slightly larger k_{Ex} than nitriles at comparable ε is consistent with greater stabilization of the unfolded state from hydrogen bonding. The low data point for EG can be attributed to its exceptionally high viscosity relative to all of the other solvents investigated here, which could lead to a significant decrease in k_{unfold} and thus k_{Ex}.

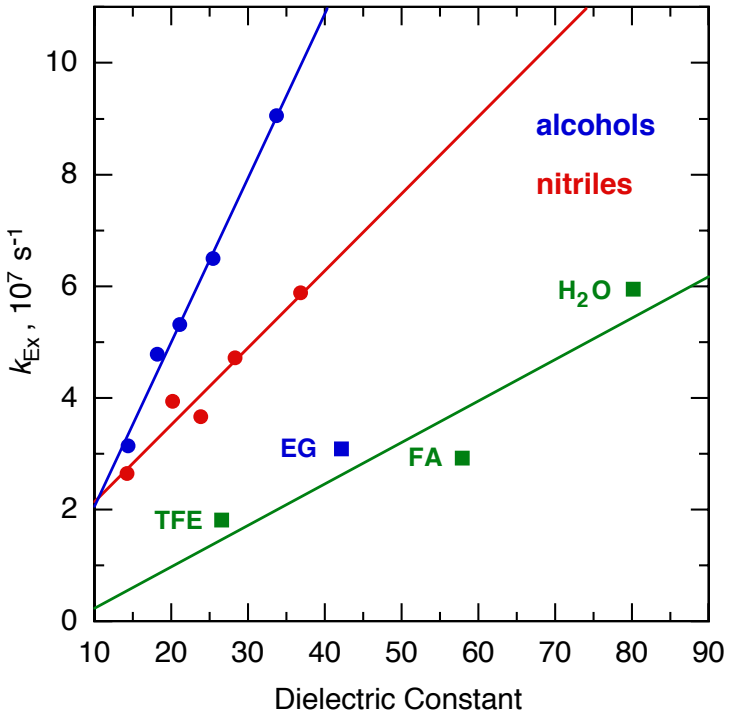
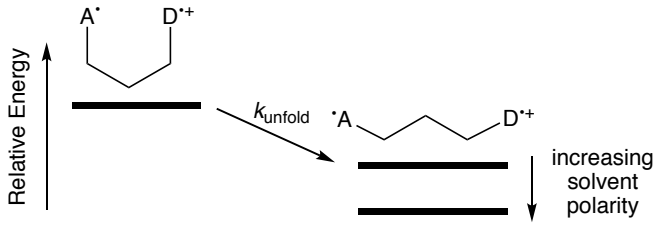
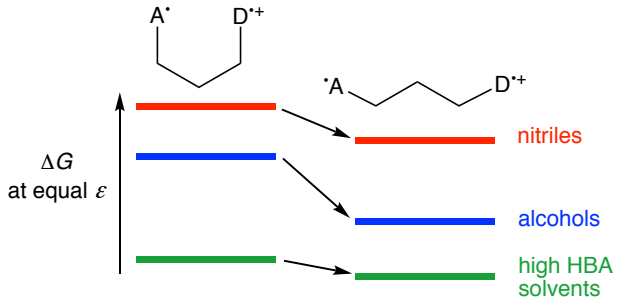


Figure 4. Dependence of the exciplex decay rate constant (k_{Ex}) on the solvent dielectric constant and functionality.



Scheme 3. Dependence of the driving force for exciplex unfolding on solvent polarity.

Interestingly, the data for the high HBA acidity solvents TFE, FA, and H_2O in Figure 4 show an opposite trend to what might be expected based on the results for aliphatic alcohols versus nitriles. These surprising results can be plausibly interpreted according to Scheme 4. As described above, at equal ε, alcohols could increase the driving force for unfolding due to greater hydrogen bonding with the isoquinolinyl radical in the unfolded versus folded state. In contrast, high HBA solvents should form a relatively strong hydrogen bond even in the folded state, that would only marginally increase in the unfolded state, thus decreasing the change in driving force for these solvents, leading to lower k_{Ex}. Additionally, high HBA solvents have smaller λ_s than alcohols of comparable ε (Figure 3) and would be expected to contribute less to the solvent stabilization of the unfolded structure.



Scheme 4. Driving force for exciplex unfolding for nitriles, alcohols, and high HBA solvents.

2.3. Solvent effect on the electronic couplings matrix elements.

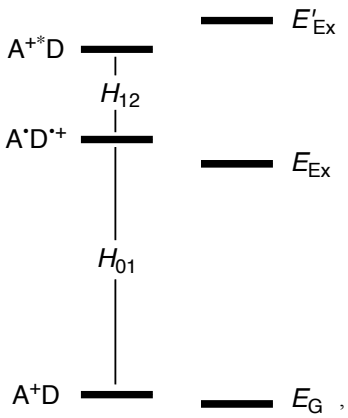
The combined data presented above indicate that several properties of the cationic exciplex of $\mathbf{1}^+$ can be influenced by hydrogen bonding to solvent molecules. These changes include spectral shifts, differences in the reorganization energies, and exciplex deactivation. It was important to test whether these changes could simply be due to

hydrogen bonding affecting the electronic coupling parameters due to changes in orbital overlap between the exciplex moieties. The exciplex electronic coupling parameters can be evaluated from the dependence of the radiative rate constants on the emission energies of the exciplex. Here we follow the previously described procedure applied to cationic exciplexes to determine these parameters.[1]

The interdependence of the radiative rate constant corrected for solvent refractive index (n), k'_f (eq 4), and the exciplex average emission frequency, $h\nu_{av}$, is governed only by two variable parameters: ($H_{01}\Delta\mu$) and H_{12}.[13] H_{01} is the electronic coupling matrix element between the ground state and the pure charge transfer (*CT*) state. $\Delta\mu$ is the difference between the static dipole moment of these two states. H_{12} is the electronic coupling matrix element between the pure *CT* state and the locally excited (*LE*) state (Scheme 5).

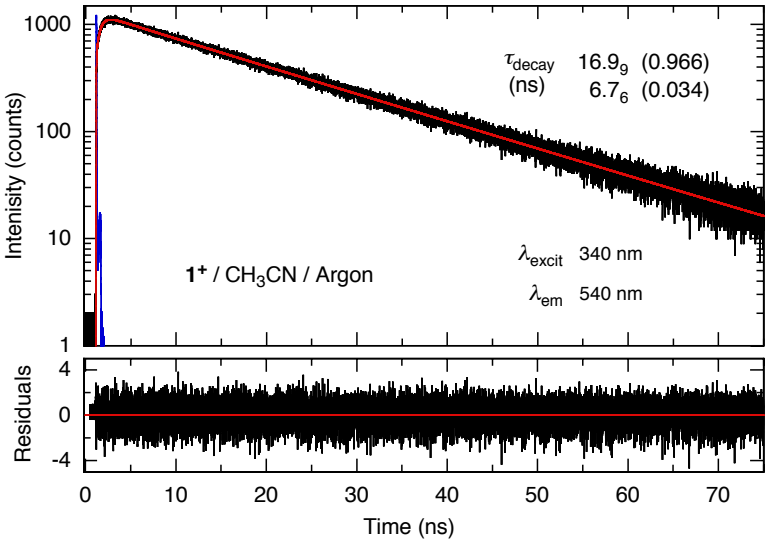
$$k'_f = k_f / f(n) \tag{4a}$$

$$f(n) = n\{(n^2 + 2)/3\}^2 \tag{4b}$$



Scheme 5. States involved in the electronic structure of a cationic exciplex. The basis states A^+D, $A^{\bullet}D^{\bullet+}$, and $A^{+*}D$ mix to form the ground, E_G, and excited states, E_{Ex} and E'_{Ex}. H_{01} and H_{12} are the electronic coupling matrix elements.

Time-correlated single photon counting (TCSPC) analyses for the exciplex of $\mathbf{1}^+$ indicated the presence of a major emissive contributor and a second, minor one. Figure 5 shows typical TCSPC data with acetonitrile and formic acid as solvents, including the lifetimes and the pre-exponentials for the major and minor exciplex emissions. The lifetimes of the exciplexes were obtained by global fitting of TCSPC data taken at 4-7 different wavelengths from 420 to 560 nm. The lifetimes of the minor exciplexes were



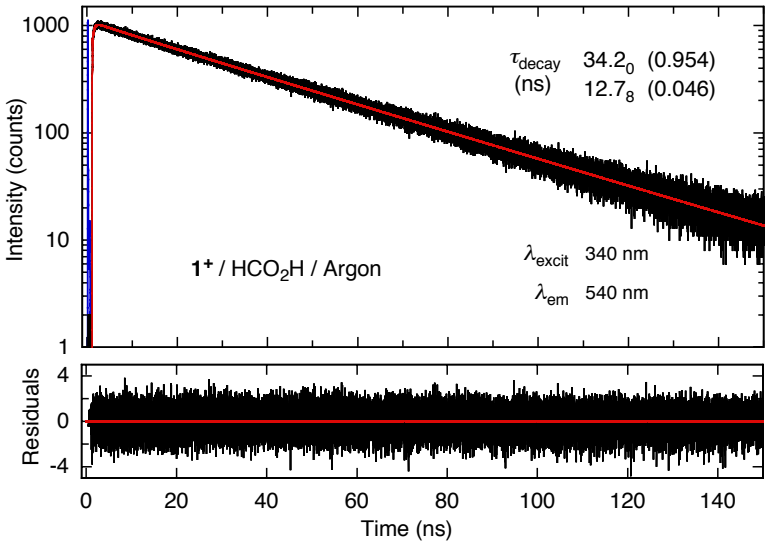


Figure 5. TCSPC measurements for the exciplexes of **1a** in argon-saturated acetonitrile (top) and formic acid (bottom) monitored at 540 nm, where contributions from the *LE* fluorescence are negligible. Experimental data in black, best fit in red, and instrument response function (IRF) in blue.

3 ± 0.5 times shorter than those of the corresponding main component. From the pre-exponential ratios of the TCSPC analyses at different emission wavelengths, the minor component was estimated to be 15-25 nm blue shifted from the main exciplex. The fraction of the minor exciplex component was obtained from eq (5), where A_1 and A_2 are the TCSPC pre-exponentials of the minor and major exciplexes, respectively, appropriately weighted by their lifetimes, τ_1 and τ_2. As described in detail elsewhere,[3] the spectral contribution of the minor exciplex can be subtracted using eq (5) from TCSPC data collected at multiple emission wavelengths. The data presented here are for the major exciplexes after subtraction of the minor components. Contributions from the minor exciplexes decrease with increasing solvent polarity from ~6% to negligible amounts in the most polar solvents. The radiative rate constants data in Table 2 are limited to solvents where the contribution from the minor component is < 3% of the total exciplex emission.

$$(A_1\tau_1)/(A_1\tau_1 + A_2\tau_2) \qquad (5)$$

The plot of k'_f versus $h\nu_{av}$ used to determine the electronic coupling parameters clearly shows no obvious deviations between the data in nitriles, alcohols, formic acid, and water (Figure 6). The electronic couplings ($H_{01}\Delta\mu$) and H_{12} that best fit the data are ~7.8 (10^3 $cm^{-1}D$) and ~1.48 (10^3 cm^{-1}), respectively, obtained as described previously.[1]

We note that these values differ slightly from those for several differently methyl-substituted analogues of $\mathbf{1}^+$ in water, where ($H_{01}\Delta\mu$) and H_{12} are 10.4 (10^3 $cm^{-1}D$) and 1.37 (10^3 cm^{-1}), respectively.[2] In that data set, the point for $\mathbf{1}^+$ in the k'_f versus $h\nu_{av}$ plot was slightly below those of the other analogues, pointing to different electronic couplings. It is noteworthy that data points for the unsubstituted and the 2,4,5-trimethylphenyl derivatives measured *in acetonitrile* fell on the same fitting curve for those in water,[2] providing additional support that differences in electronic couplings due to hydrogen bonding, if any, are minimal.

Table 2. Average emission energies, emission quantum yields, and radiative rate constants for the exciplex of $\mathbf{1}^+$ in different solvents.

solvent	n^a	$h\nu_{av}{}^b$ (10^3 cm^{-1})	$\phi^f{}_{Ex}{}^c$	$k_{Ex}{}^d$ (10^7 s^{-1})	$k_f{}^e$ (10^6 s^{-1})	$k'_f{}^f$ (10^6 s^{-1})
CH_3CN	1.3438	19.91_6	0.040_2	5.88	2.36_7	1.09_4
C_2H_5CN	1.3664	20.06_0	0.054_0	4.72	2.54_8	1.12_2
$HOCH_2CH_2OH$	1.4308	19.86_5	0.087_5	3.09	2.70_0	1.03_7
CH_3OH	1.3286	20.00_3	0.025_2	9.06	2.28_0	1.08_9
C_2H_5OH	1.3613	20.12_9	0.041_2	6.49	2.67_6	1.19_1
$1\text{-}C_3H_7OH$	1.3855	20.22_9	0.054_5	5.32	2.89_9	1.26_2
H_2O	1.3330	19.36_0	0.032_6	5.95	1.93_9	0.91_8
HCO_2H	1.3714	20.10_8	0.089_9	2.92	2.62_9	1.14_6

[a]Solvent refractive index. [b]Average emission energy (from references [2] and [3]). [c]Exciplex fluorescence quantum yield. [d]Exciplex decay constant (Table 1). [e]Exciplex radiative rate constant ($k_{Ex} \times \phi^f{}_{Ex}$). [f]Exciplex radiative rate constant corrected for the solvent refractive index (eq 4a).

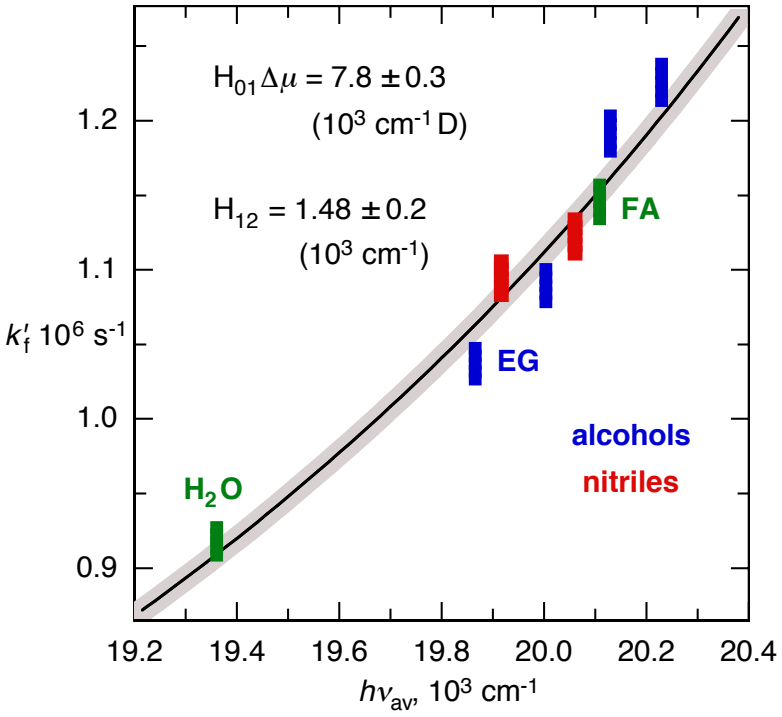


Figure 6. Plot of k'_f versus $h\nu_{av}$, for the exciplex of $\mathbf{1}^+$ in different solvents. The error bars of the data points represent ±1%. The thickness of the fitting curve indicates the uncertainty in the electronic couplings.

3. Conclusions

Emission from the cationic exciplex of $\mathbf{1}^+$ is strongly affected by solvent functionality. In the excited state, hydrogen bonding of protic solvents to the nitrogen of the isoquinolinyl radical moiety results in increased stabilization of the exciplex. As a result, at equal ε, the energy gap between the ground and excited states (ΔG) decreases from nitriles to alcohols by ~0.03 eV and the solvent reorganization energy (λ_s) by ~0.04 eV. From alcohols to high hydrogen-bond acidity solvents (HBA), the decrease in ΔG and λ_s is about three times as much, ~0.1 and ~0.14 eV, respectively. In addition, the exciplex decay via solvent insertion to form a stretched conformer is also affected by hydrogen bonding. At equal dielectric constant, increased hydrogen bonding in alcohols versus nitriles increases the driving force and the rate constant for unfolding. However, in this

case, the much stronger hydrogen bond in high HBA solvents, coupled with relatively low solvent stabilization, is proposed to lead to a *smaller* driving force for unfolding and thus lower the unfolding rate constant. In contrast to the pronounced role of hydrogen bonding on the exciplex energetics, the electronic couplings of the exciplex states were not detectably affected. It will be interesting to determine how other examples of cationic exciplexes depend on different types of solvent functionalities.

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: cationic exciplex • fluorescence • hydrogen bonds • solvatofluorochromism • spectroscopic properties

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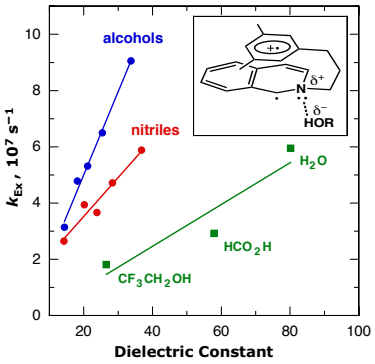
TOC graphic and accompanying text:



Hydrogen Bonding to **Cationic Exciplexes** affects the rate constants for exciplex decay (k_{EX}) in a complex way depending on the hydrogen bond donor ability of the solvent. Hydrogen bonding decreases the ground to excited state energy gaps and solvent reorganization energies, but increases the vibrational reorganization energies. In contrast, the electronic couplings between the exciplex ground, excited, and charge transfer states do not show a solvent functionality dependence.