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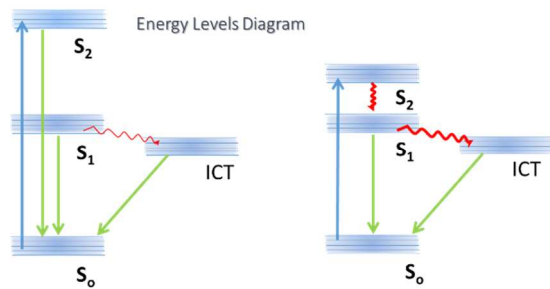


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Enhanced S₂ Emission in Carbazole-Based Ionic Liquids

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Abstract

Ionic liquids composed of a carbazoleimidazolium-based cation and various hydrophobic anions have been synthesized and characterized. Analyses of the absorption spectra of these compounds indicate significant increases in energy gaps between the first two excited singlet states, which results in inhibition of internal conversion from the S₂ to S₁ states. Detailed studies of the spectral properties of these compounds support emission from multiple excited states including possible emission from the second excited singlet state (S₂ emission) in combination with an intramolecular charge transfer state. This conclusion is also consistent with fluorescence lifetime data, which suggest fluorescence emission from multiple electronic excited states. In addition, theoretical calculations of the excited states support these conclusions.

Introduction

Emission from the second excited singlet state (S_2 emission) is an unusual phenomenon as it violates Kasha's rule, which dictates that emission should occur from the lowest excited state of a molecule of a given multiplicity.¹ This suggests that emission from a higher excited state is rare due to a relatively fast non-radiative internal conversion process, which occur among electronic excited states of the same multiplicity. However, if the first two excited states of the same multiplicity do not maintain a large energy gap, the result is a more rapid non-radiative decay as compared to radiative emission from the second excited singlet state. Nevertheless, anomalous emission from second excited singlet states are observed and were first reported in azulene.² In addition, S_2 fluorescence emission has also been observed in a few other classes of compounds such as porphyrin,³ thione,⁴ and carbazole.⁵ Two primary reasons have been invoked for S_2 emission from such compounds. These are, 1) a wide energy gap between the first two excited singlet states that inhibits internal conversion, and 2) the symmetry of the geometries in the excited states. A wide energy gap between the first two excited singlet states reduces vibronic coupling between these excited states, which diminishes the non-radiative process (internal conversion). Inhibition of non-radiative internal conversion leads to radiative emission from the second excited singlet state as observed in the aforementioned compounds. Such molecules have received considerable attention due to their utility for probing the molecular environment (e.g. polarity, viscosity, temperature). This results from dependence of these processes on the environment, and thus remarkable changes in the ratio of first excited singlet state (S_1) and second excited singlet state (S_2) emission intensities are observed in the presence of different media. However, a distinct challenge is examination of the photophysical properties of these molecules in higher excited states. This problem arises from rapid deactivation of the excited

state, as well as other energy and electron transfer processes which may occur in the excited state.^{6, 7} Thus, spectroscopic tools such as ultrafast transient absorption spectroscopy can provide valuable information about these molecules in the excited states and such studies are currently underway in our laboratory. Finally, to the best of our knowledge, all reported studies in the literature for anomalous S_2 emission are in regard to solid phase organic molecules. However, no such studies have been reported for ionic liquids.

Ionic liquids (ILs) are defined as organic salts with melting points below 100 °C. These molecules are well-known for their tunable properties and have found a multitude of applications in a variety of areas such as solvents,^{8, 9} synthesis,⁹ pH sensors,¹⁰ colorimetric sensors,^{10, 11} electrochemistry,¹² and others. Several fluorescent ionic liquids are also known, and their spectral characteristics have been thoroughly studied.^{10, 13} However, to the best of our knowledge, dual fluorescence emission has not been reported for any ionic liquids to date. Herein, we report the first observation of a possible S_2 fluorescence emission phenomenon in ionic liquids. In this study, a carbazoleimidazolium-based iodide salt was synthesized following previously reported protocol,^{14, 15} and subsequently followed with an ion exchange reactions to yield two ILs containing different counter anions, specifically trifluoromethanesulfonate (OTf) and bis(trifluoromethylsulfonyl)imide (NTf₂).

Carbazole is used for this study, which is a p-type semiconductor with two excited states in the absorption spectra and may have potential applications as semiconductor lasers.¹⁶ However, the parent compound does not exhibit any emission from higher excited state, i.e. S_2 emission, due to the small energy gap between the second excited singlet state (S_2) and the first excited singlet state S_1 . In an effort to increase the energy gap, an imidazolium ring was attached at the third carbon of carbazole which produced enhanced conjugation. Two different counteranions were

substituted at the carbazoleimidazolium cation, which produced tunable thermal stability with improved photostability. As specified earlier, these ILs were synthesized in our laboratory in order to increase the energy gap between the second and first excited singlet states by improving conjugation and through formation of an intramolecular charge transfer complex between the carbazole and imidazolium units.¹⁵ The spectral properties of these compounds were studied in order to provide estimates of excited state energies. The absorption spectra, fluorescence emission spectra, and excitation-emission matrix were recorded for each IL in order to provide better insight into spectral properties. Lifetime measurements at various excitation and emission wavelengths were also obtained in order to understand the contributions of emission processes from various excited states to the ground state, as well as between the two excited states in these ionic liquids. Quantum mechanical calculations were performed to ascertain symmetry of the orbitals and to estimate the energy gap between the excited states. Data obtained from these studies were consistent with our experimental observations.

Experimental Section

Materials

Sodium trifluoromethanesulfonate (NaOTf), lithium bis(trifluoromethylsulfonyl)imide (LiNTf₂), were purchased from Sigma Aldrich and used as received. Tetrahydrofuran (THF) was purchased from Macron chemicals and dichloromethane (DCM) was purchased from J.T Baker. Triply deionized water (18.2 M Ω cm) was obtained by use of an Elga model PURELAB ultra water-filtration system and was used for all ion exchange reactions.

Instrumentation

MPA 160 and MPA 161 DigiMelt SRS (Stanford Research System) were used to determine melting points. The phase transition thermal characteristics of these compounds were studied by

use of a Q100 differential scanning calorimeter (DSC, TA instruments, New Castle, DE). A few milligrams of ILs were weighed into an aluminum crucible and sealed with an aluminum lid. The resultant sample was scanned from -40 to 150 °C using a rate of 5 °C min⁻¹ under nitrogen flow of 50 ml min⁻¹. Thermal stability of the ILs were determined by heating a few milligrams at a scan rate of 10 °Cmin⁻¹ from 25 to 600 °C using a Hi Res Modulated TGA 2950 Thermogravimetric Analyzer.

A Shimadzu UV-3101PC and a UV-Vis-near-IR scanning spectrometer (Shimadzu, Columbia, MD) were used for absorbance measurements. All fluorescence measurements were performed on a Spex Fluorolog-3 spectrofluorimeter (model FL3-22TAU3); JobinYvon, Edison, NJ). A 0.4-cm path length quartz cuvet (Starna Cells) was used for fluorescence measurements. All fluorescence studies were performed using right angle geometry. A 0.4 cm path length quartz cuvet was used for absorbance measurements against an identical cell filled with THF as the blank solvent.

Fluorescence lifetimes were measured using a FluoroCube spectrofluorimeter (model FluoroCube, HORIBA Scientific, Edison, NJ) employing the time domain mode. A picosecond pulsed LED excitation source of 273 and 344 nm was used at 1 MHz, and emission collected at 309, 362, and 385 nm using a TBX detector. The time correlated single photon counting (TSCPC) mode was used for lifetime data acquisition with a resolution of 28 ps / Channel over a 100 ns TAC range.

Computational details

A Gaussian 09 program¹⁷ was used for all computation. The geometric structures of compounds were modelled using GaussView 5.0. Ground state geometries of each IL as a whole were optimized using density functional theory (DFT)¹⁸ and time dependent density functional theory

(TDDFT) in the gas phase. A hybrid DFT Becke's three-parameter nonlocal exchange functional^{19,20} employing the correlation functional of Lee-Yang-Parr^{21,22} (B3LYP) was used for all calculations. A split valence basis set of 6-31+G(d,p)^{22,23} was also employed. The choice of basis set with polarized and diffuse functions were used for a better description of electrons relatively far from the nuclei. Vibrational frequencies were analyzed in order to confirm the optimized structures as a local minima. Optimized structures were used for TDDFT by employing the same model chemistry (B3LYP/6-31+G (d,p)) to determine the lowest excitation energies corresponding to the HOMO-LUMO band gap.

Synthesis:

Synthesis of carbazoleimidazolium iodide was performed similar to a previously reported procedure.^{14, 15} All synthesis details and characterization schemes have been presented previously.¹⁵ Two different ionic liquids were synthesized from carbazoleimidazolium iodide (CII) using a metathesis approach. Anion exchange was performed to replace the iodide ion with trifluoromethanesulfonate (OTf) and bis(trifluoromethylsulfonyl)imide (NTf₂) ions using a standard ion exchange protocol. A biphasic mixture of CII in dichloromethane (DCM) and sodium/lithium salts of OTf or NTf₂ in water was stirred for three to four days. After separation of the DCM layer from the water layer, the DCM was rinsed several times with water to remove entrained sodium/lithium iodide impurities. The DCM solvent was removed from the dissolved ionic liquids by use of a rotary evaporator, followed by removal of final traces of water using freeze drying. The final products were characterized using ESI-MS, ¹H-NMR, and ¹⁹F-NMR. The structures of these ionic liquids are shown in Figure 1.

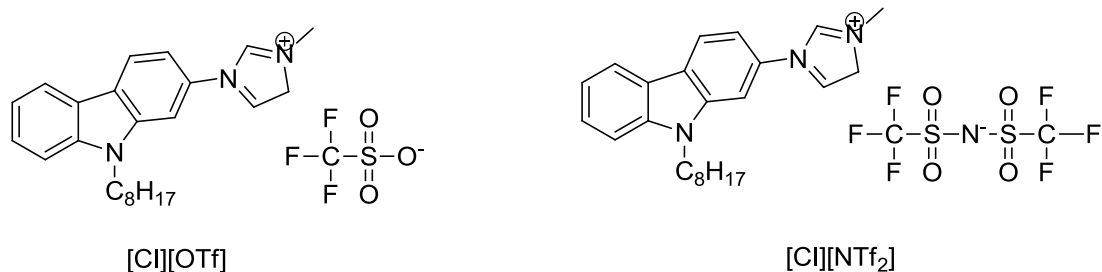


Figure 1. Structures of Synthesized ILs

Physical properties of ILs

Both ILs were light yellow viscous materials. The melting points of these compounds were determined by use of two different approaches. Differential scanning calorimetry results for measurement of melting points were consistent with results obtained from physically observed melting points measured in capillaries filled with the compounds. These latter melting points were obtained by use of an MPA 160 and MPA 161 DigiMelt SRS (Stanford Research System). The carbazoleimidazolium iodide (CII) is a white solid with a very high melting point. After exchange of the iodide ion with bulky hydrophobic anions, the melting points (T_m) of the resulting compounds were lowered substantially and these materials were then consistent with the standard definition of ILs (M.P. < 100 °C). The drops in melting points after anion exchange with relatively large anions are attributed to frustrated packing between the oppositely charged counterions. In addition to that a long alkyl chain is also responsible to acquire amorphous materials with significant decrease in melting point. The [Cl] [NTf₂] compound is a viscous jelly like liquid; hence, was difficult to fill in a capillary to record the melting point. Thermal decomposition temperature (T_d) is significantly improved in the resulting ionic liquids and X-ray diffraction (XRD) data revealed that these ionic liquids are amorphous (See Figure S1).¹⁵

Table 1. Physical properties of CII and ionic liquids

ILs	T _d °C	T _m °C
CII	310	190
[CI][OTf]	395	56
[CI][NTf ₂]	432	<100

Results and Discussion

UV-Vis Spectroscopic Studies

Carbazole and its derivatives have been known to display two major absorption bands, representing respective transitions from the ground state to the first excited singlet state (S_1) and the second excited singlet state (S_2).¹⁶ Thus, at least two peaks are expected in the absorption spectra of carbazoleimidazolium-based ionic liquids since the counter anions employed in this study do not contribute to absorbance in the wavelength range of the UV-Vis spectra of these compounds. The UV-Vis spectra of carbazole and the derived ionic liquids are provided in Figure 2. Interestingly, notable shifts in wavelength corresponding to transitions to the first excited singlet state ($S_1 = 335$ nm) and the second excited singlet state ($S_2 = 275$ nm) were observed in the absorption spectra of these ionic liquids relative to the parent carbazole compound (S_1 at 320 nm and S_2 at 293 nm). A bathochromic shift of S_1 and a hypsochromic shift of S_2 as compared to the parent compound are attributed to extended conjugation in these ionic liquids as a result of attaching the imidazolium ring at the third carbon of carbazole. Thus, this structural change leads to a significant increase in energy gap between the first two excited singlet states of these ionic

liquids. In other words, we can express these findings as

$$(\Delta E_{S_2-S_1})_{\text{carbazoleimidazole ionic liquids}} > (\Delta E_{S_2-S_1})_{\text{carbazole}}$$

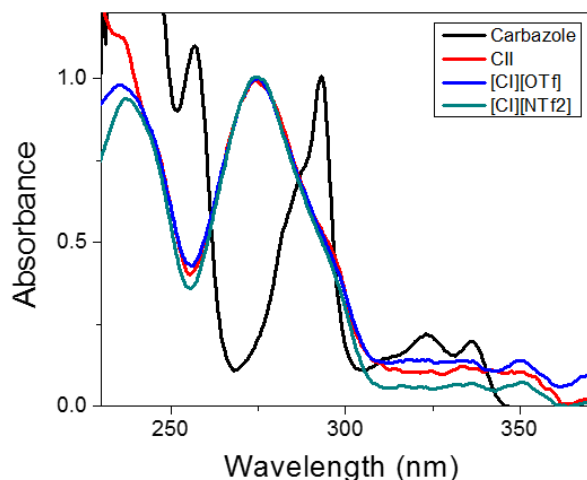


Figure 2. Normalized absorption spectra of carbazole and carbazole-based ionic liquids in THF.

Fluorescence Spectroscopic Studies

Fluorescence emission spectra of our ILs in THF were recorded at two different excitation wavelengths. In our previous studies,¹⁵ the effect of incorporating an imidazolium ring at the third carbon of carbazole was investigated. It was found that this change in structure leads to the formation of an intramolecular charge transfer state, which then results in a large Stokes shift. When excited at the S_1 maxima (335 nm), it was observed that the fluorescence emission spectra, with emission maxima at 385 nm, were very intense and broad as compared to the absorption spectra. Broadening of the emission spectra was ascribed to emission from two different excited states, i.e. the first singlet excited state (S_1 emission) and the intramolecular charge transfer state (emission from ICT). A broad peak with a clearly defined maxima at 385 nm was assigned to emission from ICT, while the shoulder observed at 362 nm, was assigned to a radiative

transition from the S_1 state. When the excitation wavelength was set at the S_2 absorption band (275 nm), a similar broad highly intense spectrum was attained with an additional small peak at shorter wavelength (305 nm) as shown in Figures 3 and S2. This high energy fluorescence peak was not observed when ILs were excited at the S_1 state. This additional peak at lower wavelength, with low intensity, possibly arises from emission of the second excited singlet state (S_2 emission), which is termed an anomalous emission process since it contradicts Kasha's rule of emission from the first excited state.¹ As discussed in the literature, S_2 emission is likely due to an absence or slow rate of internal conversion between the first two excited singlet states (S_2 and S_1) owing to an increase in energy gap and the small vibrational overlap between these two excited states (Franck-Condon).^{5, 24-27} One criterion for S_2 emission is an energy gap greater than 3000 cm^{-1} . However, S_2 emission does not solely depend on the energy gap between these two states. The value of energy gap calculated between the two excited singlet states for these ionic liquids was 6513 cm^{-1} . This value for the present ILs is extremely high relative to the stated criterion for S_2 emission ($\Delta E > 3000\text{ cm}^{-1}$). Examination of the absorption spectra showed a significant wavelength shift in opposite directions for the two excited states, S_2 and S_1 ($\sim 60\text{ nm}$ separation). In comparison, the parent carbazole compound had a gap of only $\sim 30\text{ nm}$. Thus, the primary reason for the observed dual emission in these ILs is reasoned to be the wide energy gap between the first two excited singlet states. Using the energy gap law, we estimate the rate of internal conversion as shown below in equation 1,²⁶

$$k_{IC} \propto \exp(-\beta\Delta E), \quad (1)$$

where β is a constant and ΔE is the energy difference between the two excited states (energy gap). The inverse relationship between the rate of internal conversion and the energy gap between the first two excited states can be used to support the inferred inhibition of the radiationless

deexcitation process (IC) with an increase in the energy gap. We therefore reason that the large energy gap is not the only reason for the observed S_2 emission. For example, S_2 emission also depends on symmetry restrictions and spin multiplicity.²⁵ Our contention in this regard is supported by a few reports in the literature where S_2 emission was observed despite a small energy gap. For example, the energy gap for diphenyloctatetrene^{28, 29} is about $\sim 3000\text{ cm}^{-1}$ and S_2 emission is still observed. This reported observation was explained by invoking symmetry allowed transitions. The energy gap between the first two excited singlet states of the ionic liquids developed in this manuscript are quite large as compared to the reported criteria. However, it is useful to examine the structural symmetry of these molecules. Thus, quantum mechanical calculations were conducted for a better understanding of our observations. These calculations are discussed later in this manuscript.

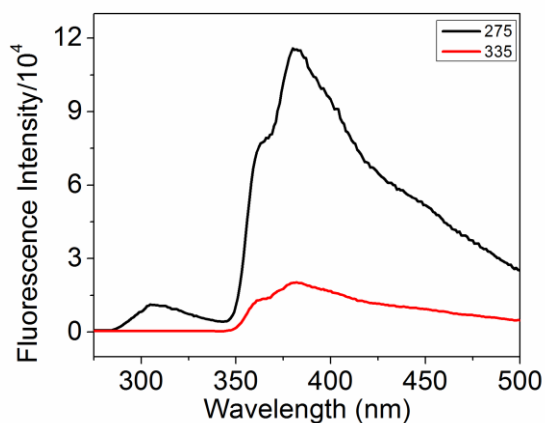


Figure 3. Fluorescence emission spectra of 5 μM solution of $[\text{CI}][\text{NTf}_2]$ in THF at two different excitation wavelengths, S_1 (335 nm) and S_2 (275 nm).

Studies of excitation-emission matrices (EEM) were designed to gain additional information regarding the observed dual emission, shape, and broadness of the peaks. Our compounds were

excited at different wavelengths (250-335 nm using intervals of 5 nm), and the measured fluorescence emissions were recorded. Within the EEM, a broad fluorescence emission peak at 385 nm with a shoulder at 362 nm was observed, while no emission was observed within the lower wavelength region from the S_2 state when the excitation wavelengths were in the range of the S_1 absorption band (335 nm) (Figure 4). It is expected that if this additional peak is arising from S_2 emission, then S_2 emission should not occur in these ILs when excited to the S_1 state (longer wavelength). This is because molecules excited at these longer wavelength can only reach the S_1 state, but are unable to reach the S_2 state due to insufficient excitation energy. Examination of the EEM also did not produce any observed excitation dependent emission from the S_1 and ICT states. The fluorescence spectra were observed to be broad when excited at different wavelengths in the region of S_1 . However, intensity changes were perceived to be the result of fewer molecules reaching the first excited singlet state when excitation wavelengths were shifted from the excitation maxima. Furthermore, another peak in the shorter wavelength region was observed when excited in the region of the S_2 maxima (see Figure 4). This peak is assigned to S_2 emission. Thus, exciting these ionic liquids in the region of the S_2 maxima produces emission from the S_1 , ICT as well as from one higher energy level which is likely the S_2 excited state.

Various derivatives of carbazole have been reported and their photodynamics explored in detail. To our knowledge, only one derivative of the carbazole molecule has been known to produce dual emission (S_2 and S_1 emission).⁶ It is very interesting to present the current data which explain the possibility of emission from more than one excited states in the ionic liquid systems based on carbazole.

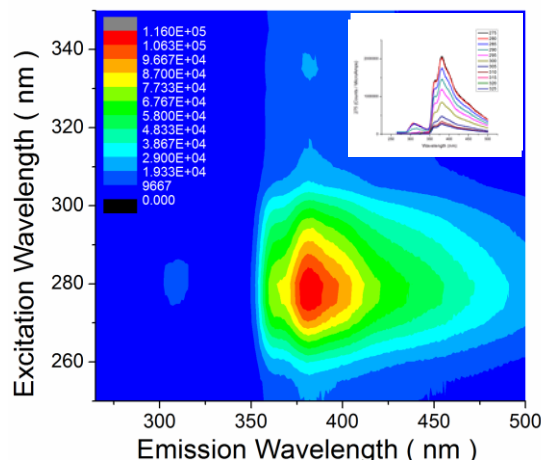


Figure 4. Excitation-emission spectra (EEM) of 5 μM solution of [CI][NTf₂] in THF.

We have further investigated the possibility of intramolecular energy transfer. The acquired absorption spectra clearly reflected (Figure 2) a higher molar extinction coefficient for the S₂ state as compared to the S₁ state. In contrast, the fluorescence emission spectra revealed strong fluorescence emission intensity from the S₁ or ICT states relative to the emission intensity of S₂. This decrease in fluorescence emission intensity of S₂ is ascribed to intramolecular energy transfer from S₂ to S₁ as a result of the moderate overlap between S₂ fluorescence emission and S₁ absorption in these ILs as depicted in Figure S3. The spectral overlap integral ($J(\lambda)$) was estimated using equation 2,³⁰

$$J(\lambda) = \frac{\int_0^{\infty} \varepsilon(\lambda)f(\lambda)\lambda^4 d\lambda}{\int_0^{\infty} f(\lambda)d\lambda}, \quad (2)$$

where ε is the molar extinction coefficient of the acceptor, $f(\lambda)$ is the normalized emission spectrum of the donor, and λ is the wavelength. The overlap integral value calculated for [CI][NTf₂] was $\sim 2.47 \times 10^{-15}$, which suggests the possibility of limited intramolecular Förster resonance energy transfer (FRET) between these two excited states. Since carbazole is a well-known hole semiconductor, there is a high probability of an S₂ \rightarrow ICT transition. We speculate

that it is possible to generate a hole at the carbazole unit after intramolecular charge transfer, followed by immediate electrons jumps from the higher excited states to fill this hole, similar to what is observed for organic light emitting diodes (OLEDs). However, another possible explanation for the less intense fluorescence emission peak of S_2 - S_0 could be a transition from the S_2 to ICT state. In order to understand these multiple emission processes from different excited states, transient absorption experiments are in progress, and will be presented in a later manuscript. These experiments will require modification of our transient absorption apparatus for carbazoleimidazolium-based ionic liquids since it is challenging to perform ultrafast spectroscopy at UV wavelengths in organic solvents.

Fluorescence Lifetime Measurements

The fluorescence lifetime decays of these ILs were measured at different excitation and emission wavelengths to gain a better understanding of the various electronic transitions. These ILs were excited at two different wavelengths, i.e. the first excited singlet state (Ex S_1 344 nm) and the second excited singlet state (Ex S_2 277 nm). Fluorescence was collected at three different wavelengths in order to provide better insight into the photophysical characteristics of emission from the different excited states. The measured emission wavelengths were set at 309 nm (possible S_2 emission), 362 nm (S_1 emission) and 385 nm (ICT emission). The resultant data were fit to a triple exponential decay, and the contributions from fluorescence in each case were determined to be primarily from three states (Table 2). The lifetime of $S_2 \rightarrow S_0$ emission was ascribed to 0.85-1.1 ns. This conclusion was drawn from our observation that the contribution of this component decreased as the collection of emission wavelength shifted from possible S_2 emission while the excitation wavelength was held constant at S_2 . In addition, the highest contribution of this component was noted when ILs were excited at S_2 wavelength and the

emission were collected at S_2 . The two other components in the lifetime data were ascribed to a radiative transition from $ICT \rightarrow S_0$ and $S_1 \rightarrow S_0$. The life time for $ICT \rightarrow S_0$ is estimated at ~ 8 to 9.5 ns, whereas 3-4 ns is ascribed to the fluorescence from $S_1 \rightarrow S_0$ after a back transition between the ICT and S_1 state. A new component of shorter life time appeared when the excitation wavelength was set at 344 nm (S_1). These short 72 ps component in [CI][NTf₂] and 691 ps in [CI][OTf] were attributed to emission from an $S_1 \rightarrow S_0$ transition. In previous studies, it has been observed that substitution of an electron withdrawing group at the third position of carbazole leads to a drop in fluorescence lifetime from 7.33 ns (unsubstituted carbazole) to 350 ps from $S_1 \rightarrow S_0$.¹⁶ Therefore, we conclude that improved conjugation due to substitution of an imidazolium unit into carbazole, leads to a decrease in fluorescence lifetime of the $S_1 \rightarrow S_0$ state into the picosecond timescale. Average lifetimes of the two ILs ([CI][OTf] and [CI][NTf₂]) for $\lambda_{ex} / \lambda_{em}$ 277/309 nm and 277/362 nm exhibit very close values. These values represent the average lifetimes of primarily the S_2 and S_1 states respectively. However, the average lifetime for $\lambda_{ex} / \lambda_{em}$ 277/385 nm representing primarily the charge transfer state are significantly different with nearly three times shorter lifetime for [CI][NTf₂] as compared to [CI][OTf] suggests that variation of the counteranion affects the charge transfer state emission behavior.

Table 2: Fluorescence lifetime data for 10 μ M solution of ILs in THF at different excitation and emission wavelengths.

sample	λ_{ex} $\lambda_{\text{em}}(\text{nm})$	α_1	τ_1 (ns)	α_2	τ_2 (ns)	α_3	τ_3 (ns)	$\tau_{\text{avg}}(\text{ns})$	χ_{red}^2
[CI][OTf]	277/309	0.36	0.985	0.55	3.095	0.09	8.014	2.76	1.042
[CI][OTf]	277/362	0.11	0.857	0.08	3.658	0.81	8.316	7.15	1.029
[CI][OTf]	344/385	0.09	0.691	0.18	3.234	0.73	8.12	6.558	1.013
[CI][NTf ₂]	277/309	0.32	1.139	0.63	3.804	0.05	9.331	3.236	1.027
[CI][NTf ₂]	277/362	0.18	0.915	0.38	4.521	0.44	9.558	6.886	1.044
[CI][NTf ₂]	344/385	0.72	0.072	0.06	2.089	0.22	8.231	1.978	1.066

Optimized Geometries of ILs

TDDFT calculations provide additional understanding of the structural, electrochemical, and optical properties of these new ILs. Optimized geometries revealed that carbazole substituents tend to be planar, while the imidazole moiety is twisted. In all of these systems, the computed HOMO is located primarily at the carbazole unit and the LUMO distributes over the imidazolium moiety (Figure 5).

These molecular orbital diagrams clearly represent electron densities of the ground and excited states (Figure 5). It is noted that the electron density is completely removed from the carbazole unit and distributed into the imidazolium ring in [CI][NTf₂]. In contrast, there is only a slight shift of electron density toward the imidazolium ring in [CI][OTf]. Thus, we conclude that the

anions are primarily responsible for the charge transfer process. Furthermore, we can assume that intramolecular charge transfer is enhanced in the presence of a more hydrophobic anion. Symmetry in the orbitals is also observed for the ground and excited states, and we conclude that S_1 and S_2 absorption peaks are due to π - π^* transitions.

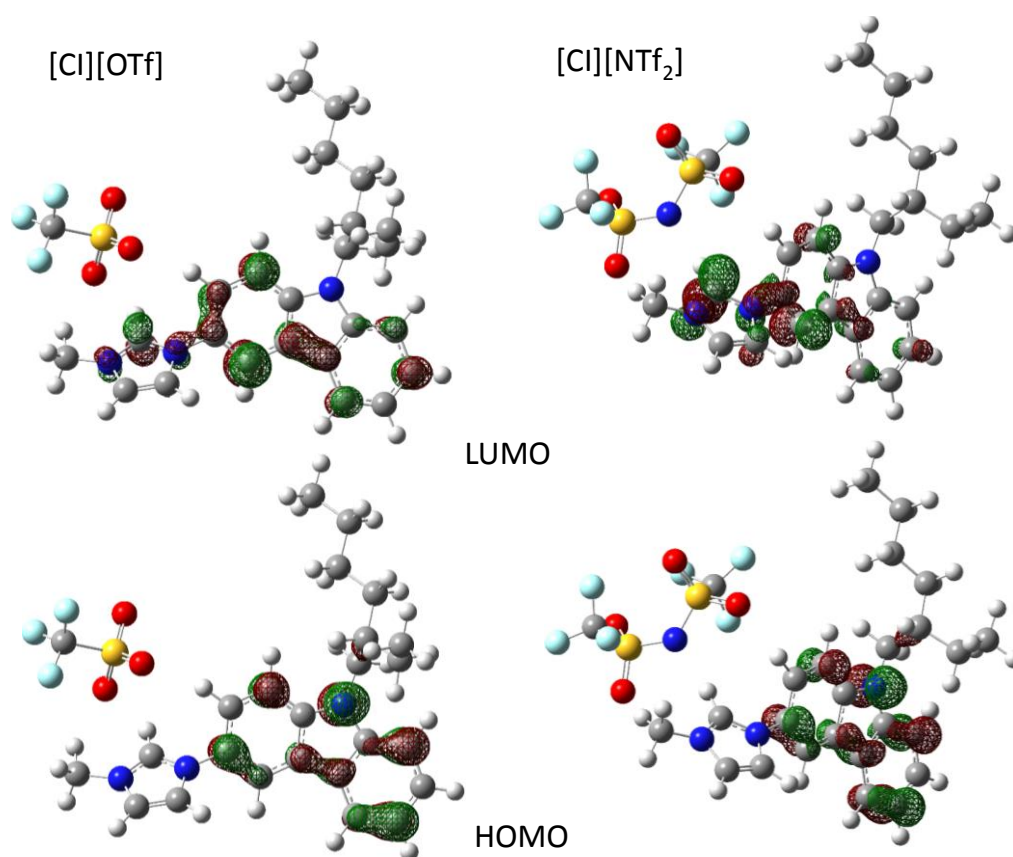


Figure 5. The frontier molecular orbital diagram for two ionic liquids representing intramolecular charge transfer process affected by counteranions.

The computed band gaps using TDDFT are tabulated in Table 3. In all cases, the TDDFT results are in excellent agreement with our experimental results.

Table 3. Computed TDDFT transition energies, excitation wavelengths, and oscillator strengths

Compound	TDDFT excitation energies (eV)	Excitation wavelength (nm)	Oscillator strength (f)	Major contribution
[CI][OTf]	3.77	328.40	0.023	H -> L (0.67)
	4.34	285.51	0.327	H-1 -> L (0.46)
[CI][NTf ₂]	3.74	331.43	0.031	H -> L (0.64)
	4.23	292.75	0.234	H-L -> L (0.64)

Two approximate excitation energies are observed for all ionic liquids as depicted in Table 3. The high oscillator strength represents a HOMO-1 \rightarrow LUMO transition, which corresponds to $S_0 \rightarrow S_2$. The first dipole-allowed electronic transitions correspond to promotion of an electron from HOMO \rightarrow LUMO. This represents the $S_0 \rightarrow S_1$ transition, which has lower oscillator strength as observed in our experimental results. An orbital diagram of these transitions are represented in Figure 6.

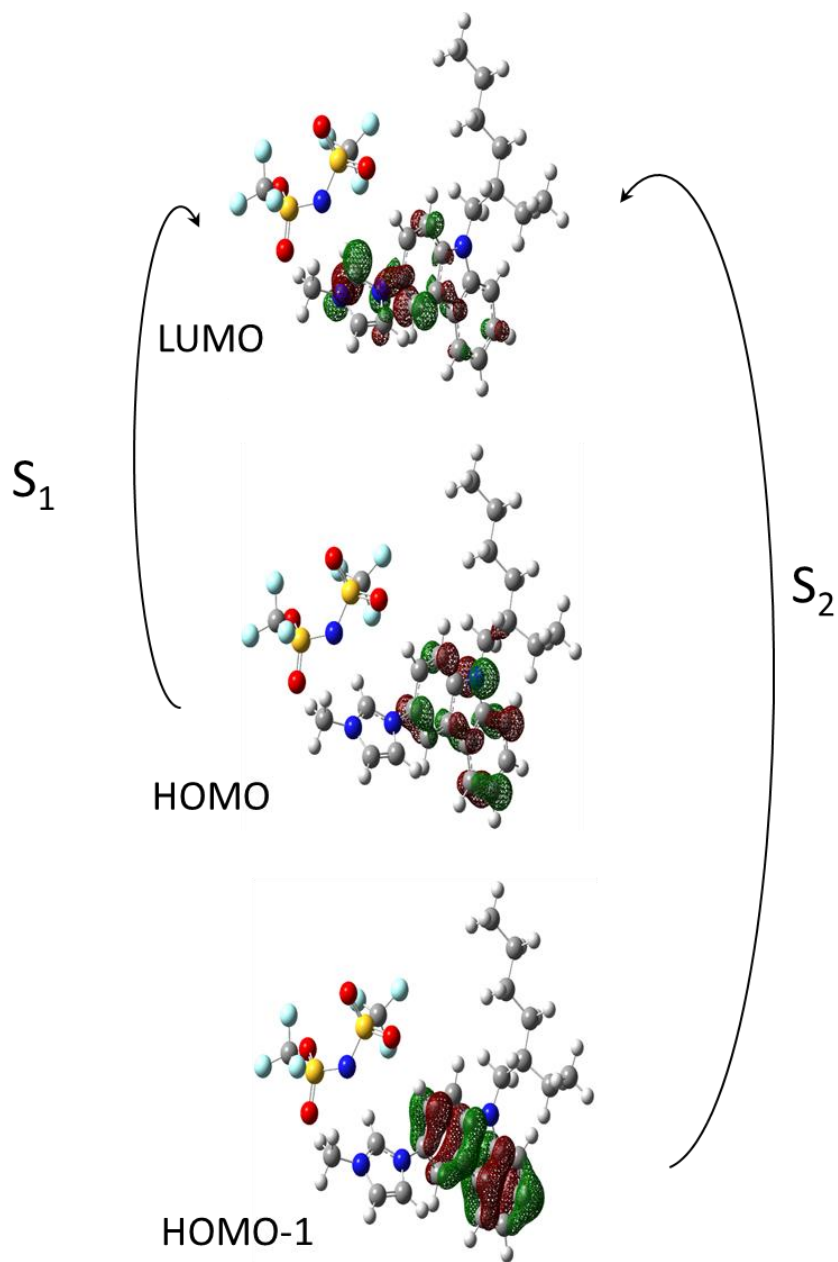


Figure 6. Molecular orbital diagram of [CI][NTf₂] representing the electron density at different excitation and ground states.

Conclusion

Carbazoleimidazolium- based ionic liquids with two different hydrophobic anions were synthesized and characterized. The hydrophobicity of the anions increased with an increase in

size of the trifluoro chain and charge transfer also depends upon the respective counteranions. Enhanced tunable thermal and photostability, which is directly associated with the structure of the counteranions, were acquired in the resultant amorphous ILs. The absorption peaks for the S_1 and S_2 transitions were observed to have a large shift due to extensive conjugation after addition of imidazole at the third carbon of carbazole. This shift of energy levels in the opposite direction increased the energy gap between two singlet excited states. The observed emission at lower wavelength (possible S_2 emission) in these ILs only when excited at S_2 state, was attributed to this significant increase in energy gap between the two excited states, in combination with enhanced symmetry. This significant increase in energy gap between these two states is responsible for suppression of the internal conversion process. Lifetime data supports our contention that fluorescence emission occurs from multiple excited states. Excited states energy levels obtained using a theoretical quantum calculation are also in good agreement with the experimental results.

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