

Supporting Information

**Intramolecular Charge Transfer with Crystal Violet Lactone in
Acetonitrile as a Function of Temperature.
Reaction is Not Solvent-Controlled**

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Absence of Excitation Wavelength Dependence of CVL Fluorescence in Ionic Liquids.

The photophysical behavior of CVL in room temperature ionic liquids (ILs) has over the last years attracted considerable attention.^{11,12,14,37,38} In the first publication of CVL in *N*-propyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ([Pr₃₁][Tf₂N]),^{11,12} the conclusion was made that analysis of the ICT fluorescence kinetics of CVL in [Pr₃₁][Tf₂N] is complicated, because the time scales of solvation, ICT reaction, and fluorescence decay are all comparable and hence mutually interfere.^{11,2} Therefore, photostationary spectra were employed.^{11,12} Also, the fluorescence quantum yield ratio $\Phi'(ICT)/\Phi(LE)$ of CVL was found to show a pronounced excitation wavelength effect, normally absent in conventional solvents, increasing by a factor of around 4 between excitation and the peak or at the longest wavelength: the so-called 'red-edge effect'.³⁹ These findings were seen as experimental evidence for a dynamic heterogeneity of the CVL location in ILs, i.e., that energetically selected subpopulations relax at distinct rates. Similar observations of red-edge effects had previously been made with other excited molecules in ILs.⁴⁰⁻⁴³ Later, it appeared that the spectra of CVL in [Pr₃₁][Tf₂N] were erroneous, probably resulting from impurity fluorescence.¹³ In support of this conclusion, only very little or negligible excitation wavelength dependence of CVL emission was detected with CVL in six different ILs.³⁷ From molecular dynamics (MD) simulations, it had been found, in contrast, that the kinetics of the LE \rightarrow ICT reaction of CVL in [Pr₃₁][Tf₂N], but not in MeCN, depends on its nonisotropic local solvent environment, which can persist for several nanoseconds, i.e., an excitation wavelength dependence was expected in ILs.³⁸

In a recent publication,¹⁴ it was stated that the ICT reaction of CVL in six ILs exhibits a behavior similar to that in aprotic dipolar solvents, although it was pointed out that the weak intrinsic CVL fluorescence and the lack of data for conventional solvents with long solvation times introduce uncertainty in this interpretation.¹⁴ Nevertheless, for a low-barrier adiabatic process as encountered with CVL in polar media, the distinction between solvation dynamics in dipolar versus ionic environments was thought to be largely irrelevant.¹⁴ Also, the relatively small value of $\Phi'(ICT)/\Phi(LE)$ in ILs as compared with solvents such as MeCN is considered to be caused by the fact that the LE and ICT excited states of CVL are not equilibrated in ILs. As a consequence, in ILs the short time τ_2 is different for the LE and ICT decays, for example, 43 ps and 110 ps for CVL in 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Im₂₁][Tf₂N]) at 25 °C.¹⁴

Isoemissive points do not appear with CVL in the ILs propyltrimethylimidazolium bis(trifluoromethylsulfonyl)imide ([N₃₁₁₁][Tf₂N]) and isopropyl dimethylimidazolium

bis(trifluoromethylsulfonyl)imide ($[N_{ip311}][Tf_2N]$), although the time-resolved spectra are clearly those of a two-state process', as the dynamic Stokes shift of the LE band, occurring simultaneously with the ICT reaction, tends to blur any isoemissive points in the spectra.³⁷ Such isoemissive points are not to be expected in ILs, contrary to the report in ref 37. There, time-resolved emission spectra (TRES) of CVL in 1-butyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide ($[bmmim][Tf_2N]$) at 23 °C for time delays between 0 ps and 8 ns were presented (instrument response function of 55 ps).³⁷ The spectra consist of two components, originating from the LE and the ICT state, even somewhat surprisingly also that at 0 ps, with an overall fluorescence quantum yield $\Phi(fl)$ in 5 ILs between 0.0002 and 0.058. Along with the ICT reaction, a red-shift of the LE emission maximum was observed, a direct indication that the equilibration of CVL in the excited state is time-dependent, because of the slow solvent relaxation in the IL. From the TRES spectra, an approximate LE \rightarrow ICT reaction time of 985 ps was determined, considered to represent the slower of the two processes involved in the ICT reaction of CVL, electron transfer and solvation of the ICT state. An average solvent relaxation time $\langle\tau_{sr}\rangle$ of 690 ps for $[bmmim][Tf_2N]$ was measured from the time-dependent fluorescence Stokes shift of coumarin 153, showing the important role of solvent relaxation in the highly viscous IL.³⁷ Nevertheless, an isoemissive point is reported in the TRES of CVL in $[bmmim][Tf_2N]$ at 23 °C, an unexpected observation when solvation dynamics is slow, as already discussed above.¹⁴

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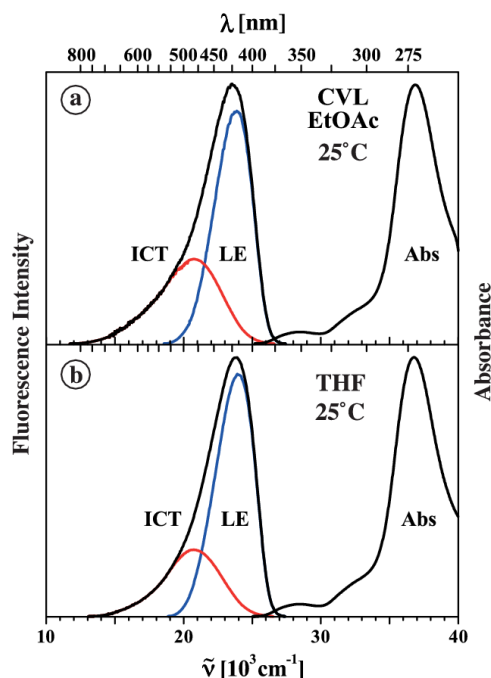


Figure S1. (a) Fluorescence and absorption (Abs) spectra of CVL, (a) in ethyl acetate (EtOAc) and (b) in tetrahydrofuran (THF), both at 25 °C. The fluorescence spectra show dual fluorescence from a LE and an intramolecular charge transfer (ICT) state, see text. Excitation wavelength: (a) 350 nm, (b) 330 nm.

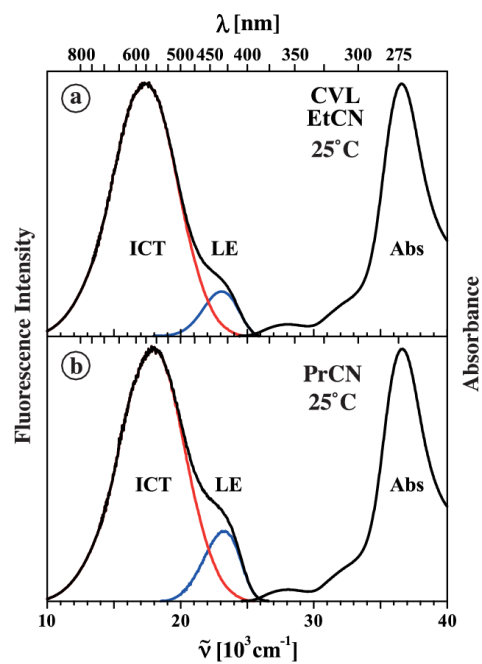


Figure S2. Fluorescence and absorption (Abs) spectra of CVL, (a) in ethyl cyanide (EtCN) and (b) in *n*-propyl cyanide (PrCN), both at 25 °C. The fluorescence spectra show dual fluorescence from a LE and an intramolecular charge transfer (ICT) state, see text. Excitation wavelength: (a and b) 340 nm.

Table S1. Data for CVL in Acetonitrile (MeCN) at Room Temperature

| | ref 5 | ref 2 | ref 18 | ref 13 | Tables 1, 2, 4 | ref 38 ^g |
|---|------------------------|------------------------|--------|-------------------|------------------------|---------------------|
| $\tilde{\nu}^{\max}(\text{S}_{1,\text{abs}})$ (cm ⁻¹) | | 27950 | | 28020 | 27995 | |
| $\tilde{\nu}^{\max}(\text{S}_{2,\text{abs}})$ (cm ⁻¹) | 36500 | | | | 36590 (S3) | |
| ε^{\max} (M ⁻¹ cm ⁻¹) | 39000 | | | | | |
| $\tilde{\nu}^{\max}(\text{ICT})$ (cm ⁻¹) | | 16950 | | 16780 | 16440 | 9480 |
| $\tilde{\nu}^{\max}(\text{LE})$ (cm ⁻¹) | 18480 (flu) | 22650 | | 23200 | 22680 | 18870 |
| $\Phi(\text{LE})$ | | 6 x 10 ⁻⁴ | | | 3.8 x 10 ⁻⁴ | |
| $\Phi'(\text{ICT})$ | 1.3 x 10 ⁻³ | 1.3 x 10 ⁻³ | | | 7.0 x 10 ⁻³ | |
| Φ'/Φ | | 6.5 | | 13.3 | 18.3 | |
| $\Phi(\text{ISC})$ | 1 | | | | 0.015 | |
| $\tau_1(\text{LE})$ (ns) | 1.8 ^a | 1.5 | | 1.2 | 1.18 ^e | |
| $\tau_1(\text{ICT})$ (ns) | 1.8 ^a | 1.4 | | 1.2 | 1.18 ^e | |
| $\tau_2(\text{LE})$ (ps) | | | 7.8 | 8 | 9.16 | |
| $\tau_2(\text{ICT})$ (ps) | | | 9.5 | 8 | 9.16 | |
| A_{12}/A_{11} (eq 9) | | | | 49.4 | 35.3 | |
| k_a (10 ⁹ s ⁻¹) | | | | 120 | 106.2 | |
| k_d (10 ⁹ s ⁻¹) | | | | 2.3 | 2.95 | |
| $\mu_e(\text{LE})$ (D) | | 10.7 ^b | | 9-12 ^d | 17 | |
| $\mu_e(\text{ICT})$ (D) | | 25.2 ^c | | 24 ^e | 33 | |
| ΔG (kJ/mol) | | | | -9.8 | -8.9 | |
| ΔG^\ddagger (kJ/mol) | | | | | 10.1 | 85.8 |

^aFrom Stern-Volmer quenchin expression $k_q \tau_1$, with assumed $k_q = 2 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. ^bWith Onsager radius $\rho = 3.6 \text{ \AA}$ and $\mu_g = 5.5 \text{ D}$. ^cWith Onsager radius $\rho = 5.8 \text{ \AA}$ and $\mu_g = 5.5 \text{ D}$. ^dWith Onsager radius $\rho = 3.6 \text{ \AA}$ (from ref 2) and $\mu_g = 6.0 \text{ D}$. ^eWith Onsager radius $\rho = 5.8 \text{ \AA}$ (from ref 2) and $\mu_g = 6.0 \text{ D}$. ^f $\tau_o(\text{ICT}) = 1.15 \text{ ns}$ (Table 4). ^gFrom molecular dynamics simulations.

Table S2. Thermodynamic and Dynamic Parameters of CVL and Other D/A Molecules

| D/A molecule ^a | CVL | DMABN | PP | PP | PP | FPP | FPP | PP4F |
|--------------------------------------|-------------|-------|------------------|------------------|------|-------------------|---------------------------|------|
| Solvent | MeCN | MeCN | MeCN | EtCN | PrCN | MeCN | EtCN | EtCN |
| Ref | Tables 4, 6 | 44 | 48 | 48 | 35 | 70 | 70 | 70 |
| ΔH (kJ/mol) | -19.7 | -27 | -10 | -6.7 | -4.6 | 14.5 ^e | -16.7 (12.8) ^e | -14 |
| ΔS (J/mol/K) | -35.8 | -38 | -28 | -27 | -23 | | -57 | -44 |
| $E(\text{FC})^b$ (kJ/mol) | 88.7 | 89 | 77 | 71 | 71 | 75e | 70 (66) ^e | |
| ΔG^b (kJ/mol) | -8.9 | -15.5 | -1.5 | 1.4 | | | | |
| ΔG^\ddagger (kJ/mol) | 10.1 | | | | | | | |
| k_a^c (10^9 s^{-1}) | 106 | 240 | 211 ^d | 111 ^d | | | | |
| k_d^c (10^9 s^{-1}) | 2.95 | 0.47 | | | | | | |
| E_a (kJ/mol) | 3.9 | 5 | 5.7 | 9 | 12.4 | | 3.7 | 5.9 |
| k_a^o (10^{11} s^{-1}) | 4.95 | 18 | 21 | 42 | 92 | | 7 | 15 |
| τ_2^c (ps) | 9.2 | 4.1 | | | | | | |

^a4-(Dimethylamino)benzonitrile (DMABN), *N*-phenylpyrrole (PP), fluorazene (FPP), 4-fluoro-*N*-phenylpyrrole (PP4F). ^bAt 25 °C. $E(\text{FC}) = E(\text{S1}) + \Delta H - \tilde{\nu}^{\text{max}}(\text{ICT}) = 305.0 \text{ kJ/mol} (25495 \text{ cm}^{-1}) - 19.7 \text{ kJ/mol} - 196.6 \text{ kJ/mol} (16440 \text{ cm}^{-1}) = 88.8 \text{ kJ/mol}$, $E(\text{S1})$ from Table 1. ^cAt 25 °C. ^dExtrapolated (ref 48). ^eDetermined from a Stevens-Ban plot, see ref 70. ^eCalculated by employing $\Delta H(\text{SB})$ from a Stevens-Ban plot, see ref 70.

Table S3. Decay Parameters for CVL in Various Solvents at 25 °C. Data Mainly from Ref 13 (Table 3).

| Solvent ^a | $\bar{\tau}_2$ (ps) | $\bar{\tau}_1$ (ns) | $A_{12}/$ A_{11} | k_a (10^9 s^{-1}) | k_d (10^9 s^{-1}) | $1/\tau'_o(\text{ICT})$ (10^9 s^{-1}) | $k_d \tau'_o$ | $\tau'_o(\text{ICT})$ (ns) | $\bar{\tau}_0(\text{LE})$ (ns) | ΔG (kJ/mol) | $\tilde{\nu}^{\text{max}}(\text{ICT})$ (cm^{-1}) |
|----------------------|------------------------|------------------------|-----------------------|------------------------------------|------------------------------------|--|------------------|-------------------------------|-----------------------------------|----------------------------|--|
| MeCN ^b | 9.16 | 1.15 | 35.4 | 106 | 2.95 | 0.89 | 2.95 | 1.12 | 39 | -8.9 | 16970 |
| MeCN | 8 | 1.2 | 49.4 | 123 | 2.45 | 0.85 | 2.89 | 1.18 | 39 | -9.7 (-9.8) ^c | 16780 |
| acetone | 22 | 3.6 | 12.2 | 42.0 | 3.40 | 0.30 | 11.4 | 3.36 | (30) | -6.2 (-6.8) ^c | 18210 |
| PrCN | 25 | 4.6 | 12.2 | 36.96 | 3.00 | 0.23 | 12.9 | 4.30 | 33.5 | -6.2 (-6.7) ^c | 18180 |
| DMF | 23 | 1.4 | 40.4 | 42.41 | 1.02 | 0.73 | 1.39 | 1.37 | 32.4 | -9.2 (-9.2) ^c | 17320 |
| DMSO | 29 | 0.71 | 66.7 | 33.96 | 0.47 | 1.43 | 0.33 | 0.70 | 32.2 | -10.6 (-10.0) ^c | 16640 |
| PC | 30 | 0.6 | 90.0 | 32.95 | 0.33 | 1.68 | 0.19 | 0.59 | (30) | -11.4 (-9.3) ^c | 16770 |
| M/A ^d 3/1 | 41 | 6.4 | 5.5 | 20.62 | 3.71 | 0.18 | $\frac{20.8}{8}$ | 5.63 | (26) | -4.3 (-3.9) ^c | |
| M/A ^d 2/1 | 40 | 5.5 | 5.0 | 20.83 | 4.11 | 0.21 | $\frac{19.5}{3}$ | 4.76 | (26) | -4.0 (-4.2) ^c | |
| M/A ^d 1/1 | 37 | 4.6 | 7.4 | 23.80 | 3.17 | 0.24 | $\frac{13.1}{3}$ | 4.14 | (26) | -5.0 (-5.2) ^c | |
| M/A ^d 1/2 | 27 | 3.5 | 11.0 | 33.94 | 3.04 | 0.31 | 9.87 | 3.25 | (26) | -6.0 (-6.0) ^c | |
| M/A ^c 1/3 | 27 | 3.1 | 12.2 | 34.22 | 2.76 | 0.35 | 7.98 | 2.89 | (26) | -6.2 (-6.3) ^c | |
| P/M ^c 1/4 | 13 | 0.93 | 54.6 | 75.52 | 1.35 | 1.09 | 1.23 | 0.91 | (26) | -10.0 (-9.8) ^c | |
| P/M ^c 2/3 | 15 | 0.83 | 66.7 | 65.66 | 0.95 | 1.22 | 0.78 | 0.82 | (26) | -10.5 (-10.6) ^c | |
| P/M ^c 3/2 | 18 | 0.77 | 66.7 | 54.72 | 0.78 | 1.32 | 0.59 | 0.76 | (26) | -10.5 (-10.2) ^c | |
| P/M ^c 4/1 | 22 | 0.76 | 81.5 | 44.88 | 0.52 | 1.33 | 0.39 | 0.75 | (26) | -11.1 (-9.8) ^c | |

^aSolvents: acetonitrile (MeCN); *n*-propyl cyanide (PrCN), or butyronitrile, incorrectly labeled BuCN in ref 13; *N,N*-dimethylformamide (DMF); dimethylsulfoxide (DMSO); propylene carbonate (PC); ^bData from Tables 4 and 6 in the present paper. ^cData in parentheses listed in *J. Phys. Chem. A* **2011**, *115*, 3746-3754 (ref 13). ^dM/A: methyl acetate/acetone. ^eP/M: PC/MeCN.

Table S4. Data for CVL and Other D/A Molecules in a Series of Solvents at Different Temperatures

| D/A molecule ^a | ref | solvent | T (°C) | $\tau_o(\text{ICT})$ (ns) | $\tilde{\nu}^{\text{max}}(\text{ICT})$ (cm ⁻¹) |
|---------------------------|-----|------------------|--------|---------------------------|--|
| MDB | 67 | toluene | 20 | 2.0 | 24760 ^b |
| | 67 | | -20 | 2.4 | |
| EDB | 67 | toluene | 20 | 2.0 | 24700 ^b |
| | 67 | | -20 | 2.3 | |
| PrDB | 67 | toluene | 20 | 2.1 | 25160 ^b |
| | 67 | | -20 | 2.4 | |
| 24DCMIA | 64 | MeCN | | | 19430 |
| 34DCMIA | 64 | DEE ^c | 25 | | 19970 |

^aMDB: 4-dimethylamino-2,6-dimethyl-benzonitrile; EDB: 4-diethylamino-2,6-dimethyl-benzonitrile; PrDB: 4-di-*n*-propylamino-2,6-dimethyl-benzonitrile; 24DCMIA: 2,4-dicyano-(*N*-methyl-*N*-isopropyl)aniline; 34DCMIA: 3,4-dicyano-(*N*-methyl-*N*-isopropyl)aniline. ^bAt 25 °C. ^cDEE: diethyl ether.

Table S5. Data for PP, PP4F, PP4CN, FPP, FPP4F, and FPP4CN in a Series of Solvents at Different Temperatures

| D/A molecule ^a | Ref | Solvent ^b | T (°C) | $\tau_o(\text{ICT})$ (ns) | $\tilde{\nu}^{\text{max}}(\text{ICT})$ (cm ⁻¹) |
|---------------------------|--------|----------------------|--------|---------------------------|--|
| PP4F | 56 | MeCN | 25 | | 25290 |
| | 65 | MeCN | -45 | 4.8 | 24740 |
| | 52 | EtCN | 25 | | 25210 |
| | 65 | EtCN | -45 | 3.9 | 25050 |
| | 52 | EtCN | -85 | 4.7 | 24860 |
| | 65 | PrCN | -45 | 4.3 | 25160 |
| FPP | 70 | MeCN | 25 | | 26540 |
| | 70 | | -45 | 15.6 | 25020 |
| | 70 | EtCN | 25 | | 27110 |
| | 70 | PrCN | 25 | | 27310 |
| | 70 | | -60 | 13.4 | 26680 |
| | 70 | | -100 | 14.8 | 26320 |
| FPP4F | 56 | MeCN | 25 | | 24920 |
| | 70, 56 | MeCN | -45 | 7.5 | 24410 |
| | 56 | EtCN | 25 | | 25560 |
| | 70, 56 | EtCN | -45 | 6.8 | 24930 |
| | 70, 56 | EtCN | -85 | 8.0 | 24640 |

^a4-Fluoro-*N*-phenylpyrrole. (PP4F), fluorazene (FPP), 4-fluorofluorazene (FPP). ^bSolvents: MeCN (acetonitrile), EtCN (ethyl cyanide), PrCN (*n*-propyl cyanide).

Table S6. Data for Tetrafluoroaminobenzonitriles, DMABN, and DIABN at 25 °C (ref 51)

| D/A molecule ^a | Solvent | $\tau'_o(\text{ICT})$ (ns) | $\tilde{\nu}^{\text{max}}(\text{ICT})$ (cm^{-1}) | $\Phi(\text{ISC})$ | $\Phi(\text{IC})$ | $\Phi(\text{LE})\times 10^{-3}$ | $\Phi'(\text{ICT})\times 10^{-3}$ |
|---------------------------|------------------|-------------------------------|--|--------------------|-------------------|---------------------------------|-----------------------------------|
| DMABN4F | <i>n</i> -hexane | 0.268 | 20860 | | | | 2.6 |
| | MeCN | 0.154 | 17300 | | | | 0.56 |
| DEABN4F | <i>n</i> -hexane | 1.5 | 21000 | 0.42 | 0.57 | | 11.3 |
| | MeCN | 0.535 | 17900 | 0.09 | 0.91 | | 1.7 |
| AZABN4F | <i>n</i> -hexane | 0.078 | 21990 | | | | 0.34 |
| | MeCN | 0.050 | 18190 | | | | 1.54 |
| MABN4F | <i>n</i> -hexane | 0.0043 | 23190 | 0.02 | 0.98 | | 0.13 |
| | MeCN | 0.018 | 19220 | 0.02 | 0.98 | | 0.46 |
| ABN4F | <i>n</i> -hexane | 0.0026 | 24930 | 0.00 | 1.00 | | 0.06 |
| | MeCN | 0.0040 | 20270 | 0.005 | 0.99 | | 0.11 |
| DMABN | <i>n</i> -hexane | | | 0.76 | 0.10 | 140 | |
| | MeCN | 3.80 | 20250 | 0.80 | 0.17 | 0.76 | 29.8 |
| DIABN | <i>n</i> -hexane | | 25720 | | | | |
| | MeCN | | 20490 | | | | |

^aDMABN4F: 2,3,5,6-tetrafluoro-4-(diethylamino)benzonitrile; DEABN4F: 2,3,5,6-tetrafluoro-4-(diethylamino)benzonitrile; AZABN4F: 2,3,5,6-tetrafluoro-4-(azetidiny)benzonitrile; MABN4F: 2,3,5,6-tetrafluoro-4-(methylamino)benzonitrile; ABN4F: 2,3,5,6-tetrafluoro-4-aminobenzonitrile; DMABN: 4-(dimethylamino)benzonitrile; DIABN: 4-(diisopropylamino)benzonitrile.

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