Lanthanoid Fluoride Nanoclusters

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# Intense Near-IR Emission from Nanoscale Lanthanoid Fluoride Clusters**

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Lanthanoid-doped fluoride glasses are intense near-IR (NIR) emission sources because of the low-energy phonon characteristics of fluoride lattices.[1–5] These materials are particularly useful in optical applications,[6–12] because fluorides are absolutely air-stable. Unfortunately, the extreme insolubility of lanthanoid ions in the presence of fluoride sources[13–15] has always presented a barrier to developing alternative synthetic approaches to $LnF_x$ materials, particularly in media that would preclude the incorporation of NIR-emission-quenching OH groups. Herein we demonstrate that by using unconventional chalcogen-based ligands we can dramatically alter the solubility characteristics of lanthanoid cations in the presence of fluoride anions. We describe the synthesis, structural characterization, and exceptional NIR emission properties of the largest known lanthanoid cluster.

Exposure of in situ prepared $Ln(SePh)_3$ to fluoride sources does not result in the immediate precipitation of solid $LnF_3$. Metathesis reactions of $Ln(SePh)_3$ with $HgF_2$, CsF, or $Me_4NF$ have yet to deliver crystalline products, but reactions of $Ln(SePh)_3$ with $NH_4F$ in pyridine with subsequent filtration and saturation of the solution (either by layering with hexane or slow cooling) result in the crystallization, in 5–20% yields, of nanoscale lanthanoid fluoride clusters that were shown, by low-temperature single crystal X-ray diffraction,[16] to be $[(py)_{24}Ln_{28}F_{68}(SePh)_{16}]$ (Ln = Pr **1**, Nd **2**; py = pyridine; Equation (1)). An ORTEP diagram of the

$$Ln(SePh)_3 + 2\,NH_4F \rightarrow [(py)_{24}Ln_{28}F_{68}(SePh)_{16}] + NH_4SePh + ?? \quad (1)$$

molecular structure of **1** and **2** is shown in Figure 1, with significant bond distances for **1** and **2** given in the caption; complete structural information is given as Supporting Information. Clusters **1** and **2** contain a central set of four 12-coordinate Ln ions encapsulated by six triply bridging and six tetrahedral fluoride ions, which coordinate to the next layer of 24 lanthanoid ions that are then further connected through additional $\mu_2$, $\mu_3$, and $\mu_4$ fluorides, with the surface of the cluster capped by pyridine and selenolates. While the internal Ln coordination numbers are 12, the surface ions are either 8- or 9-coordinate.

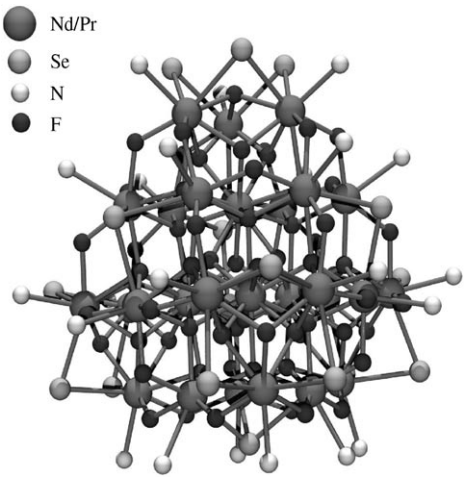


***Figure 1.*** Picture of the fluoride cluster $[(py)_{24}Ln_{28}F_{68}(SePh)_{16}]$ (Ln = Pr (**1** at 200 K), Nd (**2** at 298 K)) with the C and H atoms removed for clarity. Ranges of Ln bond lengths (for **1**/**2** in Å) are: Ln-F 2.26–2.80/2.26–2.88, Ln-Se 3.15–3.18/3.13–3.17, and Ln-N 2.59–2.72/2.57–2.71. Detailed bond geometries for **1** and **2** are given in the Supporting Information.

The surprising solubility of these $LnF_3$-containing materials can be attributed to the relative instability of the selenolate starting materials. Chalcogenolate instability has been used to rationalize the apparent stability of SePh-encapsulated lanthanoid oxo cluster compounds,[17] but in that system $Ln_2O_3$ starting materials did not appear to react with $Ln(SePh)_3$, and so thermodynamic stability of the clusters remained unproven. In the present system, suspended $LnF_3$ reacts with a solution of $Ln(SePh)_3$, but a crystalline product of this reaction has not yet been obtained. Still, the observation of a reaction is additional evidence that selenolate-encapsulated fluoride clusters are thermodynamically stable with respect to precipitation of $LnF_3$. Presumably the total energy of the system is lowered when the selenolate ligands are distributed over a number of $Ln^{III}$ ions.

The potential utility of these clusters as signal amplification sources in organic optical fibers mandates an evaluation of their emission properties. The absorption spectrum of **2**, given in the Supporting Information, is similar to $Nd^{3+}$

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spectral transitions of typical solid-state materials with comparable absorption coefficients.[18–21] The emission spectrum, obtained by exciting the metastable level $^4F_{3/2}$ with 800-nm light, is shown in Figure 2. Two well-resolved emission

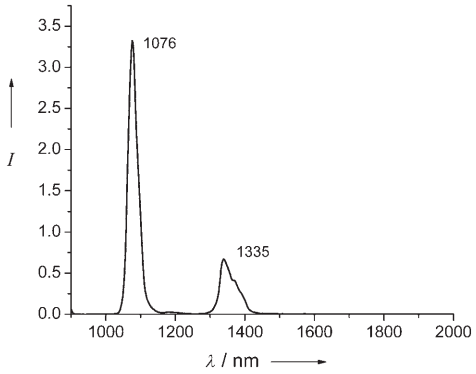


***Figure 2.*** Emission spectrum of **2** pumped with 800-nm light. The 41% quantum efficiency is more than three times greater than the efficiency from any other crystalline Nd molecule or cluster.

bands are observed at 1076 and 1335 nm, corresponding to the $^4F_{3/2}\rightarrow{}^4I_{11/2}$ and $^4F_{3/2}\rightarrow{}^4I_{13/2}$ transitions, respectively. To measure the quantum efficiency of the $^4F_{3/2}\rightarrow{}^4I_{11/2}$ transition, the fluorescence decay time ($\tau_{fl}$) was extracted from the measured decay curve shown in the Supporting Information. The decay curve was fitted with the Monte Carlo model[22] to yield a decay time of 303 μs for the 1076-nm emission. The fitting takes into account all of the cooperative energy-transfer processes between Nd atoms located in the various crystallographic sites. The experimental decay time, together with the calculated radiative decay time,[23,24] results in a calculated quantum efficiency of 41% for **2**. This compares with nearly 100% quantum efficiency for Nd-doped fluoride lattices[1–5] and is significantly greater than our previously reported molecular Nd sources, that is, 16% in $[(thf)_8Nd_8O_2Se_2(SePh)_{14}]$,[25] 12% in $[(py)_{18}Nd_{12}O_6Se_4(SePh)_4(SeSePh)_4Hg(SePh)_2]^{2+}$[17], 9% in $[(dme)_2Nd(SC_6F_5)_3]$ (dme = 1,2-dimethoxyethane),[26] or less than 4% in non-chalcogen-based coordination complexes.[27–33]

There are both distinct similarities and differences between cluster **2** and solid-state $NdF_3$. The structures are vastly different, with the ten-coordinate Nd[34] in $NdF_3$ clearly different from the coordination environments for Nd(1) (CN = 12), Nd(2, 4, 5) (CN = 9), or Nd(3) (CN = 8), although in **2** and in $NdF_3$ there are both pyramidal and tetrahedral fluoride geometries. Still, these materials clearly have solid-state characteristics. In particular, neither **2** nor $NdF_3$ emits at 1.8 μm, and yet emission at 1.3 μm is strong—the 41% quantum efficiency noted for **2** is the highest reported value for a structurally characterized Nd coordination complex. This efficiency is lower than that found in Nd-doped fluoride lattices, presumably owing to both concentration quenching[35] and the proximity of vibronically quenching C–H-containing ligands.[31,36,37]

With SePh capping ligands, Ln ions form thermodynamically stable clusters with fluoride ions to give highly emissive materials. The compounds described herein are the largest lanthanoid cluster compounds reported to date,[38] and the Nd derivative displays the highest quantum efficiency ever recorded for NIR emission from a crystalline Nd coordination complex. The clear demonstration that Ln–selenolate instability can be used to isolate previously inaccessible cluster compounds also implies the utility of this reactivity with other highly electronegative ligands.

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[1] Y. Guyot, A. Collombet, T. Somatri, A. Tkachuk, M.-F. Joubert, *J. Alloys Compd.* **2002**, *341*, 174.
[2] X. Zhang, F. Lahoz, C. Serrano, G. Lacoste, E. Daran, *IEEE J. Quantum Electron.* **2000**, *36*, 243.
[3] S. A. Payne, C. Bibeau, *J. Lumin.* **1998**, *79*, 143.
[4] L. C. Courrol, I. M. Ranieri, R. E. Samad, S. L. Baldochi, L. Gomes, A. Z. de Freitas, N. D. Vieira, Jr., *Proc. SPIE-Int. Soc. Opt. Eng.* **2006**, *6100*, 610010/1.
[5] R. Balda, I. Iparraguirre, J. Azkargorta, J. R. Fernandez, *Proc. SPIE-Int. Soc. Opt. Eng.* **2003**, *5131*, 19.
[6] J. Gottmann, L. Moiseev, D. Wortmann, I. Vasilief, L. Starovoytova, D. Ganser, R. Wagner, *Proc. SPIE-Int. Soc. Opt. Eng.* **2007**, *6459*, 64590W/1.
[7] R. Dekker, D. J. W. Klunder, A. Borreman, M. B. J. Diemeer, K. Worhoff, A. Driessen, J. W. Stouwdam, F. C. J. M. van Veggel, *Appl. Phys. Lett.* **2004**, *85*, 6104.
[8] G. A. Kumar, C. W. Chen, J. Ballato, R. E. Riman, *Chem. Mater.* **2007**, *19*, 1523.
[9] M. Zhang, S. Shi, J. Meng, X. Wang, H. Fan, Z. Yongchun, X. Xuyang, Y. Qian, *J. Phys. Chem. C* **2008**, *112*, 2825.
[10] J. Boyer, J. Gagnon, L. A. Cuccia, J. A. Capobianco, *Chem. Mater.* **2007**, *19*, 3358.
[11] H. Mai, Y. Zhang, R. Si, Z. Yan, L. Sun, L. You, C. Yan, *J. Am. Chem. Soc.* **2006**, *128*, 6426.
[12] G. A. Kumar, J. Ballato, R. Riman, E. Snitzer, *J. Appl. Phys.* **2004**, *95*, 40.
[13] O. Amano, A. Sasahira, Y. Kani, K. Hoshino, M. Aoi, F. Kawamura, *J. Nucl. Sci. Technol.* **2004**, *41*, 55.
[14] M. P. Menon, J. James, *J. Chem. Soc. Faraday Trans.* **1989**, *85*, 2683.
[15] G. Dadabaeva, D. D. Ikrami, R. Okhunov, M. Saidova, *Dokl. Akad. Nauk Tadzh. SSR* **1983**, *26*, 300.
[16] Empirical formula for **1**: $C_{346}H_{330}F_{68}N_{50}Se_{16}Pr_{28}$, $M_r = 11689.44$; space group $I\bar{4}2m$, $a = 23.5934(10)$, $c = 38.658(3)$ Å, $V = 21519(2)$ Å$^3$, $Z = 2$, $D_{calcd} = 1.804$ g cm$^{-3}$, $T = 200(5)$ K, $\lambda = 0.71073$ Å, abs coeff = 4.532 mm$^{-1}$, $R(F) = 0.0720$, $R_w(F^2) = 0.1751$, where $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_w(F^2) = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ for 7890 data with $I > 2\sigma(I)$ out of 13605 unique data with $\theta < 28.35°$. Empirical formula for **2**: $C_{346}H_{330}F_{68}N_{50}Se_{16}Nd_{28}$, $M_r = 11782.68$, space group $I\bar{4}2m$, $a = 23.7770(9)$, $c = 39.272(3)$ Å, $V = 22203(2)$ Å$^3$, $Z = 2$, $D_{calcd} = 1.762$ g cm$^{-3}$, $T = 293(5)$ K, $\lambda = 0.71073$ Å, abs coeff = 4.594 mm$^{-1}$, $R(F) = 0.0535$, $R_w(F^2) = 0.1197$, for 7247 data with $I > 2\sigma(I)$ out of 10555 unique data with $\theta < 25.37°$.
[17] S. Banerjee, G. A. Kumar, R Riman, T. J. Emge, J. G. Brennan, *J. Am. Chem. Soc.* **2007**, *129*, 5926.
[18] G. Oczko, *J. Alloys Compd.* **2000**, *300*, 414.
[19] S. Lis, *J. Alloys Compd.* **2000**, *300*, 88.

  

[20] K. E. Gubina, J. A. Shatrava, V. A. Ovchynnikov, V. M. Amirkhnov, *Polyhedron* **2000**, *19*, 2203.
[21] J. Legendziewicz, G. Oczko, R. Wiglusz, V. Amirkhanov, *J. Alloys Compd.* **2001**, *323*, 792.
[22] L. A. Díaz Torres, O. Barbosa-Garcia, M. A. Meneses-Nava, C. W. Struck, B. Di Bartolo in *Advances in Energy Transfer Processes* (Eds.: B. Di Bartolo, X. Chen), World Scientific Publishing Co., Singapore, **2000**, pp. 523–552.
[23] B. R. Judd, *Phys. Rev. B* **1962**, *127*, 750.
[24] G. S. Ofelt, *J. Chem. Phys.* **1962**, *37*, 511.
[25] S. Banerjee, L. Huebner, M. D. Romanelli, G. A. Kumar, R. E. Riman, T. J. Emge, J. G. Brennan, *J. Am. Chem. Soc.* **2005**, *127*, 15900.
[26] G. A. Kumar, R. E. Riman, L. A. Diaz Torres, S. Banerjee, M. D. Romanelli, T. J. Emge, J. G. Brennan, *Chem. Mater.* **2007**, *19*, 2937.
[27] Y. Hasegawa, T. Ohkubo, K. Sogabe, Y. Kawamura, Y. Wada, N. Nakashima, S. Yanagida, *Angew. Chem.* **2000**, *112*, 365; *Angew. Chem. Int. Ed.* **2000**, *39*, 357.
[28] M. P. O. Wolbers, F. C. J. M. van Veggel, J. W. Hofstraat, F. A. J. Geurts, D. N. Reinhoudt, *J. Chem. Soc. Perkin Trans.* **1997**, 2275.
[29] M. P. O. Wolbers, F. C. J. M. van Veggel, B. H. M. Snellink-Ruel, J. W. Hofstraat, F. A. J. Geurts, D. N. Reinhoudt, *J. Chem. Soc. Perkin Trans. 2* **1998**, 2141.
[30] S. I. Klink, G. A. Hebbink, L. Grave, F. C. J. M. van Veggel, D. N. Reinhoudt, L. H. Slooff, A. Polman, J. W. Hofstraat, *J. Appl. Phys.* **1999**, *86*, 1181.
[31] G. A. Hebbink, F. C. J. M. van Veggel, D. N. Reinhoudt, *Eur. J. Org. Chem.* **2001**, 4101.
[32] Y. Hasegawa, K. Murakoshi, Y. Wada, J. H. Kim, N. Nakashima, T. Yamanaka, S. Yanagida, *Chem. Phys. Lett.* **1996**, *248*, 8.
[33] Y. Wada, T. Okubo, M. Ryo, T. Nakazawa, Y. Hasegawa, S. Yanagida, *J. Am. Chem. Soc.* **2000**, *122*, 8583.
[34] E. Staritzky, L. B. Asprey, *Anal. Chem.* **1957**, *29*, 856.
[35] B. Di Bartolo in *Energy Transfer Processes in Condensed Matter* (Ed.: B. Di Bartolo), Plenum, New York, **1984**, p. 103.
[36] S. Yanagida, H. Hasegawa, K. Murakoshi, Y. Wada, N. Nakashima, T. Yamanaka, *Coord. Chem. Rev.* **1998**, *171*, 461.
[37] V. L. Ermolaev, E. V. Sveshnikova, *Russ. Chem. Rev.* **1994**, *63*, 905.
[38] X. Gu, D. Xue, *Inorg. Chem.* **2007**, *46*, 3212.

  