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Highly Luminescent Sm^{III} Complexes with Intraligand Charge-Transfer Sensitization and the Effect of Solvent Polarity on Their Luminescent Properties

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Supporting Information

ABSTRACT: Samarium complexes with the highest quantum yields to date have been synthesized, and their luminescence properties were studied in 12 solvents. Sensitization via a nontriplet intraligand charge-transfer pathway was also successfully demonstrated in solution states with good quantum yields.

Sensitization via the antenna effect could be achieved through different mutually nonexclusive pathways, depending on the electronic properties of the chromophore. The most common pathway is the triplet-mediated energy-transfer process.[1] Upon photoexcitation of the organic antenna, its singlet excited state undergoes intersystem crossing, where energy is subsequently transferred from the long-lived triplet excited state to the accepting state(s) of Ln^{III}. Transition-metal complexes serving as antennae by their triplet metal-to-ligand charge-transfer transitions have been vastly researched as well.[2−4] Examples of energy transfer between Ln^{III} ions are also observed but are relatively less encountered.[5] Last but not least, sensitization via an intraligand charge-transfer (ILCT) state has also garnered attention because they exhibit excellent light-harvesting opportunities in the visible-light spectrum.[6]

We have previously observed,[7] with time-resolved luminescence experiments, direct energy transfer from the singlet excited state of a 2-(*N*,*N*-diethylanilin-4-yl)-4,6-bis(pyrazol-1-yl)-1,3,5-triazine ligand to Eu^{III}, and such an ILCT state-mediated energy-transfer pathway was further confirmed[8] to effectively quench (>98%) the excited-state energy.

Sm^{III}, on the other hand, suffers from an intrinsic disadvantage of having a weaker luminescence intensity because of a smaller energy gap between the emitting state and the next lower energy level:[9] $\Delta E(^4G_{5/2}\rightarrow{}^6F_{11/2})$ of ca. 7500 cm^{-1} of Sm^{III} versus $\Delta E(^5D_0\rightarrow{}^7F_6)$ of ca. 12500 cm^{-1} of Eu^{III}. The luminescence quantum yields of Sm^{III} complexes in solution thus are normally quite weak, in which the highest quantum yield value of visible emission, to our best knowledge, is 2.7% in pyridine.[10] However, Sm^{III} offers a deeper-red emission (645 nm) than Eu^{III} and is a dual-emitting lanthanide because it emits in the near-IR (NIR) region as well; therefore; research into enhancing the luminescence quantum yields of Sm^{III} has vital potential in a variety of applications.

The optimized structure, by calculations using LUMPAC[11] with a Sparkle/RM1 model, of **Sm-1** is shown in Figure 1. **Sm-2** and **Sm-3** are structurally very similar to **Sm-1** (see the Supporting Information, SI), which is expected because the methyl groups are situated relatively peripherally on the 3 and 5 positions of the pyrazole to exert influence on the coordination environment.

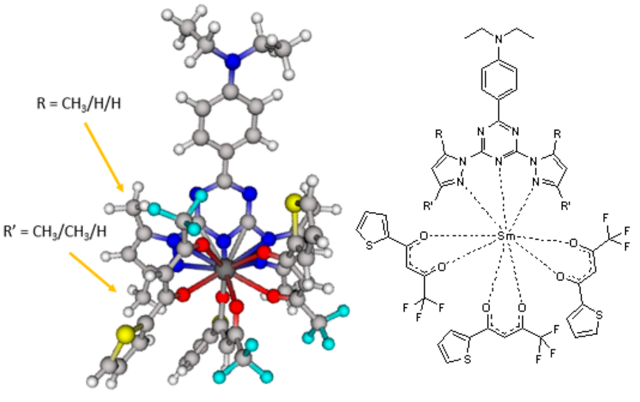

Figure 1. Optimized structure of **Sm-1** (left).

The luminescence properties were studied in 12 solvents with increasing dipole moments, including alcoholic, protic, and nucleophilic solvents. The formation of a hydrogen bond with and the protonation of the lone pair on the aniline would hinder the ILCT transition, affecting the chromophore's excited-state energy, whereas that of the Sm^{III} $^4G_{5/2}$ level would be quenched nonradiatively by resonating with the vibrational overtones of O−H oscillators of the coordinated solvent molecules (Figures 2 and 3).[12]

Our studies show that the broad and structureless ILCT band appears at different positions in the absorption spectra of different solvents and, in general, exhibits a bathochromic shift as the dipole moment of the solvent molecule increases. This phenomenon arises because the solvent is able to stabilize the ILCT ground state by dipole−dipole interaction with the donor−acceptor backbone on the chromophore, leading to a bigger energy gap.[13] The absorption bands peaking at ca. 350 nm are attributed to 2-thenoyltrifluoroacetatonate (tta), where the peak position and shape are not affected by the solvent polarities.

For **Sm-1**−**Sm-3**, excitation at 390 nm gave the highest Sm^{III} luminescence intensity in nonpolar solvents ($\mu \leq 1.6$ D),

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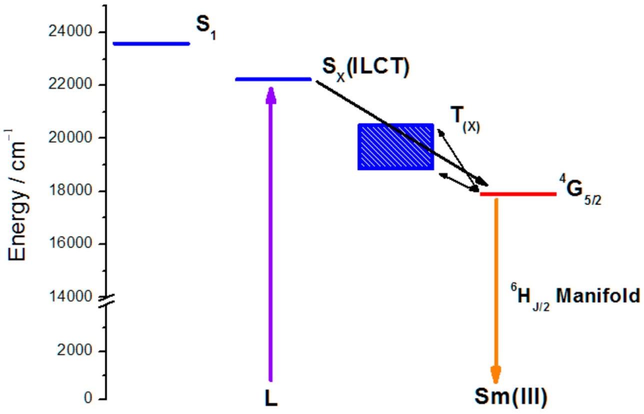

Figure 2. Energy-level diagram depicting triplet sensitization by tta as well as singlet sensitization by the ILCT state of the Sm complexes.

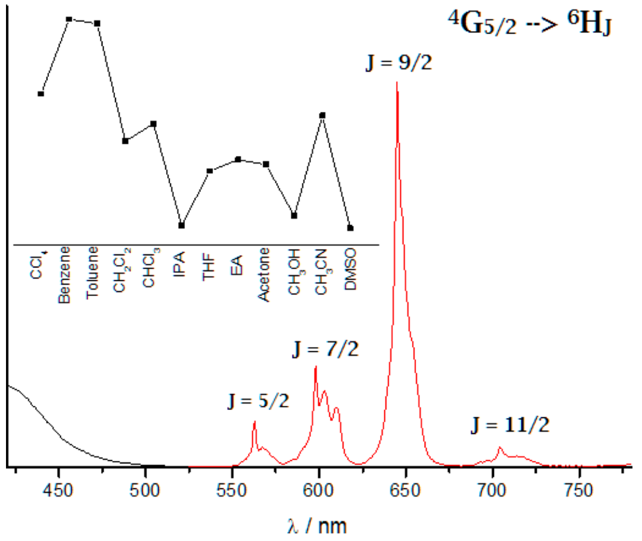

Figure 3. Emission spectrum in the visible region of **Sm-2** in benzene; λ_{ex} = 350 nm. Inset: Integrated luminescence intensities of the $^4G_{5/2} \rightarrow {}^6H_J$ transition of **Sm-2** in different solvents according to increasing dipole moments.

except for isopropyl alcohol (μ = 1.56 D), which was able to form hydrogen bonds. As the dipole moment of the solvent further increased, excitation at 390 nm gave minimal luminescence intensities and a broad ligand fluorescence emission band was observed instead (whereas in acetonitrile clearly recognizable Sm^{III} emission profiles could be observed). Nevertheless, excitation at 390 nm in nonpolar solvents, despite displaying maximum Sm^{III} luminescence, does not necessarily indicate ideal energy transfer because the residual ligand fluorescence, particularly for chloroform and dichloromethane, was at intensities comparable to those of the Sm^{III} f–f transitions.

The luminescence properties do no change much for the other analogues because modification of the tridentate ligand has a minimal effect on the energy transfer from tta to Sm^{III} and does not play a role, if any, in the ILCT transitions.

The emission lifetimes of the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition were measured, and the lifetimes in nonpolar solvents were longer than 100 μs, whereas in alcoholic and polar solvents, the lifetimes were at ca. 30 μs. However, in chloroform, dichloromethane, and acetonitrile, two distinctive luminescence lifetimes were observed, i.e., biexponential decay (Figures S39–S41 in the SI). Further kinetics studies on their UV–vis absorption properties revealed that the compound was not stable and the original species already decayed within 5 min, notably the diminishing of the ILCT band absorption (see the SI) and the possible appearance of free ligand absorption. The instability issue was observed in carbon tetrachloride as well, yet the lifetimes were well-fitted to a monoexponential decay, indicating slower deterioration. Again, the luminescence lifetime behaviors are very similar for the analogues, and the peculiar instability issues are being investigated concurrently and will be followed up on in our future work.

Luminescence lifetimes in methanol and methanol-d_4 were measured and used to calculate the number of coordinated solvent molecules (Table 1 and Figure 4). It was found that about four methanol molecules coordinated to Sm^{III}, rendering the drastic difference between the lifetimes. This result may

Table 1. Luminescence Lifetimes and Quantum Yields (Estimated Error of ±10% and 15%, Respectively) in the Visible Region for Sm-1–Sm-3 in Different Solvents[a]

		lifetime (μs)[b]			quantum yield (%)[c]		
solvent	μ (D)	**Sm-1**	**Sm-2**	**Sm-3**	**Sm-1**	**Sm-2**	**Sm-3**
CCl_4	0	134	133	159	4.3	3.9	3.9
benzene	0	114	113	106	4.5	4.9	3.8
toluene	0.31	102	103	93.5	3.9	4.2	3.1
CH_2Cl_2	1.14	27.8	26.8	22.4		*d*	
$CHCl_3$	1.15	66.3	64			*d*	
i-PrOH	1.66	22.8	21.9	22.4	0.82	0.29	0.65
THF	1.75	30.7	33.4	27.2	1.1	1.2	1.2
EA	1.88	54.7	57.7	58.7	1.4	1.4	1.4
acetone	2.69	37.8	97.2	32	0.65	1.4	0.57
CH_3OH	2.87	12.7	12.3	15.9	0.18	0.19	0.14
CH_3CN	3.44	71.2	98.1	55.6	0.50	2.3	0.31
DMSO	4.1	28.8	28.9	25.9	0.44	*e*	0.48

[a] Reported data are mean values of triplicates. [b] Emission lifetime of the $^4G_{5/2} \rightarrow {}^6H_{9/2}$ transition; λ_{ex} = 350 nm. [c] Relative to quinine sulfate in 0.1 M H_2SO_4 (λ_{ex} = 350 nm; Φ = 0.577). [d] Instability upon dilution, inappropriate for measurement. [e] Sm^{III} luminescence dominated by ligand fluorescence.

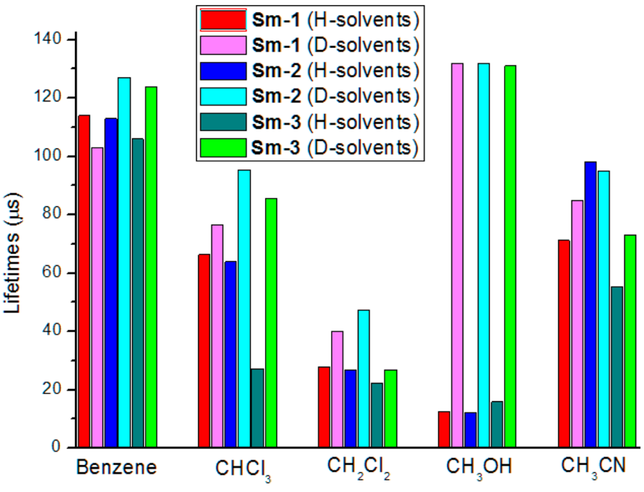

Figure 4. Luminescence lifetimes of **Sm-1**–**Sm-3** (left to right) in selected solvents and their deuterated equivalents.

shed light into the elucidation of possible species responsible for biexponential decay.

In accordance with the lifetime measurements, the quantum yields of the polar solvents are much lower than those of the nonpolar solvents, implying that the radiative lifetime is in a direct relationship with the overall quantum yield and further suggesting that the sensitization efficiencies[14] of the complex in different solvents remained similar. Although energy dissipation toward radiative transitions in the NIR region is not investigated in this work, it is reasonable to assume that the lower quantum yields in polar solvents could be attributed to (1) the (hypsochromic) shift of the excited-state energy of the antenna, rendering less efficient population of $^4G_{5/2}$ by thermally promoted back energy transfer, (2) nonradiative quenching by vibrational overtones of O−H and C−H oscillators in proximity to the Sm^{III} center, and (3) the loss of the excited-state energy via dipole−dipole coupling of the ligand and solvent molecules.

The long luminescence lifetimes and high quantum yields in the visible region in nonpolar solvents are due to the following: first, the absence of nucleophilic solvent molecules displacing the tridentate ligand prevents inner-sphere quenching of oscillators and, second, nonpolar solvent molecules lack dipole−dipole interaction with the donor−acceptor structure of the complexes but rather provide a relatively more rigid solution-state environment to minimize vibrational quenching processes.

The absolute quantum yield was also measured for complexes that were excited at their ILCT band absorption maximum, which excludes tta excitation, in order to explore nontriplet sensitization of Sm^{III} luminescence. **Sm-2** again exhibited in the highest quantum yield among all, with 4% in toluene and 3% in benzene. **Sm-1** and **Sm-3** averaged a value of 2% in both solvents. It could be concluded that excitation solely at the ILCT absorption band (410 nm) was able to sensitize Sm^{III} as well, with luminescence comparable to that of the conventional triplet-mediated excited-state energy-transfer mechanism.

■ CONCLUSIONS

Three Sm^{III} complexes have been synthesized with a diethylamino moiety, which imparts an ILCT band onto the chromophore. Proving previously that the ILCT band was able to sensitize Eu^{III} luminescence via a nontriplet energy-transfer pathway, we were able to demonstrate in this work that Sm^{III} luminescence could also be sensitized likewise. High quantum yields surpassing literature values were also recorded in solution (highest at 4.9% in benzene). The luminescence lifetimes and quantum yields were measured in 12 solvents for thorough investigation and were found, in general, to decrease as the dipole moment of the solvent increases, suggesting other nonradiative deactivation dominating the decrease. This work also showed the possibility of tuning the color of the Sm^{III} complexes in different polar environments for potential material applications. Future work on NIR emissions sensitized by the ILCT band on Sm^{III} as well as Nd^{III} and Yb^{III} complexes is ongoing, and the unexpected instability issue will also be addressed in our future work.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details, characterization, and full photophysical spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Bünzli, J.-C. G.; Piguet, C. *Chem. Soc. Rev.* **2005**, *34*, 1048−1077. (b) Moore, E. G.; Samuel, A. P. S.; Raymond, K. N. *Acc. Chem. Res.* **2006**, *42*, 542−552.

(2) Pope, S. J. A.; Coe, B. J.; Faulkner, S.; Bichenkova, E. V.; Yu, X.; Douglas, K. T. *J. Am. Chem. Soc.* **2004**, *126*, 9490−9491.

(3) Coppo, P.; Duati, M.; Kozhevnikov, V. N.; Hofstraat, J. W.; De Cola, L. *Angew. Chem., Int. Ed.* **2005**, *44*, 1806−1810.

(4) Pope, S. J. A.; Coe, B. J.; Faulkner, S. *Chem. Commun.* **2004**, 1550−1551.

(5) Faulkner, S.; Pope, S. J. A. *J. Am. Chem. Soc.* **2003**, *125*, 10526−10527.

(6) (a) D'Aléo, A.; Picot, A.; Beeby, A.; Williams, G. J. A.; Le Guennic, B.; Andraud, C.; Maury, O. *Inorg. Chem.* **2008**, *47*, 10258−10268. (b) D'Aléo, A.; Pointillart, F.; Ouahab, L.; Andraud, C.; Maury, O. *Coord. Chem. Rev.* **2012**, *256*, 1604−1620.

(7) Yang, C.; Fu, L.-M.; Wang, Y.; Zhang, J. P.; Wong, W.-T.; Ai, X.-C.; Qiao, Y.-F.; Zou, B.-S.; Gui, L.-L. *Angew. Chem., Int. Ed.* **2004**, *43*, 5010−5013.

(8) Fu, L.-M.; Ai, X.-C.; Li, M.-Y.; Wen, X.-F.; Hao, R.; Wu, Y.-S.; Wang, Y.; Zhang, J.-P. *J. Phys. Chem. A* **2010**, *114*, 4494−4500.

(9) Lunstroot, K.; Nockemann, P.; Van Hecke, K.; Van Meervelt, L.; Görller-Warland, C.; Binnemans, K.; Driesen, K. *Inorg. Chem.* **2009**, *48*, 3018−3026.

(10) Hasegawa, Y.; Tsuruoka, S.; Yoshida, T.; Kawai, H.; Kawai, T. *J. Phys. Chem. A* **2008**, *112*, 803−807.

(11) *Solvents and Solvent Effects in Organic Chemistry*, 4th ed.; Reichardt, C., Welton, T., Eds.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2011.

(12) Holz, R. C.; Chang, A. C.; Horrocks, W. D. *Inorg. Chem.* **1991**, *30*, 3270−3275.

(13) Dutra, J. D. L.; Dispo, T. P.; Freire, R. O. *J. Comput. Chem.* **2014**, *25*, 772−775.

(14) Aebischer, A.; Gumy, F.; Bünzli, J.-C. G. *Phys. Chem. Chem. Phys.* **2009**, *11*, 1346−1353.