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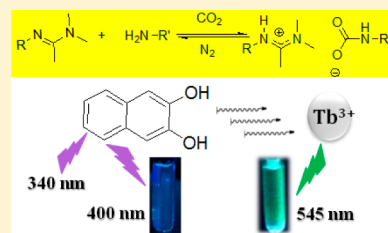
Kizhmuri P. Divya^{†,‡} and Richard G. Weiss^{*,†}

[†]Department of Chemistry and Institute for Soft Matter Synthesis and Metrology, Georgetown University, Washington, District of Columbia 20057-1227, United States

[‡]Department of Chemistry, PSMO College, Tirurangadi, Malappuram, Kerala, India 676 306

S Supporting Information

ABSTRACT: A reversible room-temperature ionic liquid (ILO) was prepared by the addition of CO₂ to an equimolar mixture of hexylamine (AD) and butylamine (AN). The ILO and AD/AN mixture were cycled repeatedly by alternating the passage of CO₂ and N₂ gases through the liquid. The ILO was utilized to sensitize very efficiently energy transfer to and emission by Tb(III) ions when 2,3-dihydroxynaphthalene (DHN) was irradiated. The emission was nearly completely quenched in the AD/AN mixture. The process described here is unique in its use of CO₂ and N₂ to “switch on and off” the emission by a lanthanide ion, Tb(III) in this case. In the corresponding amidinium dithiocarbamate ionic liquid (ILS), no appreciable Tb(III) emission was found due to quenching of the excited singlet state of DHN by thio groups. The ILS was not reconverted to the AD/AN mixture upon adding N₂; N₂ bubbling did not result in the displacement of CS₂.



Previously, we demonstrated that adding triatomic molecules, such as CO₂ or CS₂, to an equimolar mixture of an amidine and a primary amine yields room-temperature ionic liquids (RTILs).^{1–3} The CO₂-derived ionic liquids, amidinium carbamates (ILOs), can be cycled repeatedly with their amidine/amine mixtures by bubbling, in an alternating sequence, CO₂ and an “inert” displacing gas, such as N₂. The ionic liquids formed upon addition of CS₂ to amidine/amine mixtures, amidinium dithiocarbamates, are not reversible under the same conditions and undergo reaction to form thioureas and expulsion of H₂S upon heating.⁴ Various methods, including conductivity, quantification of uptake of CO₂, and NMR and IR spectroscopies, have been used to study the reversibility of amidine/amine mixtures and their corresponding RTILs.² Among other applications, these ILs have been used as the solvents for conversion of epoxides to cyclic carbonates⁵ and to study the reversible electron transfer from an amine to the excited singlet state of pyrene.⁶

Lanthanide complexes are of interest due to their wide range of applications, including bioanalytical imaging,⁷ fluorescent labeling,⁸ and use as light-emitting diodes.⁹ The spectroscopic properties of lanthanide complexes, such as intense and sharp emission bands¹⁰ and high overall quantum yields of the metals upon excitation of ligand chromophores,^{11,12} make them strong candidates for these purposes. The absorption and emission spectra of Ln(III) ions consist of f–f transitions.^{13,14} However, direct excitation of lanthanides leads to weak emission due to the forbidden nature of the transitions; the aforementioned enhancement in the complexes is achieved by avoiding direct excitation and relying upon appropriate energy matching for energy transfer.^{15–17}

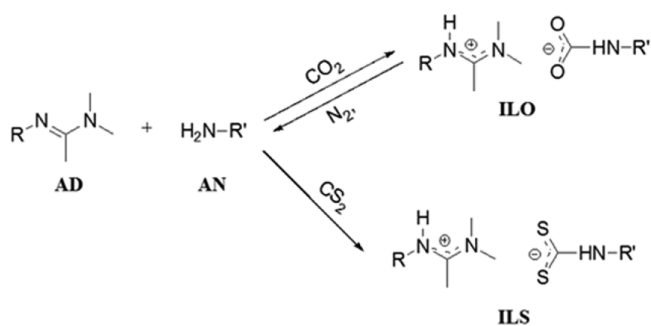
Imidazolium ionic liquids have been used as media for luminescent lanthanide complexes, and they may be able to participate in the sensitization process.¹⁸ Those studies indicate that the nonradiative deactivation processes of Ln(III) ions are decreased more in some ILs than in solid matrixes or organic solvents and result in increased energy-transfer efficiencies to Ln(III).^{19,20} Also, sensitized emission of lanthanide ions, such as Eu(III) and Tb(III) by means of energy donors, pyrene and 2,3-dihydroxynaphthalene (DHN),²¹ has been reported in cholate matrixes,^{22–24} and a 1:1 complex has been observed between Cm(III) and DHN in aqueous media by time-resolved laser-induced fluorescence spectroscopy.²⁵

Here, we report a set of experiments in which the sensitized emission of a lanthanide ion, Tb(III), by DHN in an equimolar mixture of *n*-hexylamine (AD) and *n*-butylamine (AN) can be “turned on” very efficiently by addition of CO₂ to form the ILO and “turned off” by addition of N₂ to re-establish the AD/AN mixture. The on–off emission process, a consequence of the AD/AN ↔ ILO interconversion, can be performed repeatedly by alternating the bubbling of CO₂ and N₂ through the solutions. Note that the emission is lost when N₂, a gas that normally enhances emission intensities, is bubbled through the solution. However, no discernible emission from Tb(III) is found upon excitation of DHN in *n*-hexylammonium *n*-butyl dithiocarbamate (ILS), the corresponding thiolated RTIL prepared by adding CS₂ to the AD/AN mixture (Scheme 1), as a result of very efficient quenching of aromatic excited singlet states by the thiol groups. Two very attractive attributes of the

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Scheme 1. Formation of ILO or ILS by Reaction of the AD/AN Mixture (R = Hexyl; R' = Butyl) with CO₂ or CS₂, Respectively



ILO system are its simplicity—there is no need to preform a complex between the sensitizer and the lanthanide to achieve sensitized emission—and its reversibility. This “demonstration of principle” is clearly amenable to many other ILO systems and other sensitizer–acceptor pairs.

Experimental details, including reagent sources and purities, and instrumentation and procedures are included in the Supporting Information file.

Spectroscopic Investigations in Methanol. Solutions of 10^{-3} and 10^{-5} M DHN in methanol showed characteristic absorption bands at 325, 318, and 311 nm and emission bands ($\lambda_{\text{ex}} = 300$ nm) at 330 and 345 nm, with a shoulder at 360 nm, and the singlet state lifetime was 16 ns ($\lambda_{\text{ex}} = 300$ nm; $\lambda_{\text{em}} = 360$ nm). The spectral shapes and peak positions were unaffected by saturating the solution with air, N₂, or CO₂ (Figure S1, Supporting Information), and the emission spectra were independent of excitation wavelength. However, the absorption and emission spectra changed, and the emission intensity was attenuated upon addition of 10^{-3} M Tb(OAc)₃·4H₂O in methanol that was saturated with N₂. Chelation of Tb(III) by DHN in aqueous ethanol at 303 K is reported to involve 1:1 stoichiometry by potentiometric measurements.²⁶ We assume that similar complexation occurs in methanol and is responsible for the spectral changes. Coordination with Tb(III) enhances spin–orbital coupling in DHN due to heavy atom effects.^{27,28} However, energy transfer to Tb(III) was not facilitated, irrespective of its concentration in methanol and the presence or absence of N₂ or CO₂ (Figure S2b, Supporting Information).

Also, no perceptible changes to the absorption and emission spectra of DHN were found upon addition of Tb(III) when the

saturating gas was CO₂ (Figure S2, Supporting Information). In the presence of CO₂, the methanol solution was slightly acidic. Methanol exists in equilibrium with methyl hydrogen carbonate when CO₂ is present;²⁹ the small amount of water present in the solvent could also react with CO₂ to form carbonic acid. Thus, acidification of the medium (favoring the un-ionized form of DHN) appears to attenuate complexation between DHN and Tb(III).

Spectroscopic Investigations in AD/AN and the ILO. The ILO is thermally stable at room temperature under 1 atm of CO₂ but loses CO₂ at higher temperatures or, as mentioned, if an inert gas such as N₂ is used to displace CO₂. Also as noted, the ILS cannot be reconverted to an AD/AN mixture under similar conditions (Scheme 1). Heating the ILS results in the formation of thioureas and expulsion of H₂S.³ Although both the neat AD/AN mixture and corresponding ILO are transparent above 300 nm, the absorption and emission spectra of 10^{-3} M DHN in both media differ significantly from those in methanol (Figure 1). Note that the shoulder at ~347 nm in the absorption spectrum of DHN is nearly lost in the ILO and is prominent in AD. However, the emission spectra exhibit λ_{max} near 400 nm in AD/AN and AD, but λ_{max} changes to ~385 nm in the ILO (Figure 1b). The ~347 nm absorption and ~400 nm emission peaks are attributed to DHN molecules that are deprotonated. Insofar as these attributions are correct, there must also be some adiabatic deprotonation of DHN in its excited singlet-state manifold.³⁰ These changes in spectral properties were anticipated in media such as AD/AN and the ILO, where DHN can undergo loss of one or two protons.

Evidence for the spectral assignments has been found in the absorption and emission spectra of 10^{-3} M DHN in methanol solutions containing 0.01 M NaOMe. The absorption and emission maxima of DHN are red-shifted by 4 and 14 nm, respectively, compared to the spectra in the ILO, but the shapes are very similar (Figure S3, Supporting Information). The shifts are attributed to different solvent polarities and related extents of deprotonation. The red-shifted shoulder band of 10^{-3} M DHN in AD/AN and AD is ascribed to the formation of a salt between protonated AD and deprotonated DHN or some aggregation; also, 10^{-3} M DHN may self-associate in very polar environments.

The emission spectrum of 10^{-3} M DHN in the ILO is dependent on the excitation wavelength. In contrast to the 16 ns excited singlet lifetime found for DHN in methanol, its lifetime in the ILO was <1 ns ($\lambda_{\text{ex}} = 330$ nm; $\lambda_{\text{em}} = 380$ nm). The transition dipoles of the ¹L_a (short axis of naphthalene

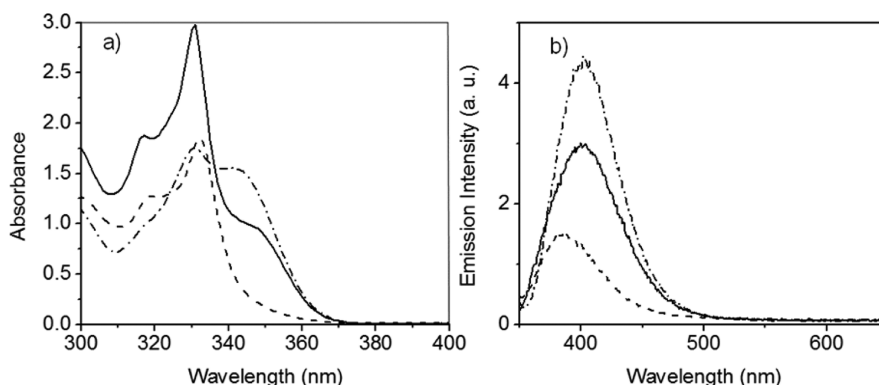


Figure 1. (a) Absorption and (b) emission spectra ($\lambda_{\text{ex}} = 340$ nm) at 295 K of 10^{-3} M DHN in AD/AN (—) and AD (---), both purged with N₂, and in the ILO (·····).

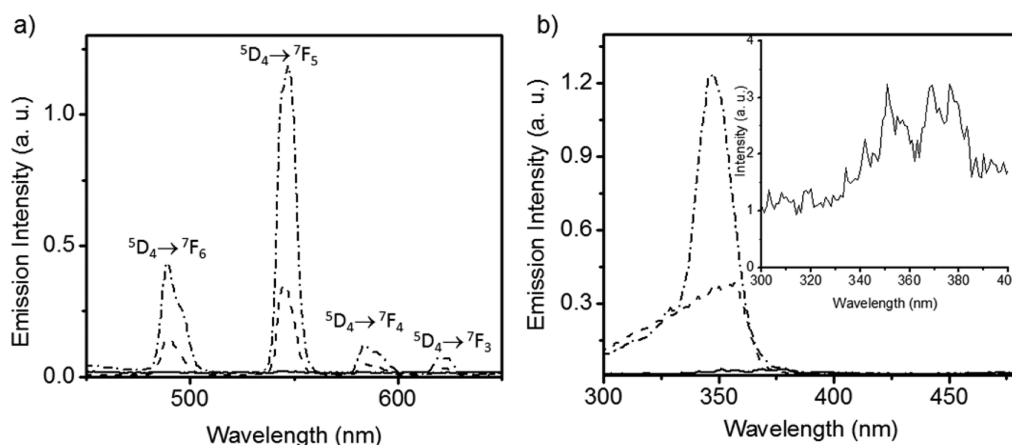


Figure 2. (a) Emission ($\lambda_{\text{ex}} = 340$ nm) and (b) excitation ($\lambda_{\text{em}} = 545$ nm) spectra at 295 K of 4×10^{-3} M $\text{Tb}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$ in AD/AN (—), in AD/AN with 2×10^{-3} M DHN (---), and in the ILO with 2×10^{-3} M DHN (— · — · —). (Inset) An enlarged portion of the excitation spectrum of 4×10^{-3} M $\text{Tb}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$ in AD/AN.

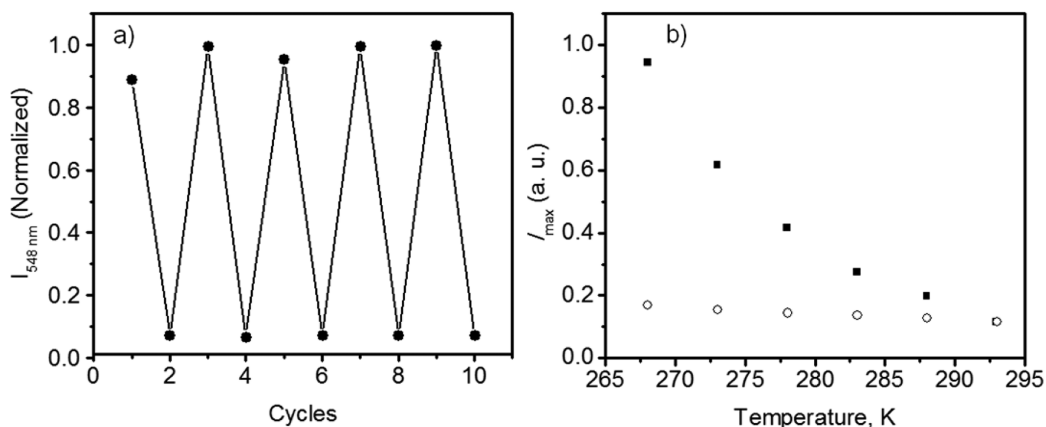


Figure 3. Relative emission intensity at 548 nm ($\lambda_{\text{ex}} = 340$ nm) of 4×10^{-3} M $\text{Tb}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$ and 2×10^{-3} M DHN in the ILO (a) upon repeated cycling between 273 (upper points) and 323 K (lower points) and (b) relative emission intensities at 547 (■) and 390 nm (○) versus temperature.

skeleton) and 1L_b (long axis) transitions of DHN are perpendicular to each other, and their absorption bands overlap partially.³¹ In poly(vinyl alcohol) films, the 327 and 313 nm absorption peaks of DHN belong to the 1L_b transition, while the 320 and weak 360 nm peaks are from the 1L_a transition. The excitation spectra of 10^{-3} M DHN in AD/AN and the ILO are red-shifted considerably with respect to their corresponding absorption spectra (Figure S4, Supporting Information), perhaps as a result of adiabatic proton transfer in the excited state and emissions from deprotonated DHN. Enhanced energy transfer from DHN to Tb(III) in the ILO indicates that the complex formed between Tb(III) and DHN allows energy transfer from the excited singlet state of DHN to Tb(III) without translational diffusion.

Addition of 4×10^{-3} M Tb(III) to 4×10^{-3} M DHN in AD/AN changed significantly the absorption spectrum of DHN (Figure S5, Supporting Information). The prominent broad absorption band at 350 nm indicates strong ground-state complexation between DHN and Tb(III) in AD/AN. However, the absorption spectra of DHN in the absence and presence of Tb(III) were similar in the ILO. Direct excitation of 10^{-3} M $\text{Tb}(\text{OAc})_3 \cdot 4\text{H}_2\text{O}$ in AD/AN at 340 nm did not show detectable Tb(III) emission. Addition of 10^{-3} M DHN to the same solution resulted in a small, but noticeable, increase in the Tb(III) emission. By contrast, a large enhancement in the

intensity of the characteristic emission peaks of Tb(III) at 489 ($^5D_4 \rightarrow ^7F_6$), 547 ($^5D_4 \rightarrow ^7F_5$), 584 ($^5D_4 \rightarrow ^7F_4$), and 620 nm ($^5D_4 \rightarrow ^7F_3$) was observed in the ILO at the same concentrations (Figure 2a). The excitation spectrum for the Tb(III) emission ($\lambda_{\text{em}} = 545$ nm) included the appearance of a new band in the 310–350 nm region, which is slightly shifted from the characteristic DHN emission; at the same time, the intensities of the characteristic bands of Tb(III) are unaltered (Figure 2b). These spectral changes are consistent with the transfer of energy from excited states of DHN to Tb(III) in the ILO due to a combination of good spectral overlap between DHN emission and Tb(III) absorption and complexation between DHN and Tb(III). Proton transfer from DHN to the ILO would enhance complexation with Tb(III) and, thereby, enhance the energy transfer. Although proton transfer may be efficient in the AN/AD mixture as well, the amino functionality in AN quenches the excited singlet state of DHN, making energy transfer to Tb(III) very inefficient. In the ILS, under similar conditions to those employed with the ILO, no emission attributable to energy transfer from DHN to Tb(III) was observed.³² In fact, the fluorescence emission from DHN was completely quenched in ILS, presumably due to quenching by the lone pairs of electrons on the sulfur atoms.³³

As mentioned, nonradiative relaxation processes of Ln(III) ions have been shown to be decreased more in imidazolium-

based ILs than in the solid state or in organic solutions.^{13,34,35} However, a major factor influencing the efficiency of energy transfer in the ILO studied here may be the extent of proton loss by DHN. That process cannot be dependent primarily on AD as the proton acceptor because virtually all of the amidine groups are protonated in the ILO and the carbamate groups are only weak bases. However, the high polarity of the ILO medium will support any of the several ionic processes that are needed to promote direct DHN–Tb(III) interactions.

An interesting consequence of the thermal reversibility of the ILO is that the fraction of AD/AN present (i.e., with expelled CO₂) increases with increasing temperature. In the flame-sealed cells employed here, the free CO₂ cannot escape and is readsorbed when the temperature is reduced again. The change in the equilibrium between AD/AN/CO₂ and the ILO can be followed therefore by changes in the intensity of the sensitized Tb(III) emission (Figure 3).

As seen in Figure 3a, heating to 323 K and cooling to 273 K repeatedly leads to very similar minimum and maximum Tb(III) emission intensities, and the gradual loss of Tb(III) emission intensity with increasing temperature is documented in Figure 3b. Over the same temperature range, the intensity of the emission from DHN at 390 nm changes very little.

Stoichiometry of the DHN/Tb(III) Complex and Conditions for Maximum Energy Transfer in the ILO. Chelation of Tb(III) by DHN in aqueous ethanol at 303 K was found to involve 1:1 stoichiometry by potentiometric measurements,²⁶ and no coordination between DHN and Tb(III) was indicated by emission measurements in a cholate gel matrix.¹⁵ However, a plot using Job's method of continuous variation,^{36,37} with the maximum Tb(III) emission intensity as the monitor, indicates a 1:2 DHN/Tb(III) stoichiometry in the ILO at 295 K (Figure 4). Thus, we conclude that significant ground-state association

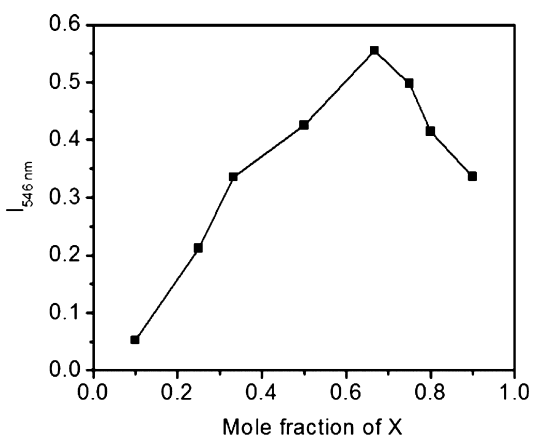


Figure 4. Job plot of emission intensities at 546 nm versus the molar ratios of DHN and Tb(III) in the ILO at 295 K. A 1:2 DHN/Tb(III) stoichiometry is indicated by the maximum.

exists between DHN and Tb(III), and it is a primary cause of the extensive energy transfer found in our studies. The Job plot also suggests that DHN is in its dianionic (i.e., doubly deprotonated) form under the conditions of the experiments.

Using the data for the complexation stoichiometry as a starting point, additional experiments were performed to determine the conditions of maximum energy transfer between DHN excited singlet states and Tb(III) ions. The relative energy-transfer efficiencies were calculated^{38,39} at different concentrations of DHN and a fixed concentration (4×10^{-3}

M) of Tb(OAc)₃·4H₂O (Table S1, Supporting Information). A maximum efficiency of 61% was achieved at 2×10^{-3} M DHN in ILO at 295 K.⁴⁰ As mentioned, under similar conditions, no emission from Tb(III) or from DHN was observed upon excitation of DHN in the ILS.³⁴ Moreover, much of the incident radiation was absorbed by the ILS.⁶

Conclusions. Although both DHN and Tb(OAc)₃·4H₂O are very soluble in the reversible RTILs examined, ILO and ILS (as well as in methanol), only in the ILO did electronic excitation of DHN lead to measurable emission from Tb(III). The ILS absorbs strongly at the excitation wavelengths of DHN, and its thio groups are known to quench efficiently excited singlet states of aromatic molecules such as DHN. In CO₂-saturated methanol, DHN and the Tb(III) ions appear to remain dissociated, and thus, direct (diffusion-controlled) collisional energy transfer is very inefficient due to the very short excited-state lifetimes. However, the solution-phase emission of Tb(III) can be enhanced significantly (i.e., up to 61% emission efficiency) by energy transfer from excited singlet states of DHN in ILO. The substantial emission is attributed to in situ formation of complexes with 2:1 Tb(III)/DHN stoichiometry that allow energy transfer from the excited singlet state of DHN to Tb(III) without translational diffusion.

Although there are other reports of sensitized lanthanide emission in ionic liquids, the process described here is unique in its ability to turn on and off the emission by modulating the presence or absence of CO₂ in the solvent. Two different methods have been used to accomplish this change: (1) by alternating the bubbling of CO₂ and N₂ gases through a solution of the amidine/amine components of the ILO and (2) by adsorbing or displacing the CO₂ within the ILO by cooling or heating the solution in a sealed tube. In addition, there is no need to preform a complex between the lanthanide ions and the sensitizer to ensure efficient sensitized emission; complexation occurs in situ upon simple mixing of the reagents in the ILO solvent.

Future research will explore the sensitization efficiency of Tb(III) by DHN under higher CO₂ pressures and the ability of other aromatic sensitizers to sensitize the emission of a variety of lanthanides in amidine/amine-based reversible ionic liquids that contain different functional groups.^{2,3}

■ ASSOCIATED CONTENT

§ Supporting Information

Additional absorption spectra, fluorescence spectra, sample preparation procedures, and relative energy-transfer efficiencies. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: weissr@georgetown.edu. Fax: +1 2026876209. Tel: +1 2026876013.

Notes

The authors declare no competing financial interest.

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