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Solvent Dependence of Cationic-Exciplex Emission: Limitation of Solvent Polarity Functions and the Role of Hydrogen Bonding

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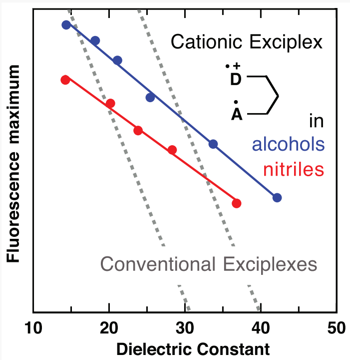
ABSTRACT: Conventional exciplexes are products of excited-state charge generation reactions between neutral reactants (e.g., $A^* + D \rightarrow A^{\bullet-}D^{\bullet+}$), whereas cationic exciplexes are products of charge shift reactions of cations with neutral donors (e.g., $A^{+*} + D \rightarrow A^{\bullet}D^{\bullet+}$). Compared herein is the solvent-dependent fluorescence of a cationic exciplex with extant data for conventional exciplexes. Although linear correlations of conventional exciplex emission maxima with the Lippert−Mataga solvent polarity function are well documented in low to moderate polarity solvents, the correlations are often poor in more polar solvents. A number of such plots in moderate to high polarity solvents show a strong curvature. Intriguingly, for these same cases, plots of emission maxima versus the solvent dielectric constant (ε) are remarkably linear. Interestingly, emission maxima for the cationic exciplex of **1**$^+$ in nitrile and alcohol solvents also correlate linearly with ε. The solvent dependency for cationic exciplex emission maxima on ε is ca 1/3 of that for conventional exciplexes, which is ascribed to solvent stabilization of both the excited state *and the ground state* for cationic exciplexes. Differences in exciplex emissions between nitrile and alcohol solvents for **1**$^+$ are attributed to hydrogen bonding, with larger differences in higher hydrogen-bond acidity solvents.



1. INTRODUCTION

A characteristic feature of exciplexes is the bathochromic shift of their fluorescence spectra with increasing solvent polarity.[1−4] The spectral shift is usually the result of increased stabilization of the excited state and increased reorganization energies. We recently reported a new class of exciplexes in which the acceptor is a cation reacting with a neutral donor, which differs from the conventional exciplexes, where both reactants are neutral.[5] Formation of conventional exciplexes represents a charge formation reaction, eq 1, whereas for cationic exciplexes, it is a charge shift reaction, eq 2.

$$A + D \xrightarrow{h\nu} A^*D \leftrightarrow A^{\bullet-}D^{\bullet+} \tag{1}$$

$$A^+ + D \xrightarrow{h\nu} A^{+*}D \leftrightarrow A^{\bullet}D^{\bullet+} \tag{2}$$

We recently synthesized a series of isoquinolinium electron acceptors tethered to alkylbenzene donors that showed remarkably strong fluorescence in water, extending the potential of using exciplex emission to probe aqueous media.[6] Given the importance of solvent effects on exciplex emission, it was of interest to compare the effect of solvent polarity on cationic exciplex fluorescence with that for conventional exciplexes.

2. EXPERIMENTAL SECTION

2.1. Materials. In general, solvents were fractionally distilled before use. Following an earlier procedure used to purify acetonitrile,[7] octanenitrile was treated by heating with $AlCl_3$ (100°, 1 h), decanted, and distilled. The distilled material was then heated with $KMnO_4/Li_2CO_3$ (100°, 1 h) and fractionally distilled. **1**$^+$ PF_6^- was prepared as previously described.[6]

2.2. Fluorescence Measurements. Fluorescence spectra were measured using a Fluorolog-3 spectrofluorometer (Jobin Yvon, HORIBA) at 20 °C and were 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

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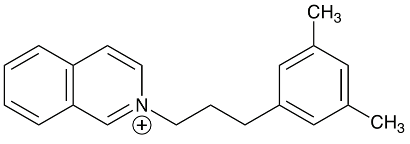
optical densities of solutions typically varied between ∼0.05−0.25 depending on the excitation wavelength.

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 $(1 - 10^{-\mathrm{OD}})$. *N*-Methylisoquinolinium in air-saturated acetonitrile ($\phi_f = 0.50$)[5] and 9,10-dicyanoanthracene in air-saturated acetonitrile ($\phi_f = 0.80$)[6] were used as actinometers.

2.3. Time-Correlated Single Photon Counting. Fluorescence lifetime measurements were made at 20 °C 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 the excited states between laser pulses. The excitation beam (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 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 software package (PicoQuant, ver. 4.6.0.0).

3. RESULTS AND DISCUSSION

The symmetrically substituted 3,5-dimethylphenyl derivative, $\mathbf{1}^+$, was used to investigate solvent effects on cationic exciplex emission. $\mathbf{1}^+$ was chosen because its exciplex has a high degree of charge transfer character and, as described earlier, a symmetrically substituted donor decreases the number of folded, exciplex-like conformers from four to two.[6]



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

The choice of solvents was limited to those with relatively high dielectric constants (ε) to avoid potential ion pairing effects. We focused on two series of solvents, alcohols and nitriles, with varying polarities (Table 1). The relatively high fluorescence quantum yields (∼0.03−0.1) in comparison to conventional exciplexes, along with the absence of any degradation or product formation during the measurements, made it possible to average many spectra to minimize noise. Emission spectra were measured using different excitation wavelengths, which result in spectra with varying contributions of residual uncomplexed A^{+*} and exciplex emissions. This allowed for accurate extraction of the exciplex spectra (see the heavy red curve in Figure 1) and for determining reliable differences in emission maxima over a rather narrow range (additional figures in Supporting Information).

TCSPC was used to determine the exciplex lifetimes (τ_{Ex}). Besides the exciplex data listed in Table 1, TCSPC analyses monitored at emission wavelengths between 420 and 560 nm indicated the presence of a second, minor exciplex. The lifetimes of the minor exciplex are 3.0 ± 0.5 times shorter than those of the corresponding main component. From the pre-exponential ratios at different emission wavelengths, the minor component is estimated to be 15−25 nm blue-shifted from the main exciplex. The highest contribution of the minor exciplex is ∼6% in the least polar solvents (octanenitrile and 3-pentanol) and decreases to ≤3% in the other solvents. The data presented in Table 1 and in the figures are of the major exciplex after subtraction of the minor component (see Supporting Information for the subtraction procedure and possible structures for the major and minor exciplexes). Similar to earlier results with $\mathbf{1}^+$ in $\mathrm{H_2O}$,[6] emission spectra and TCSPC data show that exciplex formation occurs from both folded and stretched conformers. With increasing excitation wavelength, the fraction of exciplex formation from folded conformers increases, leading to an increase of exciplex emission relative to excitation of uncomplexed A^+ (Figure 1).

3.1. Limitation of the Lippert−Mataga Solvent Polarity Function f_{solv}. The dependence of exciplex spectra on solvent polarity is usually evaluated by plotting the inverse of the exciplex maximum ($\lambda_{\max}^{-1}$), from $I(\lambda)$ versus wavelength, versus the Lippert−Mataga (LM) solvent function, f_{solv}, eq 3.[8−10] For data in low to moderate polarity solvents, such plots are reasonably linear, and their slopes are commonly used to determine exciplex dipole moments.[8,9] When the data are extended to high polarity solvents, however, noticeable scatter from the linear trend is often observed. It has also been pointed out that f_{solv} tends to level off at high solvent dielectric constants, and then, it becomes more difficult to establish a clear correlation with exciplex emission maxima.[11] When limited to moderate to high polarity solvents, plots of $\lambda_{\max}^{-1}$ versus f_{solv} for a variety of exciplexes with aromatic amines as electron donors show a systematic, but nonlinear, correlation (Figure 2a). In one case with an aliphatic amine as the electron donor, Lewis and Cohen pointed out that in a series of medium to high polarity solvents, no linear dependency of $\lambda_{\max}^{-1}$ on f_{solv} was observed; a linear dependency on the solvent dielectric constant (ε) was found instead.[11] Interestingly, plots of $\lambda_{\max}^{-1}$ versus ε for the exciplex data in Figure 2a are remarkably linear (Figure 2b), demonstrating that Lewis' results seem to be more general than previously recognized. These correlations are clearest for solvents belonging to a homologous series, as in several examples in Figure 2.

$$f_{\mathrm{solv}} = [(\varepsilon - 1)/(2\varepsilon + 1)] - [(n^2 - 1)/(4n^2 + 2)] \tag{3}$$

3.2. Solvent Dependency of Charge Shift Versus Charge Formation Exciplex Emissions. One of the objectives in this study was to compare the solvent polarity dependencies of conventional and cationic exciplex emissions. As shown in Section 3.1, for medium to high polarity solvents, the emission maxima of conventional exciplexes correlate linearly with ε, not f_{solv}. Moreover, although the LM solvent function is usually adequate for conventional exciplexes in *less polar* solvents, it relied on the assumption that the initial and final charge distributions of the acceptor/donor pair can be modeled as point dipoles. This assumption cannot describe a cationic exciplex unless it is ion-paired, and we are not aware of a suitable alternative theory. Interestingly, plots of $\lambda_{\max}^{-1}$ versus ε

Table 1. Exciplex of 1^+ in Different Solvents

solvent	ε[a]	λ_{max}[b]	$h\nu_{max}$[c]	$h\nu_{av}$[d]	fwhm[e]	τ_{Ex}[f]
CH_3CN	36.80	477.3	20.39	19.91_6	4.85_4	17.1
C_2H_5CN	28.32	474.5	20.53_5	20.06_0	4.82_5	20.8
n-C_3H_7CN	23.82	473.5	20.59	20.09_5	4.77_5	27.3
n-C_4H_9CN	20.18	472.1	20.67	20.17_2	4.73	25.5
n-$C_7H_{15}CN$	14.23	470.9	20.73	20.24_6	4.70_4	37.7
$HOCH_2CH_2OH$	42.14	477.0	20.37_5	19.86_5	4.95_1	29.9
CH_3OH	33.71	474.2	20.52	20.00_3	4.95_1	10.9
C_2H_5OH	25.41	471.8	20.64_5	20.12_9	4.87_6	15.4
n-C_3H_7OH	21.10	469.9	20.74	20.22_9	4.82_9	18.9
n-C_4H_9OH	18.16	468.9	20.80	20.28_6	4.80_7	27.3
$(C_2H_5)_2CHOH$	14.35	468.1	20.85_5	20.33_9	4.77_7	31.8
H_2O[g]	80.16	488.8	19.83	19.37_3	5.11_6	16.8
HCO_2H	57.9	473.3	20.62_8	20.10_8	4.71_9	34.0
CF_3CH_2OH	26.53	467.7	20.93	20.43_1	4.52_6	55.0

[a] Dielectric constant. [b] Exciplex emission maximum (nm) from the spectral irradiance, $I(\lambda)$, versus wavelength. [c] Emission maximum (10^3 cm^{-1}) of reduced spectrum ($I(\lambda)/\tilde{\nu}^3$ versus wavenumber $\tilde{\nu}$. [d] Average emission energy (10^3 cm^{-1}); based on data in ref 6, these $h\nu_{av}$ values indicate that the charge transfer character *in all listed solvents* is >90%. [e] fwhm of the reduced spectrum (10^3 cm^{-1}). [f] Exciplex lifetime (ns). [g] From ref 6.

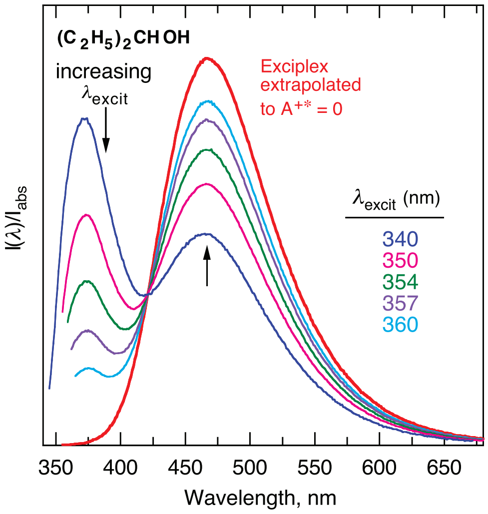


Figure 1. Emission spectra of **1**$^+$ in 3-pentanol at different excitation wavelengths, corrected for the fraction of absorbed light (I_{abs}). Heavy red curve is the average exciplex spectrum after subtracting contributions from uncomplexed A^{+*} fluorescence ($\lambda_{max} \approx 370$ nm).

for the cationic exciplex of **1**$^+$ also show a good linear correlation in each series of solvents, nitriles and alcohols (Figure 3). The emission maximum of **1**$^+$ previously reported in water[6] also fits well on the linear correlation. Because the emission maxima of both conventional exciplexes and the exciplex of **1**$^+$ all correlate linearly with ε, we use these empirical correlations to compare the solvatochromic behaviors of the two types of exciplexes.

The plots of λ_{max}^{-1} versus ε for the conventional (charge formation) exciplexes (Figure 2b) have similar slopes of ≈−44 cm^{-1}, with one exception involving an aliphatic amine rather than an aromatic amine as the donor moiety (curve 1, Figure 2b). The larger slope with the aliphatic amine as the electron donor (−67 cm^{-1}) can be attributed to higher charge localization, which leads to larger solvent interaction with the amine radical cation. By comparison, the corresponding slopes for the cationic (charge shift) exciplex of **1**$^+$ in nitriles and alcohols are −12.7 and −14.7 cm^{-1}, respectively (Figure 3). To understand these differences, it is useful to briefly review how solvent polarity affects the emission maxima of exciplexes.

Two primary factors contribute to the effect of solvent polarity on exciplex emission maxima, and their effects are additive: (1) solvent stabilization of charged species and (2) the solvent reorganization energy.[16,17] These factors are illustrated in Scheme 1a for a conventional exciplex and Scheme 1b for a cationic exciplex, which compare a pair of solvents for each exciplex, with solvent 2 being the more polar. There is no attempt to compare the absolute stabilization of each exciplex relative to the stabilization in a nonpolar solvent, and the relative displacements among the "potential energy" curves will depend on which exciplex of either kind is chosen for the comparison.

In a conventional exciplex, increasing solvent polarity generally stabilizes the zwitterionic excited state, but it has relatively little effect on the energy of the neutral, equilibrium ground state. Thus, with increasing solvent polarity (from solvent 1 to solvent 2, Scheme 1a), the energy gap between the excited state and the ground state (ΔG) decreases ($\Delta G_2 < \Delta G_1$), contributing to a shift of the emission to lower energy (see discussion of $h\nu_{av}$ below). In contrast, for cationic exciplexes such as those of **1**$^+$, increasing solvent polarity tends to stabilize *both* the ground and the excited states. In a case where the ground and excited states are stabilized equally, ΔG will be constant regardless of the solvent polarity ($\Delta G_2 = \Delta G_1$).[18,19] More generally, the dependence of ΔG on solvent polarity is expected to be much weaker for cationic exciplexes than for conventional exciplexes, and the direction of the dependency will depend on whether the excited state is stabilized more than the ground state, or vice versa.

The reorganization energy also affects the emission energies of both exciplexes because the energy of the final state of the emission process (Franck−Condon ground state) is higher than the equilibrium energy of the ground state. In Scheme 1, the horizontal displacement of the "potential energy" curve for the excited state in either solvent, relative to that for the ground-state, represents schematically the displacement of low frequency coordinates (mostly involving solvent motion) and of high-frequency coordinates (intramolecular vibrations). The resulting decrease of the energy gap between the minimum of the excited-state curve and the ground-state curve represents

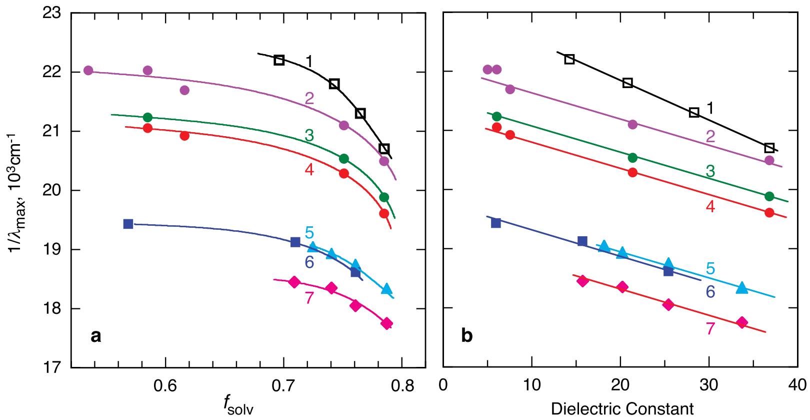


Figure 2. Plot of literature-reported exciplex emission maxima vs (a) f_{solv}, and (b) dielectric constant. (1) Phenanthrene linked at C9 via a trimethylene chain to a dimethylamino group (ref 11) in nitrile solvents. (2,3,4) Pyrene linked at C1 via a trimethylene chain to indole at N1 and to *N*-methylindole at C2 and C3, respectively, in mixed classes of solvents (ref 12). (5) Pyrene linked at C1 via a trimethylene chain to the para-position of *N*,*N*-dimethylaniline in alcohols (ref 13). (6) Anthracene linked at C9 via a trimethylene chain to the para-position of *N*,*N*-dimethylaniline in alcohols (ref 14). (7) Anthracene/*N*,*N*-diethylaniline in alcohols (ref 15). The lines in (b) have a slope of −67 cm^{-1} for (1) and an average of −44 cm^{-1} for (2−7).

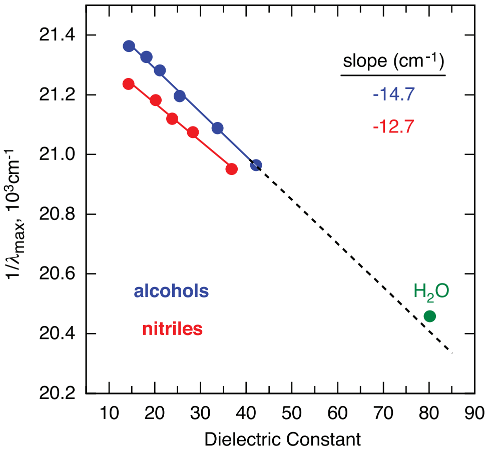
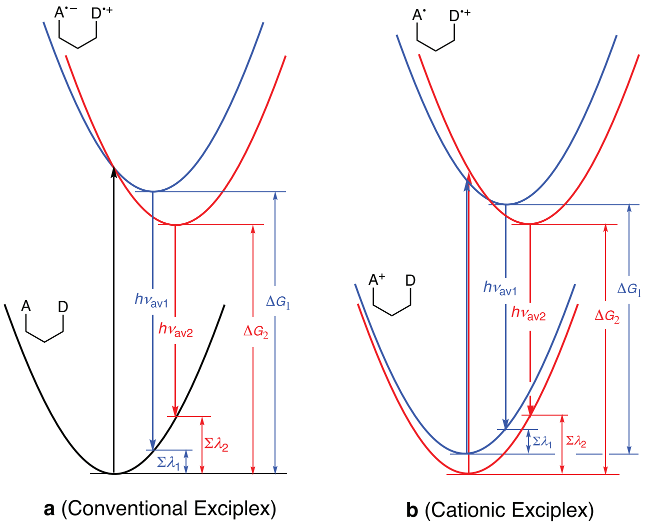


Figure 3. Plot of emission maxima for exciplexes of $\mathbf{1}^+$ in alcohol and nitrile solvents (from Table 1) vs dielectric constant.

Scheme 1. Dependence of Potential Energy Curves of (a) Conventional and (b) Cationic Exciplexes on Solvent Polarity[a]



a (Conventional Exciplex) **b** (Cationic Exciplex)

[a] Blue, less polar solvent; red, more polar solvent; black, both solvents.

the total reorganization energy, $\Sigma\lambda$, which is the sum of a (mostly) solvent component, λ_s, and a high-frequency vibrational component λ_v. The reorganization energies in the two solvents are labeled $\Sigma\lambda_1$ and $\Sigma\lambda_2$ in Scheme 1. In general, the actual values will depend on which two exciplexes are chosen for comparison; but, when comparing exciplexes with similar structures, it is reasonable to expect that the reorganization energies will be roughly the same for a conventional and a cationic exciplex (see below).

According to Marcus,[16] λ_s depends on the distribution of the charge that is transferred between the acceptor and the donor but not on the net charge of the exciplex. Thus, λ_s can reasonably be expected to have a similar value for a conventional exciplex and a cationic exciplex whenever the acceptor/donor pair has a similar size and shape in both exciplexes. For conventional exciplexes in solvents of low to moderate polarity, λ_s increases with increasing polarity; we assume that the same is true in highly polar solvents even though an appropriate theory is lacking (cf. Figure 2). The vibrational reorganization energies (λ_v) of conventional and cationic exciplexes with similar molecular skeletons are also expected to be similar. Therefore, the total reorganization energy (the sum of the two components, $\Sigma\lambda = \lambda_s + \lambda_v$), is also expected to be similar for typical conventional and cationic exciplexes, as depicted in Scheme 1.

For a conventional exciplex, the solvent-dependencies of both ΔG and $\Sigma\lambda$ contribute to a decrease of the emission maximum with increasing solvent polarity. For a cationic exciplex, the dependency of $\Sigma\lambda$ is expected to be similar, whereas ΔG is expected to be weakly solvent-dependent, if at all. This expectation is borne out by the smaller slopes of $\lambda_{\max}^{-1}$ versus ε for cationic versus conventional exciplexes (Figure 2b vs Figure 3).

The controlling parameters, ΔG and the reorganization energies λ_s and λ_v, can be determined from a quantitative analysis of the charge-transfer reduced spectrum, $I(\lambda)\tilde{\nu}^{-3}$ versus wavenumber $\tilde{\nu}$.[17] Reduced exciplex spectra of $\mathbf{1}^+$ are shown in Supporting Information. The factor of $\tilde{\nu}^{-3}$ does three things: converts a spectrum $I(\lambda)$ from counts per second per nm at wavelength λ to counts per cm^{-1} per second at wavenumber $\tilde{\nu}$, eliminates the factor of $\tilde{\nu}^3$ that appears in the standard formula for the rate of spontaneous emission,[20,21] and compensates for the dependence of the transition moment on photon energy.[22] The energy of an emitted photon, averaged over the reduced spectrum, is denoted $h\nu_{av}$, and it is related to the parameters described above by eq 4. An important feature of the reduced spectrum is that the *bandshape* does not depend on ΔG; two spectra with the same reorganization parameters but different values of ΔG can be superimposed simply by shifting the energy scale of one spectrum by an amount equal to the difference in ΔG.[17]

$$h\nu_{av} = \Delta G - \Sigma\lambda \tag{4}$$

There is a relationship between ΔG and $\Sigma\lambda$ for a typical conventional exciplex. Consider the corresponding *absorption* process for a neutral and nonpolar (negligible dipole moment) A/D pair in the geometry of a conventional exciplex (black arrow in Scheme 1a). The energy of an absorbed photon, averaged over the appropriately reduced spectrum, $h\nu'_{av}$, obeys an equation similar to eq 4, namely, $h\nu'_{av} = \Delta G + \Sigma\lambda$.[16] Even if the solvent is highly polar, the molecules surrounding the A/D pair in the equilibrium ground state are not oriented, and they are still not oriented immediately after the absorption event (i.e., in the Franck−Condon excited state), so $h\nu'_{av}$ is approximately independent of the polarity of the solvent. Thus, as one solvent is replaced by another, ΔG and $\Sigma\lambda$ must change by approximately equal and opposite amounts. Returning to the exciplex *emission* (red and blue arrows in Scheme 1a), with increasing polarity of the solvent, the two factors should make approximately equal contributions to the decreasing emission energy $h\nu_{av}$. Data for the conventional exciplexes of 2,6,9,10-tetracyanoanthracene with several alkylbenzene donors provide experimental support of this connection between ΔG and $\Sigma\lambda$, where the increases in $\Sigma\lambda$ are ~1.15 times the decreases in ΔG.[26]

As described above, for cationic exciplexes, the ground and excited states are both expected to be increasingly stabilized with increasing solvent polarity. If the two states are stabilized equally, then ΔG will be constant and the decrease in $h\nu_{av}$ and λ_{max}^{-1} with increasing solvent polarity will be due to only the increase in solvent reorganization energy (λ_s), that is, only one of the two nearly equal factors that would affect the emission energies of conventional exciplexes. Because λ_s is expected to have similar values for conventional and cationic exciplexes, the dependency of λ_{max}^{-1} on solvent polarity for the cationic exciplex should be approximately half that of conventional exciplexes. As judged by their dependencies of λ_{max}^{-1} on ε, the slope for $\mathbf{1}^+$ is even less than half that for the conventional exciplexes shown in Figure 2b. A possible explanation revealed by spectral fitting is described in Section 3.3.

3.3. Specific Solvent−Solute Interactions, Nitriles Versus Alcohols.

As shown in Figure 3, at the same dielectric constant, exciplex spectra for $\mathbf{1}^+$ in nitrile solvents are slightly *red-shifted* relative to those in alcohols. Evidently, at equal values of ε, either ΔG is slightly smaller and/or $\Sigma\lambda$ is slightly larger in the nitrile solvents. Both ΔG and $\Sigma\lambda$ affect the position of the band (specifically, $h\nu_{av}$), whereas only $\Sigma\lambda$ affects the bandshape, so the bandshape is the key to which factor or factors contribute to the difference between the two sets of solvents. As depicted in Scheme 1, for the solvent with the larger reorganization energy (the larger horizontal displacement of the excited-state curve), the ground-state curve under the bottom of the excited-state curve is steeper, implying a broader distribution of emission energies. In fact, the emission spectra in the alcohols are *broader* than in the nitriles at comparable ε, as indicated by the plot of fwhm versus ε in Figure 4.[27] Spectral fitting revealed a rather surprising explanation of the blue-shifted and broader spectra in the alcohols.

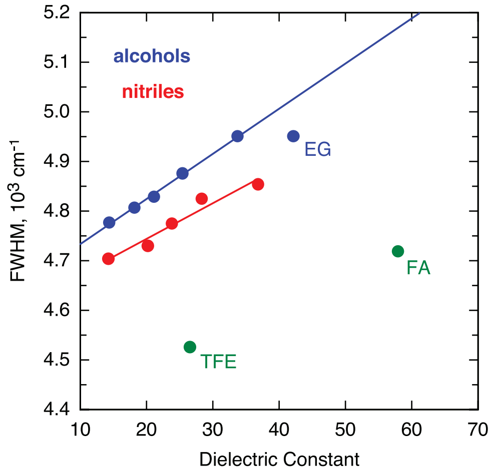


Figure 4. Plot of fwhm of exciplex spectra vs solvent dielectric constant. Solvents: blue points (alcohols), red points (nitriles), EG (ethylene glycol), TFE (trifluoroethanol), and FA (formic acid).

As described previously, the parameters ΔG, λ_s, and λ_v can be determined by fitting the spectra to a theoretical model.[17] To fit the overall bandshapes of $\mathbf{1}^+$ with sufficient accuracy, it was found necessary to consider two reorganized (displaced) normal modes, with energies $h\nu_{v1} = 0.174$ and $h\nu_{v2} = 0.33$ eV (1400 and 2660 cm^{-1}) in both the alcohols and the nitriles. In this context, the quantity λ_v is defined by ($\lambda_{v1} + \lambda_{v2}$). It is worth noting that the spectral model makes no use of the dielectric constant, refractive index, or other solvation parameters that may determine the actual values of ΔG or λ_s.

Results of the fitting procedure are summarized in Table 2 and Figure 5. Over approximately the same range of dielectric constant, both ΔG and λ_s are larger in the nitriles than in the alcohols, and both ΔG and λ_s increase with increasing solvent polarity, with ΔG increasing only half as rapidly as λ_s. Although the two vibrational modes (1400 and 2660 cm^{-1}) have their own reorganization energies (λ_{v1} and λ_{v2}), the latter is relatively small and approximately the same in both the nitriles and the alcohols (~0.04 eV), whereas the values of λ_{v1} differ by more (0.115 eV in the nitriles, 0.160 eV in the alcohols).[28]

According to eq 4, $h\nu_{av}$ is given by ($\Delta G - \lambda_s - \lambda_v$). Within the present range of dielectric constants, upon going from any nitrile to an alcohol with the same value of ε, the three contributions change by approximately -0.03_5, +0.08, and −0.037 eV, respectively (Table 2 and Figure 5). The changes nearly cancel out, resulting in the slightly redder spectra in the nitriles than in the alcohols (lower $h\nu_{av}$, Figure 6, and lower λ_{max}^{-1}, Figure 3).

For values around the present parameters, the simulation model indicates that the fwhm increases much more rapidly (~4 fold) with an increase in λ_v than with an equal increase in λ_s. Thus, the effect of the ~0.037 eV larger λ_v for alcohols outweighs that of the ~0.08 eV smaller λ_s. Remarkably, the exciplex has a broader spectrum (larger fwhm) in the solvents with the smaller total reorganization energies (the alcohols, Figure 4).

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Table 2. Fitting Parameters of Exciplex Spectra

solvents	ΔG (eV)	λ_s (eV)	λ_v (eV)	$h\nu_{av}$ (10^3 cm^{-1})
nitriles	3.35−3.38	0.68−0.75	0.162 ± 0.002	19.92−20.25
alcohols	3.31−3.34	0.59−0.66	0.199 ± 0.002	19.87−20.34
formic acid	3.26_3	0.56_4	0.20_6	20.11
trifluoroethanol	3.20_6	0.46_4	0.20_8	20.44

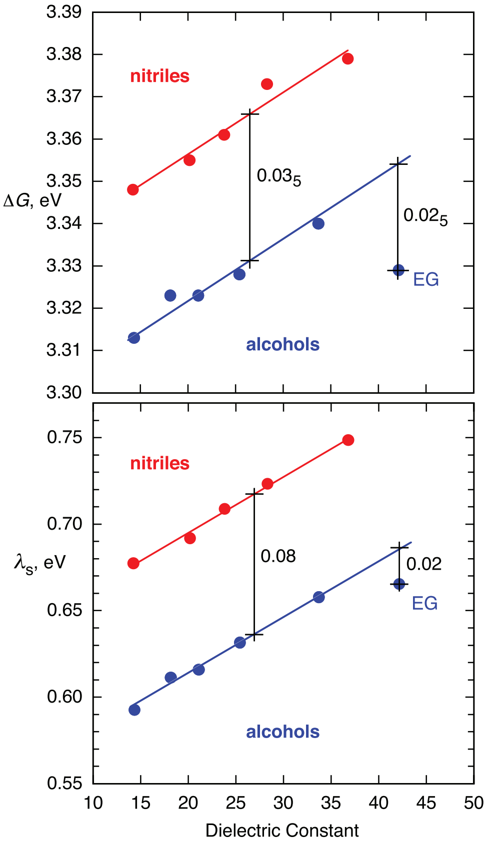

Figure 5. Dependence of ΔG (top) and λ_s (bottom) on solvent dielectric constant. Solvents: red points (nitriles), blue points (alcohols), and EG (ethylene glycol).

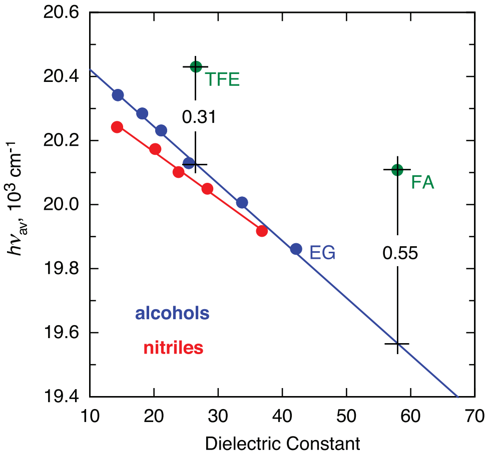

Figure 6. Dependence of the average emission energy, $h\nu_{av}$, on solvent dielectric constant. Solvents: blue points (alcohols), red points (nitriles), EG (ethylene glycol), TFE (trifluoroethanol), and FA (formic acid).

As mentioned above, ΔG increases with increasing solvent polarity (Figure 5). Evidently, *in the case of* $\mathbf{1}^+$, the equilibrium ground state is stabilized to a somewhat greater extent than the excited state as the solvent is made more polar. Were it not for the increasing ΔG—that is if λ_s was the only factor that depended on solvent polarity—the slopes of λ_{max}^{-1} versus ε in Figure 3 would be −23.7 for the nitriles and −25.7 cm^{-1} for the alcohols, which are close to half as large as for most of the conventional exciplexes (−44 cm^{-1}, Figure 2b), as anticipated in Section 3.2.

For ethylene glycol, the ΔG, λ_s, and fwhm data (points labeled EG in Figures 4 and 5) deviate from the trend of the other alcohols, whereas the λ_{max}^{-1} and $h\nu_{av}$ data (Figures 3 and 6) fit the respective trends well. The negative deviations in ΔG and λ_s for ethylene glycol (Figure 5) have opposite and nearly equal effects on the emission maximum (both ~0.02−0.02_5 eV), and therefore negligible net effect on $h\nu_{av}$ and λ_{max}^{-1}. The fwhm does not depend on ΔG but decreases with decreasing λ_s, hence the deviation of the ethylene glycol point (Figures 4 and 5).

The differences between alcohols and nitriles described above might be explained by the potential for alcohols to participate in hydrogen bonding, which could affect the structure of the exciplex. The lesser ΔG (Figure 5) and the greater λ_v in alcohols (Table 2) could be due to hydrogen bonding to the isoquinolinyl radical moiety, which would stabilize the excited state and somewhat alter its vibrational reorganization. To test this hypothesis further, we investigated the effect of solvents with stronger hydrogen bonding abilities.

3.4. Solvents with High Hydrogen-Bond Acidity.

To test the possible influence of hydrogen bonding on the exciplex emission of $\mathbf{1}^+$, we investigated two solvents with relatively high hydrogen-bond acidity, trifluoroethanol and formic acid. In both solvents, the emission spectra were blue-shifted relative to alcohols with comparable dielectric constants (much larger $h\nu_{av}$ and λ_{max}^{-1}; points TFE and FA in Figures 6 and S8 in Supporting Information). In these solvents, the higher energy exciplex emission is accompanied by a noticeably smaller fwhm (Figure 4), indicating smaller reorganization energies relative to alcohols of comparable polarity.

Spectral fitting revealed opposing effects on $h\nu_{av}$ in these strongly hydrogen bonding solvents (Table 2, Figure 7). Relative to the alcohols at equal values of the dielectric constant, both ΔG and $\Sigma\lambda$ are decreased. Individually, these factors would decrease or increase $h\nu_{av}$ (eq 4), but as shown in Figure 7, the decrease of $\Sigma\lambda$ for TFE and FA (0.161 and 0.175 eV) is larger than the corresponding decrease of ΔG (0.124 and 0.107 eV, respectively). The net effect is the larger $h\nu_{av}$ shown in Figure 6 for these two solvents: (0.161−0.124) = 0.037 eV ≈ 310 cm^{-1} for trifluoroethanol and (0.175−0.107) = 0.068 eV ≈ 550 cm^{-1} for formic acid (Figure 6). Compared with the alcohols, λ_v is only slightly larger in these two strongly hydrogen-bonding solvents. Thus, the decrease in fwhm relative to that of alcohols at equal ε (Figure 4) is due to smaller λ_s.

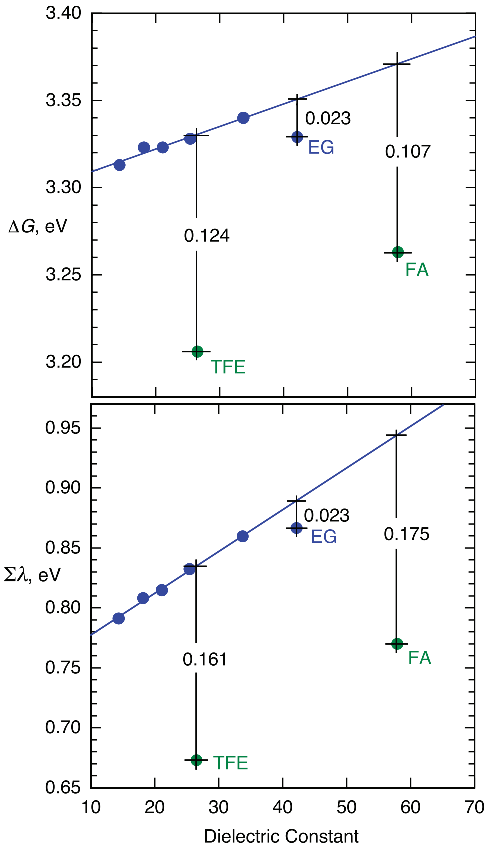

Figure 7. Dependence of ΔG (top) and $\Sigma\lambda$ (bottom) on solvent dielectric constant. Solvents: blue points (alcohols), points labeled EG (ethylene glycol), TFE (trifluoroethanol), and FA (formic acid).

The 0.08 eV smaller λ_s for alcohols versus nitriles (Figure 5) and the further ~0.16−0.17 eV decrease in λ_s in the higher hydrogen-bond acidity solvents trifluoroethanol and formic acid versus the alcohols (Figure 7) is likely due to hydrogen bonding. The nitrogen of the isoquinolinyl radical in the excited state is expected to be a reasonable hydrogen bond acceptor. Hydrogen bonding to the isoquinolinyl radical by protic solvents would be expected to impart some partial positive charge to this exciplex fragment and, correspondingly, some partial negative charge to the hydrogen bond donor. The negative charge on the hydrogen bond donor might be expected to be rather diffuse because of the network of hydrogen bonds with other solvent molecules. If the positive charge on the isoquinolinyl radical fragment is comparatively more localized, this could result in a partial orientation of the solvent dipoles around the isoquinolinyl fragment that somewhat resembles that in the ground state isoquinolinium cation. To the extent this is the case, one might expect a decrease in λ_s for protic solvents.

4. CONCLUSIONS

There are three main conclusions of the work described here.

(i) Although prior data show emission maxima ($\lambda_{\max}^{-1}$) for conventional exciplexes correlating linearly with the Lippert−Mataga solvent polarity function in low to moderate polarity solvents, we show that the correlations can be strongly curved in moderate to high polarity solvents, pointing to limitations of the solvent polarity function. Interestingly, plots of the same data as $\lambda_{\max}^{-1}$ versus solvent dielectric constant (ε) turn out to be remarkably linear. A suitable theoretical model to explain these results would clearly be desirable.

(ii) Fluorescence spectra of a cationic exciplex ($\mathbf{1}^+$) in sets of nitrile and alcohol solvents also yield a linear correlation of $\lambda_{\max}^{-1}$ versus ε, but the spectral shift with increasing ε is ~1/3 of that for conventional exciplexes. In the case of conventional exciplexes, which are produced by charge formation reactions of neutral ground state reactants, only the excited state is stabilized increasingly with increasing ε. In the case of cationic exciplexes, which are produced by charge shift reactions of a cation with a neutral donor, the stabilization of *both* the ground- and the excited-state increases with increasing ε. If both states are equally stabilized, the slope of $\lambda_{\max}^{-1}$ versus ε would typically be 1/2 of that for conventional exciplexes. Spectral fitting shows that for the cationic exciplex of $\mathbf{1}^+$, the ground state is stabilized more with increasing ε than the excited state, resulting in the even smaller slope in the $\lambda_{\max}^{-1}$ versus ε plot. This finding suggests the intriguing possibility that a cationic exciplex could be designed to further increase the stabilization of the ground state relative to that of the excited state such that the emission maxima might become medium-independent. Work along these lines is in progress.

(iii) Differences in emission maxima, fwhm, and energetic parameters between the spectra of the $\mathbf{1}^+$ exciplex in nitrile versus alcohol solvents are likely a consequence of hydrogen bonding to the isoquinolinium radical moiety in the excited state. Consistent with this hypothesis are additional spectral shifts and energetic parameters in high hydrogen-bond acidity solvents, trifluoroethanol, and formic acid.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpca.0c01774.

Emission spectra as a function of excitation wavelength, minor exciplex component, exciplex fluorescence spectra in nitriles, exciplex fluorescence spectra in alcohols, and emission maxima versus dielectric constant (PDF)

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Notes

The authors declare no competing financial interest.

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(27) The linear dependence in Figure 4 is likely to be a consequence of the narrow range of fwhm rather than more fundamentally significant reason. As shown later (Figures 5 and 7), plots of λ_s and $\Sigma\lambda$ are also linear, but the fwhm is usually expected to be a nonlinear function of the reorganization energy (ref 16).

(28) Because equal increments of λ_{v1} and λ_{v2} are associated with very different frequencies, they should affect the bandshape and the fwhm differently. Nevertheless, because λ_{v2} varies only slightly (±0.002 eV), the discussion of the fwhm will not distinguish between the two contributions to λ_v.