

Electrolyte-Concentration and Ion-Size Dependence of Excited-State Intramolecular Charge-Transfer Reaction in (Alkylamino)benzonitriles: Steady-State Spectroscopic Studies

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Steady-state spectroscopic studies have been performed with three intramolecular charge-transfer molecules, 4-(1-azetidinyl)benzonitrile (P4C), 4-(1-pyrrolidinyl)benzonitrile (P5C), and 4-(1-piperidinyl)benzonitrile (P6C), in ethyl acetate and acetonitrile in presence of lithium perchlorate (LiClO_4) at room temperature to investigate the effects of electrolytes on excited-state intramolecular charge-transfer reaction. Electrolyte-concentration and ion-size dependences of several spectroscopic properties such as quantum yield, absorption and emission transition moments, radiative and nonradiative rates, and changes in reaction free energies associated with $\text{LE} \rightarrow \text{CT}$ conversion have been determined for these molecules and reported. For P4C, quantum yield decreases by a factor of ~ 7 at the highest electrolyte concentration relative to that in pure ethyl acetate whereas it is a factor of ~ 4 for both P5C and P6C. However, in acetonitrile with 1.0 M LiClO_4 , quantum yield reduces to almost half of that in the pure solvent. Formation of a *charge-transfer* (CT) state is found to be strongly favored over the *locally excited* (LE) state as the electrolyte (LiClO_4) concentration is increased, electrolyte effects being more pronounced in ethyl acetate than in acetonitrile. Relative to pure ethyl acetate, reaction free energy change ($-\Delta G_r$) increases by a factor of ~ 5 , ~ 4 , and ~ 2 for P4C, P5C, and P6C, respectively, at 2.5 M LiClO_4 in this solvent. $-\Delta G_r$ for P4C exhibits a change in sign (from *negative* to *positive*) upon addition of electrolyte in ethyl acetate. In acetonitrile, however, these changes are within a few percent, except for P4C where it is about 4 times greater at 1.0 M LiClO_4 than that in pure acetonitrile. The electrolyte-induced total red shift of the CT band of these TICT molecules is 3 times higher in ethyl acetate than in acetonitrile. Although both the quantum yield and CT emission peak frequency decrease linearly with the increase in ion size, $-\Delta G_r$ remains largely insensitive. Further studies using a nonreactive probe (coumarin 153) in concentrated electrolyte solutions also show qualitatively similar results.

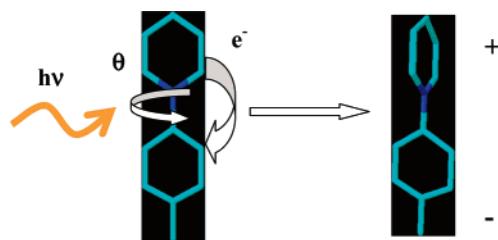
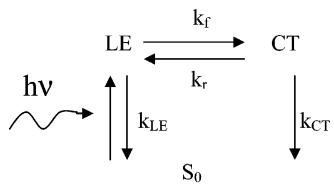
I. Introduction

Excited-state intramolecular charge-transfer reactions in substituted aminobenzonitrile derivatives have been an area of intense research for quite some time now.^{1–5} These molecules, upon photoexcitation, show an anomalously red-shifted fluorescence that occurs in addition to the normal fluorescence in polar solvents. The emergence of this red-shifted fluorescence has been a matter of considerable debate and discussion.^{3–14} Even though several models have been proposed to understand the nature of the anomalously red-shifted fluorescence, none of them could explain satisfactorily all aspects of the excited-state intramolecular charge-transfer reaction. However, all these models attribute the anomalous fluorescence to an electronic state of charge-transfer (CT) character. The state that emits normal fluorescence is assumed to possess charge distribution similar to that of the ground state and is termed as a locally excited (LE) state. Upon photoexcitation, a substantial amount of charge is transferred from the amino group to the benzonitrile ring with some intramolecular rearrangement. Several mechanisms are in vogue to rationalize the intramolecular rearrangement, although many experimental, theoretical, and semiempirical calculation studies support the twisted intramolecular charge-transfer mechanism (TICT).^{8–16} In this mechanism, charge transfer occurs simultaneously with a twisting of the alkyl

group from a conformation roughly coplanar with the benzonitrile ring to a perpendicular arrangement. This is shown in Scheme 1. However, this model is also not universally accepted because there has been much experimental evidence^{6,7} that is difficult to explain by using TICT mechanism.

Recently, Maroncelli and co-workers⁵ studied the excited-state charge-transfer reactions of 4-(1-azetidinyl)benzonitrile (P4C), 4-(1-pyrrolidinyl)benzonitrile (P5C), and 4-(1-piperidinyl)benzonitrile (P6C) in several solvents of varying polarity. These authors have explained their results by assuming the validity of twisted intramolecular charge-transfer (TICT) mechanism and found that the rate of reaction in these molecules is substantially modified by the dynamical modes of the solvent in which the reaction is studied. Here we extend the above study into the realms of electrolyte solutions in low to high concentrations. Addition of electrolyte in a polar solvent is likely to increase the polarity of the solution that may modify reactions in a similar manner. However, electrolyte solutions at moderate to high concentrations in strongly polar solvents and even at low concentrations in weakly polar solvents contain free ions, ion pairs (solvent shared and solvent separated), triple ions, and neutral triple ions in varying proportions.^{17–47} For example, dielectric and infrared spectroscopic studies of perchlorate salts of alkali and alkaline earth metal ions in acetonitrile at room temperature²⁰ suggest that contact ion-pair concentration increases from $\sim 10\%$ to about 50% for LiClO_4 and to about 30%

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SCHEME 1**SCHEME 2**

for NaClO_4 for increasing electrolyte concentration from 0.1 to 0.9 M. On the other hand, solvent-separated ion-pair concentration decreases from $\sim 10\%$ with electrolyte concentration to almost negligible proportion at higher concentrations.²⁰ For $\text{Mg}(\text{ClO}_4)_2$ and $\text{Ca}(\text{ClO}_4)_2$, however, the estimated concentration of a contact ion pair is large ($\sim 30\text{--}50\%$) even at 0.1 M, and varies nonmonotonically with electrolyte concentration. Moreover, an appreciable amount of triple and neutral triple ions is present in solutions of these bivalent metal perchlorates in acetonitrile.²⁰ Conductivity studies of LiClO_4 solutions in ethyl acetate^{17,22,39–44} suggest that the ion-pair concentration is appreciable even at electrolyte concentrations as low as 0.01 M. In addition, the formation of triple ions is found to make a significant contribution to the overall conductivity, suggesting strong ion–solvent interactions leading to structure enhanced ion association^{40,48} and formation of composite species such as triple ions, cyclic ion-pair dimers, and apolar aggregates. The ion pairs are characterized by large dipole moments^{17,20,21} that take part in modifying the interaction of a polarity probe with the environment and its dynamics. Moreover, the presence of other composite species significantly affects the structure and hence dynamics of the medium through Coulomb and non-Coulomb interactions.⁴⁸ Therefore, reactions occurring in these media would be affected in a more complicated manner than expected from the enhanced polarity of the medium alone.

Further inputs to the understanding of electrolyte solutions originate from the studies on solvation dynamics in electrolyte solutions.^{17–19,49} These studies indicate that the solvation time scale of a polarity probe in electrolyte solutions of acetonitrile and ethyl acetate is in the nanosecond regime, which is at least 1000 times slower than those in pure solvents. Huppert and co-workers^{17–19} used the Debye–Falkenhagen theory to explain the slowing down of the dynamics due to ion-atmosphere relaxation, but Maroncelli and co-workers⁴⁹ used the idea of direct probe–ion interactions through a limited solvate model to account for the inhomogeneous kinetics observed in such media. As the time scale of the barrier crossing is in the picosecond regime even for a reaction with a considerably broad barrier,^{50,51} the effects of such slow dynamics on the TICT reaction should be thoroughly investigated. A detailed study of electrolyte effects on the rate of TICT reactions in these TICT molecules has been carried out, and results are reported in the accompanying Article.⁵²

Scheme 2 represents photoexcitation of a TICT molecule and the subsequent formation of charge-transferred (CT) state where k_f and k_r are respectively the forward and backward rate

constants. k_{LE} and k_{CT} represent the net (radiative *plus* nonradiative) rate constants for LE and CT states, respectively. S_0 depicts the ground state. Interconversion between LE and CT states is the charge-transfer reaction. The rate of this interconversion depends *crucially* on two factors: intramolecular twisting and solvation.⁵ Naturally, therefore, modification of one of these factors affects the rate at which the reaction progresses. These molecules possess higher dipole moments in CT⁵ states and hence formation of CT population is favored when the solvent becomes polar. Because addition of electrolyte further enhances the average polarity of the medium,^{49,53} formation of CT population is likely to increase with electrolyte concentration. The direct interaction of CT state with various ionic species present in electrolyte solution also contributes to the enhancement of the CT population. All these are equilibrium solvation effects that need to be understood.

In this Article we report steady-state results on the excited-state intramolecular charge-transfer reactions of 4-(1-azetidinyl)benzonitrile (P4C), 4-(1-pyrrolidinyl)benzonitrile (P5C), and 4-(1-piperidinyl)benzonitrile (P6C) in electrolyte solutions of several alkali and alkaline earth metal perchlorates at different concentrations. We use the TICT model to analyze our data as done earlier.⁵ Note here that the above three compounds were first studied by Rettig and co-workers.^{8–12} Zachariasse and his group¹³ investigated the excited-state charge-transfer reaction in the above group of compounds containing three- to eight-membered rings and represented them as PnC series (n being the number of atoms constituting the ring). In addition to these experimental studies, semiempirical,^{14,15} density functional,¹⁶ and ab initio calculations¹⁵ have also been carried out with these molecules. However, studies of electrolyte effects on TICT reactions have not been performed before and such a study is reported here for the first time to the best of our knowledge. In addition, we have performed similar steady-state spectroscopic studies with a nonreactive probe, namely, coumarin 153 (C153) in these electrolyte solutions to compare the electrolyte effects on a nonreactive excited state. Note here that similar studies with C153 in acetonitrile and ethyl acetate in the presence of 1.0 M LiClO_4 or NaClO_4 have already been carried out.^{17,49} Our studies with C153 in these solvents at higher electrolyte concentrations indicate a natural extension of the low-concentration data already reported in the literature^{17–19,49} and hence are complimentary to these earlier data.

The main results of this paper are as follows. Quantum yields, radiative and nonradiative rates, and other steady-state properties (mainly spectral characteristics) for P4C, P5C, and P6C molecules are determined as a function of lithium perchlorate concentration in ethyl acetate and acetonitrile, and as a function of ion (cation) size. Both the absorption and emission spectra of these molecules show red shifts upon increasing the electrolyte concentration. These shifts are associated with spectral broadening (for absorption) and narrowing (for emission). Although the CT emission band shifts appreciably with electrolyte concentration, the LE band shows very little or no shift. Quantum yields for these molecules have been determined in the presence of electrolyte in solutions and found to decrease exponentially with electrolyte concentration. We have also measured these quantities for C153 in electrolyte solutions, which show electrolyte dependence similar to that observed for these TICT molecules. Addition of electrolyte is found to substantially modify the equilibrium constant for the $\text{LE} \rightarrow \text{CT}$ conversion reaction in the TICT molecules studied here. Electrolyte effects are found to be stronger for P4C than in the other two TICT molecules. Also, the electrolyte effects seem

to be more pronounced in ethyl acetate than in acetonitrile. The ion-size dependence of emission peak shift, quantum yield, and change in reaction free energies has also been studied. The ion-size-dependent results, however, need careful interpretation as the fluorescence emission from probes dissolved in a solution containing ions with large values of z/r_{ion} (valence/ionic radius) may arise from an unequilibrated excited state due to a considerable slowing down of the medium dynamics.⁴⁹ Also, as the degree of dissociation is different for these perchlorate salts, they are likely to produce different species as the concentration is varied in ethyl acetate and acetonitrile.^{17–22} Therefore, the observed ion-size dependence may *not* reflect the effects of ion size alone. The conductivity of LiClO_4 solutions in ethyl acetate has also been measured, which shows a steady increase in conductivity up to 2.0 M, indicating the dominance of a triple ion in determining the solution conductivity even in highly concentrated solution.

The organization of the rest of the paper is as follows. Experimental details are given in the next section. Section III contains experimental results from our steady-state spectroscopic studies. Supporting information is given wherever necessary. The Article then ends with concluding remarks in section IV.

II. Experimental Details

4-(1-Azetidinyl)benzonitrile (P4C), 4-(pyrrolidinyl)benzonitrile (P5C), and 4-(1-piperidinyl) benzonitrile (P6C) were synthesized by following the protocol given in ref 8. P4C and P6C were recrystallized from cyclohexane (Merck, Germany) and P5C from kerosene-free petroleum ether (recrystallized thrice). The purity of these compounds were checked by thin layer chromatography and monitoring the excitation wavelength dependence of fluorescence emission. Coumarin 153 was purchased from Exciton and used as received.

Ethyl acetate and acetonitrile were used as received (spectrophotometric grade) from Aldrich. Tetrabutylammonium perchlorate ($^t\text{Bu}_4\text{NClO}_4$), lithium perchlorate (LiClO_4), sodium perchlorate (NaClO_4), magnesium perchlorate ($\text{Mg}(\text{ClO}_4)_2$), calcium perchlorate ($\text{Ca}(\text{ClO}_4)_2$), and strontium perchlorate ($\text{Sr}(\text{ClO}_4)_2$) were obtained from either Aldrich or Fluka (anhydrous and/or highest available grade) and vacuum-dried before use. Solutions were prepared by dissolving a measured amount of electrolyte in a 10 mL volumetric flask and stirring the solution for $1/2$ h. Caution was exercised to ensure the complete dissolution of the added electrolyte. An aliquot of this stock solution was then transferred into a quartz cuvette of optical path length 1 cm. Subsequently, a small grain of solute (P4C/P5C/P6C) was dissolved and stirred the solution for about 10 min and the absorption spectrum was recorded (Model UV-2450, Shimadzu). The emission spectra were recorded (SPEX Fluoromax-3, Jobin-Yvon, Horiba) after adjusting the absorbance of the solution to 0.1 or less with excitation wavelength fixed at 305 nm. This wavelength was chosen to minimize the loss of the fluorescence spectrum at both blue and red ends. Solvent blanks were subtracted from the emission spectra prior to analysis and converted to frequency representation after properly weighting the intensity with λ^2 . A few samples were bubbled with dry argon gas to investigate the effects of dissolved oxygen on the absorption and emission spectra. These initial runs showed very little or no effects on the overall appearance of the spectra and hence most of the samples were not deoxygenated. This was also the observation in one of the earlier studies with these TICT molecules.⁵

We then deconvoluted each emission spectrum into two fragments by using the emission spectrum of the corresponding

TICT molecule in perfluorohexane as reference.⁵ This deconvolution provided area under each fragment (measure of population under a particular band) that was then used to calculate the equilibrium constants and change in reaction free energies for the LE to CT conversion. Emission peak frequencies were calculated as follows. Shifts of the emission spectra from the peak of the reference emission spectrum were calculated and added to the *average* peak frequency of the reference emission spectrum. The *average* of the reference emission peak was calculated by averaging the numbers obtained by fitting the upper half of the reference emission spectrum with an inverted parabola, first moment and the arithmetic mean of the frequencies at half intensities on both blue and red ends of the emission spectrum.^{54–56} Absorption peak frequencies were obtained by calculating the first moments of the absorption spectra. Conductivity measurements of electrolyte solutions were performed using a multimeter (Sension 378, Hach) fitted with a conductivity cell of cell constant 0.45 ($\pm 10\%$). The electrode was dipped in the sample until equilibrium was reached and reading becomes stable. After proper calibration, selected samples were checked three times and no significant differences were observed. Lifetime data for measuring radiative and nonradiative rates for the TICT molecules and C153 in electrolyte solutions were obtained from time-correlated single photon counting (Lifespec, Edinburgh Instruments) apparatus with excitation wavelengths at 299 and 293 nm for TICT molecules, and 409 nm for C153. All the measurements reported here were performed at $T = 298.15 \pm 0.1$ K, unless otherwise mentioned.

III. Results and Discussion

In this section we will present and discuss results obtained from the steady-state absorption and fluorescence emission studies of TICT (P4C, P5C, and P6C) molecules in perchlorate solutions of ethyl acetate and acetonitrile. We have also used a nonreactive probe (coumarin 153) molecule to compare the electrolyte effects on a nonreactive probe and on molecules that undergo intramolecular charge-transfer reaction upon photoexcitation. Because solvation statics and dynamics of electrolyte solutions in ethyl acetate and acetonitrile have already been studied using C153 as a probe with perchlorate concentration up to 1.0 M, our results with C153 will be complimentary to the existing data. Therefore, results obtained with C153 in electrolyte solutions will be discussed here briefly with data presented largely in the Supporting Information as the present Article focuses mainly on the electrolyte effects on TICT reaction.

Let us first begin with the conductivity of LiClO_4 solutions in ethyl acetate that have been measured up to 2.5 M. The results are shown in Figure 1. Conductivity data for the same solutions up to 1.0 M reported by Huppert et al¹⁷ are also shown in the same figure for comparison. As usual, the conductivity of the solution decreases with the addition of electrolyte at low LiClO_4 concentration and then increases. The increase in conductivity after initial drop is well-known and has been explained in terms of triple ion formation.^{23,24} Fuoss-Krauss analysis of experimental conductivity of LiClO_4 in ethyl acetate up to 1.0 M by Huppert and co-workers¹⁷ indicates that the concentrations of ion pair and triple ion increase with electrolyte concentration. Moreover, concentrations of both ion pair and triple ion become at least an order of magnitude larger than that of free ion at ~ 0.02 M. The present data clearly indicate that the concentration of triple ion continues to increase even up to 2.0 M and then decreases probably due to the formation of dipolar or apolar

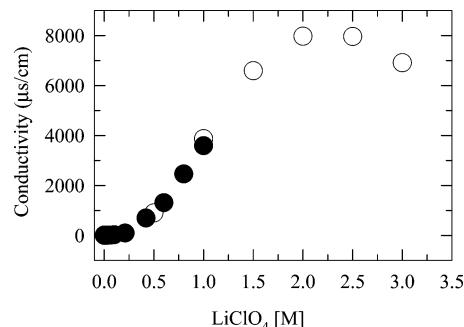


Figure 1. Conductivity of LiClO_4 solutions in ethyl acetate. Open circles represent the conductivity data recorded by us. Filled circles represent the data reported by Huppert and co-workers.¹⁷

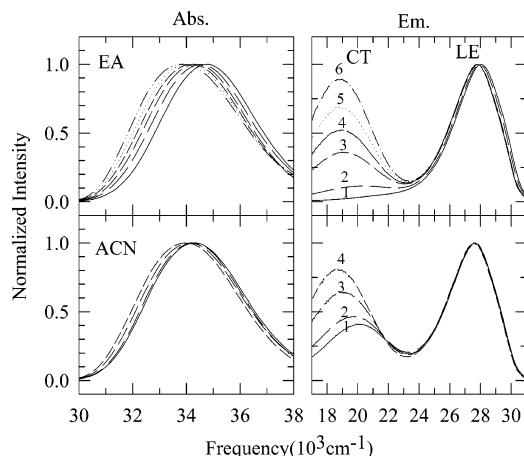


Figure 2. Absorption and emission spectra of 4-(1-azetidinyl)-benzonitrile (P4C) in several concentrations of LiClO_4 in ethyl acetate (upper panel) and acetonitrile (lower panel). For ethyl acetate solutions, spectra shown here are for the following LiClO_4 concentrations (M): 0.0 (1), 0.5 (2), 1.0 (3), 1.5 (4), 2.0 (5), 2.5 (6). For acetonitrile solutions, spectra shown here correspond to the following concentrations (M): 0.0 (1), 0.1 (2), 0.5 (3), 1.0 (4).

species at concentrations higher than 2.0 M. Fourier transformed infrared and dielectric spectroscopic studies, as done with electrolyte solutions in acetonitrile²⁰ and other solvents,⁵⁷ would have been very useful to estimate the concentration of various ionic, polar and apolar species in the medium. However, even without those studies, it is obvious that ion pair and triple ions are present in these solutions at large proportions and their effects on TICT reactions will be significant.

A. Spectral Properties. Representative absorption and emission spectra of P4C in several concentrations of LiClO_4 in ethyl acetate and acetonitrile are shown in Figure 2. Similar absorption and emission spectra for P5C and P6C are provided in the Supporting Information (Figures S1 and S2). It is interesting to note that the solubility of LiClO_4 in ethyl acetate is more than that in acetonitrile though the static dielectric constant (ϵ_0) of the former is 6 times less than that of the latter.⁵⁸ Formation of cluster between the electrolyte and the solvent is believed to be the reason for such a large solubility of LiClO_4 in ethyl acetate.⁵⁹ As a result, we could extend the LiClO_4 concentration up to 2.5 M in ethyl acetate whereas we could go only up to 1.0 M in acetonitrile. As expected, the presence of electrolyte does not alter the shape of the absorption spectrum of P4C other than inducing a total red shift $\Delta\nu_{\text{abs}}^{\text{ea}} = [\nu_{\text{abs}}^{\text{ea}}(0\text{M}) - \nu_{\text{abs}}^{\text{ea}}(2.5\text{M})] \approx 600 \text{ cm}^{-1}$ in ethyl acetate and $\Delta\nu_{\text{abs}}^{\text{acn}} = [\nu_{\text{abs}}^{\text{acn}}(0\text{M}) - \nu_{\text{abs}}^{\text{acn}}(1\text{M})] \approx 300 \text{ cm}^{-1}$ in acetonitrile. Interestingly, at 1.0 M LiClO_4 the absorption peak shift (relative to that in pure solvent) is $\sim 300 \text{ cm}^{-1}$ in both ethyl acetate and acetonitrile. For P5C

TABLE 1: LiClO₄-Concentration Dependence of Radiative and Nonradiative Rates of TICT Molecules in Ethyl Acetates^a

conc (M)	<i>n</i> (ref index)	P4C		P5C		P6C	
		$k_{\text{LE}}^{\text{rad}}$	$k_{\text{LE}}^{\text{nr}}$	$k_{\text{LE}}^{\text{rad}}$	$k_{\text{LE}}^{\text{nr}}$	$k_{\text{LE}}^{\text{rad}}$	$k_{\text{LE}}^{\text{nr}}$
0.0	1.368	3.60	4.00	4.53	25.86	1.93	22.69
0.1	1.369	2.82	5.49	3.57	40.29	1.47	39.69
0.25	1.371	3.44	7.81	3.66	75.95	1.23	58.10
0.5	1.374	3.27	11.74	3.54	124.65	1.06	92.49
1.0	1.382	2.88	18.23	3.06	160.98	1.26	150.4
1.5	1.387	2.76	23.99	3.79	285.34	1.16	172.30
2.0	1.392	2.26	27.86	3.14	269.96	1.15	185.07
2.5	1.395	2.05	32.91	2.59	302.77	1.13	195.96

^a $k_{\text{LE}}^{\text{rad}}$ (in units of 10^7 s^{-1}) and $k_{\text{LE}}^{\text{nr}}$ (in units of 10^8 s^{-1}) denote respectively the radiative and nonradiative rates associated with LE band.

TABLE 2: Ion-Size Dependence of Spectral Properties and Transition Moments of TICT Molecules in 0.5 M Perchlorate Solutions in Ethyl Acetate

P4C							
ion	z/r_{ion}	$\nu_{\text{abs}}(\text{a})$	Γ_{abs}	$\Gamma_{\text{CT}}^{\text{inh}}$	$\alpha_{\text{CT}}/\alpha_{\text{LE}}$	$k_{\text{LE}}^{\text{rad}}$	$k_{\text{LE}}^{\text{nr}}$
Na^+	0.980	34.60	4.08	3.8	0.29	2.97	10.32
Li^+	1.351	34.67	4.19	4.19	0.29	3.27	11.74
Sr^{2+}	1.724	34.47	4.59	3.33	0.76	1.78	25.73
Ca^{2+}	2.000	34.56	4.47	3.80	0.57	3.32	23.37
Mg^{2+}	2.780	34.26	4.62	3.58	0.27	2.03	9.72
P5C							
ion	ν_{abs}	Γ_{abs}	$\Gamma_{\text{CT}}^{\text{inh}}$	$\alpha_{\text{CT}}/\alpha_{\text{LE}}$	$k_{\text{LE}}^{\text{rad}}$	$k_{\text{LE}}^{\text{nr}}$	M_{LE}
Na^+	34.53	4.20	4.29	4.03	3.46	158.38	0.89
Li^+	34.35	4.17	4.73	3.93	3.54	124.65	0.90
Sr^{2+}	34.24	4.42	4.19	6.06	3.13	232.25	0.86
Ca^{2+}	33.99	4.42	4.64	4.84	3.77	256.03	0.86
Mg^{2+}	34.07	4.65	4.57	4.09	4.00	232.25	0.95
P6C							
ion	ν_{abs}	Γ_{abs}	$\Gamma_{\text{CT}}^{\text{inh}}$	$\alpha_{\text{CT}}/\alpha_{\text{LE}}$	$k_{\text{LE}}^{\text{rad}}$	$k_{\text{LE}}^{\text{nr}}$	M_{abs}
Na^+	34.29	4.41	4.35	12.51	1.09	61.241	0.52
Li^+	34.16	4.39	4.77	15.10	0.07	92.490	0.51
Sr^{2+}	33.98	4.59	3.54	19.90	0.69	94.271	0.43
Ca^{2+}	33.80	4.91	4.10	13.60	0.90	93.368	0.49
Mg^{2+}	34.09	4.63	4.68	15.61	0.85	78.655	0.45

^a Peak frequencies (ν) and band widths (Γ , fwhm) are in units of 10^3 cm^{-1} . $\alpha_{\text{CT}}/\alpha_{\text{LE}}$ denotes the area ratio between the CT and LE emission bands. r_{ion} is in the units 10^{-8} cm .

and P6C, $\Delta\nu_{\text{abs}}^{\text{ea}}$ is approximately twice as large as that in P4C whereas $\Delta\nu_{\text{abs}}^{\text{acn}} \approx 400 \text{ cm}^{-1}$ (see Figures S1 and S2 of Supporting Information). Also, the absorption peak shifts for P5C and P6C are ~ 500 and $\sim 400 \text{ cm}^{-1}$ at 1 M LiClO_4 in ethyl acetate and acetonitrile, respectively. This difference in behavior for P4C from the other two solutes can be understood if we consider the net absorption transition moments of the composite ($S_0 \rightarrow L_a + S_0 \rightarrow L_b$) absorption bands given in Table 3. The concentration-averaged net absorption transition moment ($\langle M_{\text{abs}} \rangle$) for P4C in ethyl acetate is $\sim 3.9 \text{ D}$, and those for P5C and P6C are ~ 5 and 4.9 D , respectively. If we now consider that the major contribution to $\langle M_{\text{abs}} \rangle$ comes from the more polar $S_0 \rightarrow L_a$ transition,⁵ it becomes clear why the absorption peak shift in P4C is smaller than those in P5C and P6C.

The electrolyte (LiClO_4)-concentration dependence of the absorption, CT and LE emission peak frequencies (ν_{abs} , ν_{CT} , ν_{LE}) and absorption line width (Γ_{abs}) of P4C, P5C, and P6C in ethyl acetate and acetonitrile is shown in Figure 3. The inhomogeneous CT and LE line widths are also shown in the same figure. It is clear from Figure 3 that the electrolyte-induced

TABLE 3: LiClO₄-Concentration Dependence of Transition Moments of TICT Molecules in Ethyl Acetates^a

conc (M)	P4C			P5C			P6C		
	M_{LE}	M_{CT}	M_{abs}	M_{LE}	M_{CT}	M_{abs}	M_{LE}	M_{CT}	M_{abs}
0.0	1.5	3.8	1.03	0.65	4.95	0.69	0.77	4.79	
0.1	1.3	4.3	0.91	0.71	4.96	0.60	0.83	4.89	
0.25	1.5	3.8	0.94	0.73	4.97	0.55	0.76	4.72	
0.5	1.4	0.92	3.9	0.90	0.76	5.11	0.51	0.72	4.97
1.0	1.3	0.92	4.0	0.84	0.66	5.08	0.56	0.72	4.95
1.5	1.3	0.94	3.7	0.92	0.66	4.81	0.55	0.67	5.08
2.0	1.2	0.90	4.0	0.83	0.58	5.23	0.54	0.66	5.00
2.5	1.1	0.89	3.9	0.75	0.54	5.09	0.54	0.58	5.06

^a M_{LE} , M_{CT} , and M_{abs} are in Debye units. Because the amounts of CT for P4C in ethyl acetate in the presence of 0.0, 0.1, and 0.25 M LiClO₄ concentrations are very small, the error associated with the calculation of M_{CT} at these concentrations are very large. Hence, these values are not cited here.

shift in the CT emission band is very large due to its more polar nature but the LE band shows very little or no shift upon addition of electrolyte in these solvents. Also, the peak frequency of the CT emission band of these TICT molecules decreases exponentially with the increase in LiClO₄ concentration.⁶⁰ For P4C, an increase in concentration of LiClO₄ from 0.0 to 2.5 M in ethyl acetate enhances the CT/LE area ratio by a factor of ~ 27 (relative to that in pure ethyl acetate) and shifts the CT emission peak toward lower energy by about 3000 cm⁻¹. In acetonitrile, the enhancement factor is ~ 2 and the CT peak shift is ~ 1100 cm⁻¹ for increasing the LiClO₄ concentration from 0.0 to 1.0 M. Note that the amount of CT is very small in pure ethyl acetate and at low LiClO₄ concentrations and hence the error associated with the CT peak determination in such cases is ± 500 cm⁻¹. This large error is reduced to ± 150 cm⁻¹ as the CT population grows with further addition of electrolyte. In cases where the population (LE or CT) is found to be less than 10%, the peak shift (relative to the reference) and the inhomogeneous width have been fixed. This removes any inconsistency in the peak-shift determination and band area calculation. It is interesting to note that in presence of 1.0 M LiClO₄ the CT emission peak shift of these TICT molecules is in the range of 2500 cm⁻¹ in ethyl acetate and that in acetonitrile is ~ 1000 cm⁻¹. Also, for these molecules at 1.0 M LiClO₄ solutions the area ratio (CT/LE) relative to that in pure solvent is several times larger in ethyl acetate than in acetonitrile. All these observations seem to indicate that for these TICT molecules in general and for P5C and P6C in particular that the effects of electrolyte on the LE \rightarrow CT conversion are stronger in ethyl acetate than in acetonitrile. This may be due to the fact that acetonitrile, being more polar (static dielectric constant, ϵ_0 , being 35.94 for acetonitrile as compared to 6.02 for ethyl acetate),⁵⁸ could probably supply almost all of the energy for P5C and P6C required for the conversion and subsequent solvent stabilization of CT state. Naturally, therefore, the formation of CT population predominates for P5C and P6C in pure acetonitrile and there is not much left to be driven by the enhanced interaction between the solute (P5C or P6C) and various species present in electrolyte solutions (see Figures S1 and S2 of Supporting Information). It may also be linked to the solvent polarity dependence of activation barrier⁵ associated with the LE \rightarrow CT conversion (static solvent effects).

An important feature to be noted in Figure 3 is the variation of width in both absorption and CT emission bands with electrolyte concentration in these solvents. Due to the interaction with the environment, the absorption spectra of these molecules in electrolyte solutions are shifted to lower frequency and broadened with broadening ranged between 200 and 400 cm⁻¹

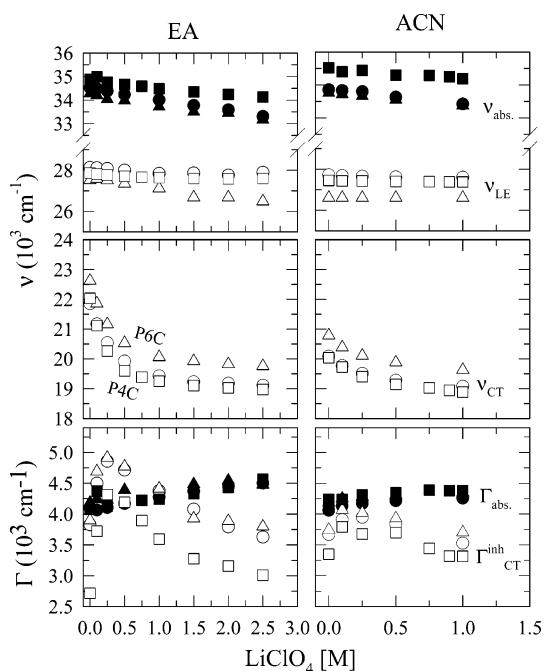


Figure 3. Electrolyte (LiClO₄)-concentration dependence of absorption (ν_{abs}) and emission (ν_{LE} , ν_{CT}) peak frequencies and line widths (full width at half-maxima, Γ) of the absorption spectra and CT bands of 4-(1-azetidinyl)benzonitrile (P4C), P5C, and P6C in ethyl acetate (left panel, marked with “EA”) and acetonitrile (right panel, marked with “ACN”). The squares represent the solute P4C, and the circles and triangles are P5C and P6C respectively. Filled symbols represent absorption peak frequencies (ν_{abs}) and line widths (Γ_{abs}). LE and CT peak frequencies (ν_{LE} and ν_{CT}) and the inhomogeneous line width ($\Gamma_{inh, CT}$) for CT band are represented by open symbols. These quantities have been obtained after deconvoluting the experimental emission spectra by broadening and shifting a reference spectrum with a Gaussian function (representing inhomogeneous solvent broadening). For further details, see text and ref 5. The estimated uncertainty in frequencies and widths is ± 300 cm⁻¹ (except when the LE is too small).

in ethyl acetate and acetonitrile. This broadening is due to the microscopic heterogeneity in the environment surrounding a solute in the solution. The CT emission band shows narrowing with the increase in electrolyte concentration with a maximum narrowing ~ 1000 cm⁻¹. If we now recall that ϵ_0 of electrolyte solution increases with electrolyte concentration,⁵³ these peak shifts and variations in spectral widths could be termed as similar to those observed earlier with C153 in neat polar solvents⁵⁴ and in electrolyte solutions (discussed later). However, the narrowing of CT emission band in these TICT molecules is 3–4 times more than what has been observed with C153 in neat solvents, suggesting a more complex interaction between the excited state of a TICT molecule and the environment surrounding it. One therefore needs further study to understand the reasons for such a large electrolyte-induced narrowing of emission width in these molecules.

Before going further into the discussion about the steady-state results with these TICT molecules, we would like to digress here briefly to relate the concentration-dependent peak shifts and spectral widths observed for the above molecules to those obtained for C153 in LiClO₄ solutions of ethyl acetate and acetonitrile. Data summarized in Table S2 in the Supporting Information indicate that the total absorption peak shift of C153 between 0.0 to 2.5 M LiClO₄ in ethyl acetate is ~ 1500 cm⁻¹, which is similar in magnitude to what has been found for P5C and P6C molecules in this concentration range in ethyl acetate. In acetonitrile, the absorption peak shift (between 0.0 and 1.0 M) of C153 is similar to what has been found (~ 400 cm⁻¹) for

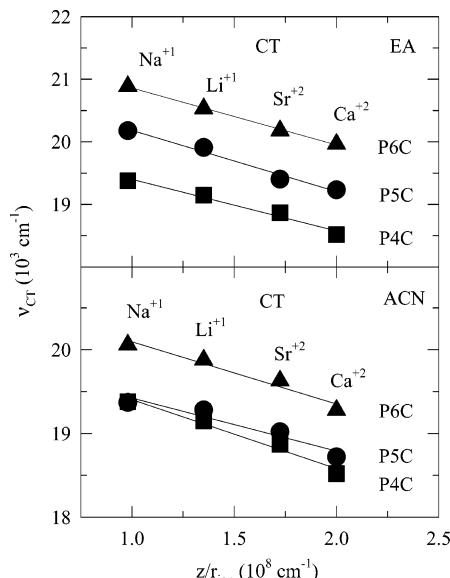


Figure 4. Ion-size dependence of emission peak frequencies of P4C, P5C, and P6C in 0.5 M perchlorate solution of ethyl acetate. In this figure, squares represent P4C and P5C and P6C are represented by circles and triangles, respectively. Perchlorate salts of the following cations have been used: Na^+ , Li^{+1} , Sr^{+2} , Ca^{+2} , and Mg^{2+} . Note that Mg^{2+} has not been shown in the figure. In the presence of Mg^{2+} ion in ethyl acetate, the values of v_{CT} (in 10^3 cm^{-1}) for P4C, P5C, and P6C, respectively, are 19.33, 19.90, and 20.61. In acetonitrile, the corresponding values are 19.33, 19.32, and 20.01.

the TICT molecules studied here. The corresponding emission peak shift in electrolyte solutions of ethyl acetate is $\sim 2000 \text{ cm}^{-1}$, which is approximately two-thirds of the CT emission peak shift found for the TICT molecules considered here. In acetonitrile, however, the emission peak shift in C153 is similar to what has been found for TICT molecules upon increasing the LiClO_4 concentration from 0.0 to 1.0 M. These spectral shifts are associated with spectral broadening (for absorption) and narrowing (for emission). We will see later that quantum yield and other relevant quantities of C153 also exhibit similar concentration dependence as those found for P4C, P5C, and P6C molecules. Therefore, these data indicate that the effects of electrolyte on these two types of molecules (nonreactive and reactive) are qualitatively similar and hence, study of electrolyte effects using one (type) of these molecules as probe would be able to explain the general behavior of the other in electrolyte solutions.

The ion-size dependence of v_{CT} for P4C, P5C, and P6C in ethyl acetate and acetonitrile containing 0.5 M perchlorate of different metal cations is shown in Figure 4. Other relevant quantities obtained from the steady-state studies in ethyl acetate are summarized in Table 2. Corresponding data for acetonitrile are provided in the Supporting Information (Table S1). Two important features are to be noted in this figure. First, except for Mg^{2+} , the CT emission frequencies of these molecules in perchlorate solutions of ethyl acetate and acetonitrile show a linear dependence on z/r_{ion} . Second, the CT emission frequency shifts by ~ 900 and $\sim 750 \text{ cm}^{-1}$, respectively, in ethyl acetate and acetonitrile (see Table S1, Supporting Information) as one moves from Na^+ to Ca^{+2} . This indicates that the solute–ion interaction becomes stronger as z/r_{ion} becomes larger.⁴⁹ The absorption frequencies (see Table 2 and Table S1) of these solutes in ethyl acetate and acetonitrile also exhibit linear z/r_{ion} dependence for all ions examined here. Similar behavior is also found earlier in the context of solvation studies in electrolyte solutions using several nonreactive probes.⁴⁹ It has been

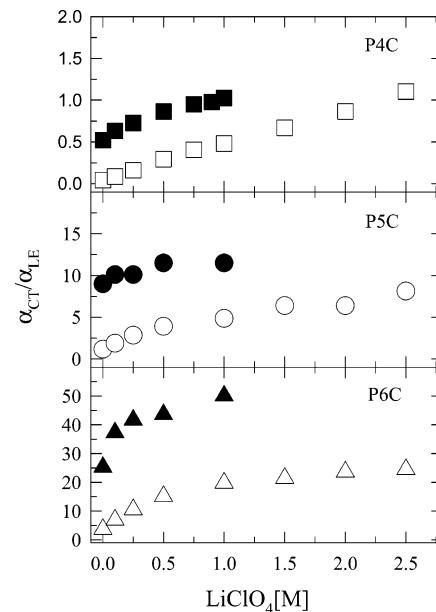


Figure 5. Electrolyte-concentration dependence of formation of CT population in ethyl acetate (open symbols) and acetonitrile (filled symbols). The ratio ($\alpha_{\text{CT}}/\alpha_{\text{LE}}$) between areas under the CT and LE bands (obtained after deconvolution as discussed in the text and in ref 5) are shown as a function of LiClO_4 concentration. Squares represent the ratio for P4C in the upper panel, circles for P5C in the middle panel, and triangles for P6C in the lower panel. The uncertainty for CT band area is typically within $\pm 10\%$.

argued^{17–19,49} that the emission shift saturates with z/r_{ion} because the environment dynamics slows down considerably as z/r_{ion} increases and the equilibrium solvation cannot be attained during the probe's lifetime. Therefore, in the presence of Mg^{2+} the CT emission is occurring from an improperly equilibrated excited state and hence the observed peak frequency is larger than what would have been for a properly equilibrated one.

Figure 5 shows the CT/LE area ratio ($\alpha_{\text{CT}}/\alpha_{\text{LE}}$) for P4C, P5C, and P6C in ethyl acetate and acetonitrile as a function of LiClO_4 concentration. The area under each band (α_x , $x = \text{CT}$ or LE) has been calculated as discussed earlier and in ref 5. Note here that the CT/LE ratio increases as the electrolyte concentration is increased, indicating the formation of the CT state is strongly favored upon addition of electrolyte. For the three molecules, formation of CT states is more favored in pure acetonitrile than in ethyl acetate due to the larger static dielectric constant of acetonitrile. However, the electrolyte-concentration dependence is stronger in ethyl acetate than in acetonitrile. As the area ratio is connected to the equilibrium constant (K_{eq}), the change in reaction free energy (ΔG_r) for the $\text{LE} \rightarrow \text{CT}$ conversion is calculated from the following relation⁵

$$\Delta G_r = -RT \ln K_{\text{eq}} = -RT \ln [\alpha_{\text{CT}} v_{\text{LE}}^3 / \alpha_{\text{LE}} v_{\text{CT}}^3] \quad (1)$$

and shown in Figure 6. As expected, ΔG_r in acetonitrile is larger due to its larger dielectric constant. As expected, ΔG_r is following the trend of $\alpha_{\text{CT}}/\alpha_{\text{LE}}$ depicted in the previous figure (Figure 5) and the possible reasons discussed. Note that the concentration-dependent $-\Delta G_r$ for P4C in ethyl acetate varies from negative to positive values, indicating that an unfavorable $\text{LE} \rightarrow \text{CT}$ conversion reaction in pure ethyl acetate becomes highly favorable upon addition of electrolyte. In fact, the equilibrium constant for the $\text{LE} \rightarrow \text{CT}$ conversion reaction in P4C is ~ 50 times larger in presence of 2.5 M LiClO_4 than in pure ethyl acetate. For P5C and P6C in ethyl acetate at 2.5 M LiClO_4 , $-\Delta G_r$ is enhanced by a factor of ~ 4 and ~ 2.5 ,

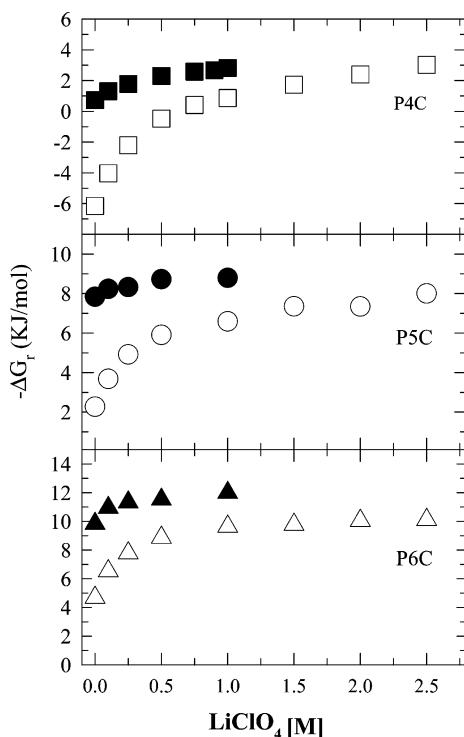


Figure 6. Electrolyte-concentration dependence of the change in reaction free energy ($-\Delta G_r$) for $\text{LE} \rightarrow \text{CT}$ conversion for P4C, P5C, and P6C in ethyl acetate (open symbols) and acetonitrile (filled symbols). ΔG_r is obtained from the area ratio (shown in Figure 5) by using eq 1. Squares (open and filled) denote $-\Delta G_r$ for P4C in the upper panel. Circles (open and filled) denote $-\Delta G_r$ for P5C in the middle panel. The results for P6C are shown by open and filled triangles in the lower panel.

respectively. This means that the equilibrium constant is increased by an order of magnitude for P5C and doubled for P6C in ethyl acetate at 2.5 M LiClO_4 with respect to the values in the absence of electrolyte. For P4C in acetonitrile with 1.0 M LiClO_4 , $-\Delta G_r$ is ~ 4 times larger than that in the absence of electrolyte but it is limited to $\sim 10\text{--}20\%$ for P5C and P6C. Therefore, the electrolyte-concentration dependence of the $\text{LE} \rightarrow \text{CT}$ conversion reaction is stronger in P4C than in P5C and P6C. The large activation barrier (ΔE_{act}) in P4C is probably the reason for such a strong electrolyte-concentration dependence. The ion-size dependence⁶¹ of $-\Delta G_r$ for these molecules in ethyl acetate and acetonitrile containing 0.5 M perchlorate salts of different cations has also been studied. It has been found that $-\Delta G_r$ shows a very weak dependence on z/r_{ion} (see Figure S3 in the Supporting Information).

B. Quantum Yields and Transition Moments. We have measured quantum yield, radiative and nonradiative rates, and transition moments for P4C, P5C, and P6C in various concentrations of LiClO_4 in ethyl acetate and acetonitrile. The following well-known relation has been used to determine the quantum yield⁵

$$\Phi_S = \Phi_R \left(\frac{n_S}{n_R} \right)^2 \left(\frac{I_S}{I_R} \right) \left(\frac{1 - 10^{-0.5A_S}}{1 - 10^{-0.5A_R}} \right) \quad (2)$$

Quinine sulfate dihydrate in 0.05 M H_2SO_4 has been used as reference ($\Phi_R = 0.508$).⁶² In eq 2, n_x represents refractive index of the reference solution (R) and sample (S), I the integrated emission intensity, and A the absorbance. Refractive indices of the electrolyte solutions have been measured (296.15 ± 1 K)

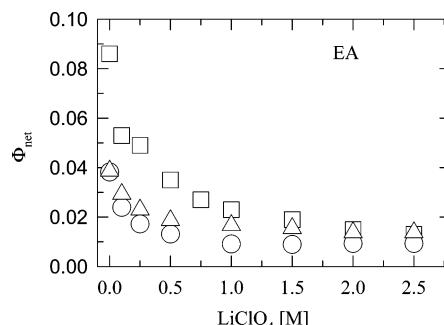


Figure 7. Electrolyte (LiClO_4)-concentration dependence of quantum yield (Φ) for P4C, P5C, and P6C in ethyl acetate. Open squares show the quantum yield for P4C, open circles show that for P5C, and the quantum yield of P6C has been shown by open triangles. Estimated errors for these calculations are within $\pm 10\%$ about the average for most of the cases.

and are reported in Table 1. Values of net quantum yields for both P5C and P6C in cyclohexane have been reproduced within $\pm 10\%$ uncertainty⁶³ about the value reported in the literature. Figure 7 depicts the electrolyte (LiClO_4)-concentration dependence of net quantum yield in ethyl acetate. Quantum yields of individual parts (LE and CT) for these molecules in various concentrations of LiClO_4 in ethyl acetate have also been determined and provided in Figure S4 of the Supporting Information. It is clear from these figures that the presence of electrolyte decreases the quantum yield appreciably. For example, the net quantum yield for these TICT molecules at 2.5 M LiClO_4 in ethyl acetate is reduced by a factor of ~ 7 from the value obtained in pure ethyl acetate. The net quantum yield of these molecules in acetonitrile at 1.0 M LiClO_4 is almost half of that in the pure solvent (see Figure S6, Supporting Information). Note that the concentration dependence of the net quantum yield for these molecules could also be fitted to a biexponential function of electrolyte concentration.⁶⁴ Values for radiative (κ_{rad}) and nonradiative (κ_{nr}) rates and average lifetimes ($\langle \tau_{\text{avg}} \rangle$) have been determined by using our experimental data in the relations given in literature.⁵ For individual parts, however, we use the following relations:⁵ $k_{\text{LE}}^{\text{rad}} = \phi_{\text{LE}}/\langle \tau_{\text{LE}} \rangle$, where the average LE lifetime has been calculated from the amplitudes (a_i) and time constants (τ_i) obtained by fitting the relevant LE emission decays as follows:⁵ $\langle \tau_{\text{LE}} \rangle = \sum_i a_i \tau_i / \sum_i a_i$. The nonradiative rate for LE ($k_{\text{LE}}^{\text{nr}}$) is then calculated by using the relation⁵ $k_{\text{LE}}^{\text{nr}} = (1 - \phi_{\text{LE}})/\langle \tau_{\text{LE}} \rangle$. For CT, the radiative rate is obtained as follows:⁵ $k_{\text{CT}}^{\text{rad}} = \phi_{\text{CT}} k_{\text{dec}} (1 + K_{\text{eq}}^{-1})$, where the average excited-state population decay constant (k_{dec}) is determined from the net rate constants k_{LE} and k_{CT} using $k_{\text{dec}} = (k_{\text{LE}} + k_{\text{CT}})/2$, and by assuming rapid equilibrium between LE and CT states.⁵ These quantities have been calculated for P4C, P5C, and P6C in electrolyte solutions and are summarized in Table 1. The decay parameters necessary for the calculations of $\langle \tau_{\text{LE}} \rangle$ and k_{CT} are discussed in the accompanying Article.⁵² The error bar associated with the calculation of these radiative and nonradiative rates is typically $\pm 15\%$ about the values reported here. Data in Table 1 indicate that radiative and nonradiative rates show a weak to moderate electrolyte-concentration dependence. The ion-size (z/r_{ion}) dependence of quantum yield is shown in Figure 8. It is evident from this figure that quantum yield of these TICT molecules behave as a function of z/r_{ion} in a manner similar to what has been observed for CT emission peak frequency (see Figure 4). The corresponding values for radiative and nonradiative rates are listed in Table 2 and show no particular dependence on ion size.

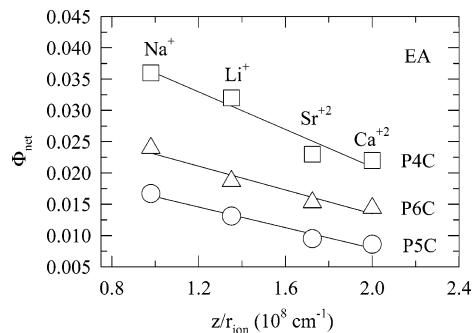


Figure 8. Ion-size dependence of quantum yield of P4C, P5C, and P6C in 0.5 M perchlorate solution of ethyl acetate. In this figure, squares represent P4C and circles and triangles represent P5C and P6C, respectively. Perchlorate salts of the following cations have been used: Na^+ , Li^+ , Sr^{2+} , Ca^{2+} , and Mg^{2+} . Note that Mg^{2+} has not been shown in the figure. In the presence of Mg^{2+} ion in ethyl acetate, the values of (Φ) for P4C, P5C, and P6C, respectively, are 0.026, 0.011, and 0.018.

Transition dipole moment of the radiative transitions, \mathbf{M}_x , has been determined from the radiative rate data by using the following relation^{5,65}

$$\mathbf{M}_x/D = 1785.7 \left(\frac{\kappa_x^{\text{rad}}/\text{s}^{-1}}{n^3 (\bar{\nu}_x^3/\text{cm}^{-3})} \right) \quad (3)$$

where $\bar{\nu}_x^3 = \{ \int F_x(\nu) d\nu / \int F_x(\nu) \nu^{-3} d\nu \}^{-1}$ with $F_x(\nu)$ denoting the fluorescence spectrum of species $x = \text{LE}$ or CT . The results are summarized in Table 3. Transition moments for CT of P4C, P5C, and P6C determined here in ethyl acetate are consistent with the reported values for these molecules in methyl acetate (ϵ_0 for methyl acetate and ethyl acetate are 6.68 and 6.02, respectively). The error bar is typically $\pm 15\%$ but is larger when the emission spectrum is overwhelmingly dominated by either LE or CT bands. It is interesting to note in Table 3 that the CT transition moment is very weakly dependent on (or even *insensitive* to) the LiClO_4 concentration. Similar results have also been found with these molecules in neat (pure) solvents where polarity had either very weak or no effects on the transition dipole moments.⁵ Data on transition moments for these molecules given in Table 3 suggest that the electrolyte-concentration-averaged LE transition moment follows the order P4C > P5C > P6C. Also, the CT transition moments for P6C in various concentrations of LiClO_4 in ethyl acetate are slightly larger than for P5C in similar conditions. Similar results have also been observed earlier in neat solvents.⁵ Note in Table 3 that the CT transition moments for P4C at low electrolyte concentrations are not reported because these values are associated with large errors as the CT band areas are very small at these electrolyte concentrations. The cation-size dependence of these transition moments is investigated and the results are summarized in Table 2. These data indicate that the transition moments are insensitive to z/r_{ion} .

We have further calculated the net absorption transition moments of the composite absorption band ($S_0 \rightarrow L_a + S_0 \rightarrow L_b$) by using the following relation^{65,66}

$$\mathbf{M}_{\text{abs}}/D = 9.584 \times 10^{-2} \left[\frac{1}{n} \int_{\text{abs}} (\epsilon(\nu)/\text{M}^{-1} \text{ cm}^{-1}) \frac{d\nu}{\nu} \right]^{1/2} \quad (4)$$

where $\epsilon(\nu)$ is the molar decadic extinction coefficient. The results for P4C, P5C, and P6C in LiClO_4 solutions of ethyl acetate are summarized in Table 3. Again, these absorption transition moments do not show any dependence on electrolyte

concentration. Note that the average net absorption transition moment obtained here is very close to the average value obtained for both these molecules in neat (pure) solvents. The net absorption transition moments of these molecules have also been determined in ethyl acetate and acetonitrile solutions containing perchlorate salts of different cations. The results are shown in Table 2 with a maximum error bar $\pm 15\%$. Again, there are no effects of z/r_{ion} on net absorption transition moment.

We have also measured quantum yield, radiative and non-radiative rates, and transition moments for C153 in various concentrations of LiClO_4 in ethyl acetate and acetonitrile. These data are summarized in Figure S5 and Table S2 of the Supporting Information. It is clear from these data that at the highest LiClO_4 concentrations studied in these solvents the quantum yield of C153 decreases by $\sim 40\%$ from those in the absence of electrolyte. This is in contrast with what have been observed for TICT molecules where the reduction in quantum yields are by *at least* a factor of 4 and 2 at LiClO_4 concentrations 2.5 M in ethyl acetate and 1.0 M in acetonitrile, respectively. The ion-size-dependent quantum yield of C153 (see Table S3 of the Supporting Information), however, is found to be linear with z/r_{ion} , which is also the observation (except for Mg^{2+}) with the TICT molecules studied here.

IV. Conclusion

Let us first summarize the main results of this work. Steady-state fluorescence studies with P4C, P5C, and P6C in ethyl acetate and acetonitrile indicate that the addition of electrolyte continuously shifts the absorption and emission spectra toward lower energy and does *not* alter the shape of the bands. The shifts in the absorption and emission spectra are associated with spectral broadening (for absorption) and narrowing (for emission). These observations are consistent with earlier studies with C153 in neat polar solvents and also in electrolyte solutions. Addition of electrolyte decreases the quantum yield of these TICT molecules appreciably, but the reduction for C153 is only $\sim 40\%$ from that in the absence of electrolyte. The enhancement of CT/LE area ratio upon addition of electrolyte is much larger in ethyl acetate than in acetonitrile. Because the area ratio is related to the change in reaction free energy ($-\Delta G_r$) via equilibrium constant, $-\Delta G_r$ for P4C in ethyl acetate is found to vary between negative and positive values, indicating that the unfavorable $\text{LE} \rightarrow \text{CT}$ conversion reaction in pure ethyl acetate becomes highly favorable at large electrolyte concentration. This is much less in acetonitrile, being $\sim 20\%$ for both P5C and P6C molecules. Also, the electrolyte effects are more pronounced in P4C than those found for P5C and P6C. For example, upon increasing the LiClO_4 concentration from 0.0 to 2.5 M the equilibrium constant for the $\text{LE} \rightarrow \text{CT}$ conversion reaction is enhanced by a factor of ~ 50 for P4C, ~ 10 for P5C, and ~ 2 for P6C compared to those in pure ethyl acetate. In acetonitrile, however, the modification of the equilibrium constant in the presence of electrolyte is confined within 2–4 times only. The ion-size-dependent study indicates that, $-\Delta G_r$ depends very weakly on z/r_{ion} . Linear correlations with z/r_{ion} are observed for the CT emission frequency (ν_{CT}) and quantum yield of these TICT molecules. Quantum yield and emission peak frequency of a nonreactive probe such as C153 in electrolyte solutions are also found to be linear with z/r_{ion} . In all these cases, however, values obtained in the presence of Mg^{2+} deviate from the observed linearity. This may be due to a considerable slowing down of environmental dynamics in the presence of ions with large values of z/r_{ion} that inhibits the photoexcited probe from attaining the complete equilibrium

during its fluorescence lifetime.⁴⁹ Because the degree of dissociation is different for different electrolytes in the same solvent and also different for the same electrolyte in different solvents, the apparent ion-size dependence may derive contributions from different species present in electrolyte solutions.^{20,57} Therefore, further investigation is required to quantify the effects of ion size in electrolyte solutions.

Because probe–ion and ion–solvent interactions for cations are known to be different from those for anions,⁶⁷ it would be interesting to study the anion-size dependence of simple spectral shifts and its consequences on quantum yields for these molecules in solution phase. Extension of the electrolyte-concentration dependence study to even higher electrolyte concentrations (solubility permitting) could be interesting, as it may indicate what to expect in mixtures of ionic liquids with polar solvents. Steady-state studies of TICT molecules in binary polar mixtures may also provide interesting information regarding the effects of preferential solvation and mole-fraction-induced solvent structure breaking⁶⁸ on TICT reactions. Study of TICT reactions in the polar solvent pool in a confined geometry is another interesting problem where one can study not only the effects of enhanced viscosity but also those arising from slow solvent dynamics. Recent dielectric spectroscopic studies of aqueous solutions containing LiCl and Li₂SO₄ indicate that ion-pairing processes are very weak in these solutions, with ion-pair concentration as low as 0.15 M at 1.0 M and even higher electrolyte concentration. Study of TICT reactions in aqueous solutions of these electrolytes where free ions are present at such a large proportion would make an important contribution to the understanding of the interaction between the Li⁺ ion and TICT molecules. Some of the studies discussed here are already in progress.^{69,70}

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Supporting Information Available: Tables of concentration- and ion-size-dependent steady-state spectral properties of P4C, P5C, P6C and C153, and figures showing emission spectra of P5C and P6C in LiClO₄ solutions of ethyl acetate and acetonitrile, changes in reaction free energy ($-\Delta G_r$), electrolyte-concentration-dependent quantum yields associated with LE and CT bands of these TICT molecules and quantum yield of C153 in electrolyte solutions of ethyl acetate and acetonitrile are provided. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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