

Visible-Range Sensitization of Er^{3+} -Based Infrared Emission from Perfluorinated 2-Acylphenoxide Complexes

Yu Peng,^{†,‡} Huanqing Ye,[‡] Zhe Li,^{†,‡} Majid Motevalli,[†] Ignacio Hernández,^{*,§} William P. Gillin,^{*,‡,||} and Peter B. Wyatt^{*,†}

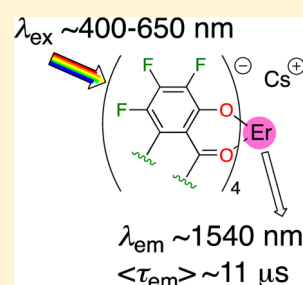
[†]Materials Research Institute, School of Biological and Chemical Sciences and [‡]Materials Research Institute, School of Physics and Astronomy, Queen Mary University of London, London E1 4NS, United Kingdom

[§]Departamento CITIMAC, Facultad de Ciencias, Universidad de Cantabria, Avda. Los Castros, s/n 39005 Santander, Spain

^{||}College of Physical Science and Technology, Sichuan University, Chengdu 610064, People's Republic of China

S Supporting Information

ABSTRACT: Five new fully fluorinated acylphenoxide ligands, which are aromatic analogues of β -diketonates, provide visible photosensitization of the $\text{Er}^{3+} {}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ emission at ~ 1540 nm (of interest for telecommunications) via the “antenna effect”, as observed in $\text{Cs}[\text{ErL}_4]$ compounds. Depending on the chemical functionalization, the excitation wavelength can be tuned in the 400–650 nm range. Decay times for the solids are in the range of 7–16 μs , proving that the complexes can be of interest for a number of optoelectronic and photonic applications.



SECTION: Spectroscopy, Photochemistry, and Excited States

Lanthanide ions are noted for their sharp electronic transitions between different 4f configurations. The potentially long-lived emission of erbium(III) (${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$) at around $1.5 \mu\text{m}$ is minimally absorbed by silica-based optical fibers and thus of particular interest in telecommunications.^{1–3} The f–f transitions have weak absorption coefficients; therefore, laser sources, tuned to the narrow absorption ranges, are required to excite the erbium-doped fibers that are currently used for optical amplification.

The absorption bands of organic chromophores are typically much broader and more intense than those of lanthanide ions. Coordination of organic chromophores to lanthanide ions can sensitize their excitation, giving greatly enhanced emission intensity and potentially enabling the use of broad-band sources to pump devices such as low-cost erbium optical amplifiers. Recent work has demonstrated population inversion of erbium ions under low power excitation in an organic composite system where the erbium ions and the chromophores were separated onto different molecules.³ Other applications of IR-emitting lanthanides exist in the field of biological labeling and imaging,^{1,4} where the use of longer, less-damaging, optical wavelengths can be advantageous in terms of tissue penetration and specificity.

C–H and O–H bonds are high-energy vibrational oscillators, and their presence in the lanthanide complexes should be avoided because they can cause severe vibrational quenching of the electronic excitation, particularly for erbium(III).^{5,6} Fluorinated or chlorinated⁷ ligands could solve this problem due to the lower energy of the C–X bond vibrations. Replacing hydrogen by halogens, with their higher atomic numbers, could

also have favorable effects on the sensitization; intersystem crossing within the photoexcited chromophore is thereby facilitated, and it is expected that a spin number change is required for the energy to be transferred to the lanthanide.⁸

Examples of erbium complexes showing interesting IR-emitting properties with perfluorinated ligands include $\text{Er}\{\text{N}[(\text{C}_6\text{F}_5)_2\text{PO}]_2\}_3$, bis(perfluorophenyl)- and bis(perfluorotolyl)-phosphinate systems.^{9–13} However, simple perfluoroaryl groups such as C_6F_5 or $\text{CF}_3\text{C}_6\text{F}_4$ absorb strongly only in the ultraviolet range. Chromophores that absorb visible light are more desirable as more efficient energy conversion is possible. Visible light is also less likely to degrade organic materials or to be absorbed by molecules other than the chromophore. A very few examples of perfluorinated ligands with absorption in the visible region are already known; these include the 3,4,5,6-tetrafluoro-2-nitrophenoxide ion¹⁴ and the conjugate base of 3-trifluoromethyl-4-hydroxyimino-1-pentafluorophenyl-1H-pyrazol-5-one.¹⁵ However, these species have demonstrated only weak sensitization of erbium ions by visible light.

In this work, we introduce a new family of perfluorinated ligands (Figure 1) including more conjugated systems that can excite the erbium IR emission at wavelengths of up to 650 nm. These ligands are the conjugate bases of 2-acylphenol derivatives and can be considered aromatic analogues of β -diketonates, which are important ligands, especially for lanthanides.^{16–18} We have produced and studied the $\text{Cs}[\text{ErL}_4]$

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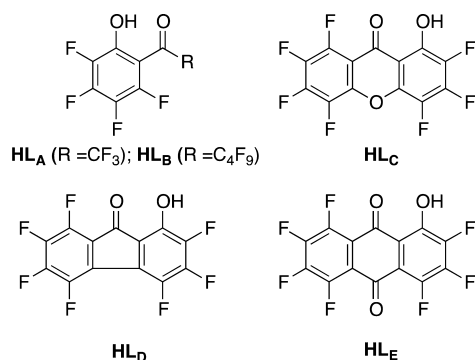


Figure 1. Structures of the perfluorinated ligands **HL_{A–E}**.

compounds, in which the negatively charged erbium tetrakis complexes show sensitization across the visible spectrum, with decay times in the 7–16 μ s range.

The ligands fall into two categories, monocyclic and tricyclic. In the former group (**HL_{A,B}**) the ketone carbonyl groups bear a single-ring aromatic substituent together with perfluoroalkyl groups of varying chain lengths. **HL_{C–E}** are tricyclic ligands with the carbonyl group contained in the central ring, to which fluorinated benzenoid rings are fused on either side. Although only subtle variations in structure are made on the middle rings, the synthetic approaches are unique for each ligand (see the Supporting Information (SI) for detailed synthesis schemes and procedures).

Erbium complexes $CsErL_4$ have been prepared from ligands **HL_{A–E}** (see the SI) and in the following discussion are designated complexes **A–E** according to the ligand used. Crystals of **B** and **D** were suitable for X-ray diffraction, and their fully refined structures show coordination of erbium by the eight oxygen atoms of the ligands (Figure 2). In this respect, they resemble the previously studied⁵ hexafluoroacetylacetonate derivative $Cs[Er(hfa)_4]$. The erbium to phenoxide oxygen distances in **B** and **D** are shorter than the 2.30–2.35 Å erbium to diketonate oxygen distances in $Cs[Er(hfa)_4]$, whereas the erbium to carbonyl oxygen distances in **B** and **D** are longer.

UV–vis diffuse reflectance spectra of the compounds in the solid state are shown in Figure 3. Their corresponding solution absorption spectra in acetonitrile are given in the SI. The absorption maxima of the solids based on single-ring ligands occur at around 400 nm. Complexes **C–E**, containing the more extensively conjugated tricyclic ligands, absorb visible light comparatively strongly, and their absorbance maxima are shifted to longer wavelengths; these complexes also display significant photoluminescence in the visible region (Figure 4).

The NIR emission of these complexes is shown in Figure 5, the $Er^{3+} {}^4I_{13/2} \rightarrow {}^4I_{15/2}$ transition showing very little dependence on the composition. Figure 5 also shows the excitation spectra for the different complexes recorded at 1535 nm. The two single ring complexes each show sensitization (broad excitation from ~400–650 nm). The peaks at ~520 and 660 nm are due to direct absorption into the ${}^2H_{11/2}$ and ${}^4F_{9/2}$ states of the erbium ion, respectively. Even though the observation of these bands suggests that the sensitization efficiency is not as large as that recently observed in a composite system,³ it is still considerably greater than, for example, the factor of 2 typically seen with Yb sensitization.

The impossibility of measuring meaningful line strengths due to the nature of the sample precludes accurate characterization of emission and sensitization efficiencies.¹⁷ Therefore, because

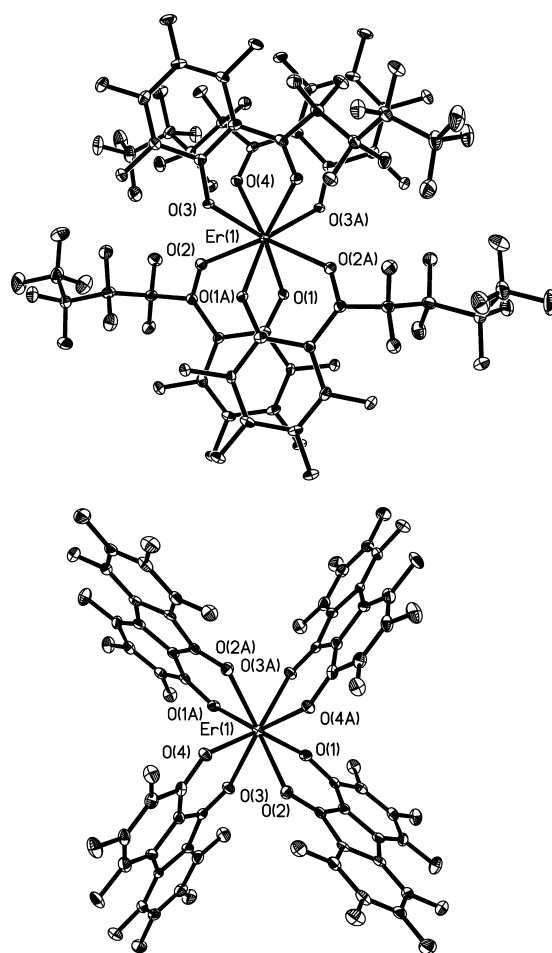


Figure 2. (a) Upper structure: coordination of Er^{3+} in $CsEr(L_B)_4$ with ellipsoids at 50% probability. Er–O distances: O(1) 2.26, O(2) 2.39, O(3) 2.27, and O(4) 2.38 Å. Angles: O(1)–Er(1)–O(2) = 70.5 and O(3)–Er(1)–O(4) = 74.1°. (b) Lower structure: coordination of Er^{3+} in $CsEr(L_D)_4$ with ellipsoids at 35% probability. Er–O distances: O(1) 2.27, O(2) 2.42, O(3) 2.43, and O(4) 2.28 Å. Angles: O(1)–Er(1)–O(2) = 78.4 and O(3)–Er(1)–O(4) = 78.0°.

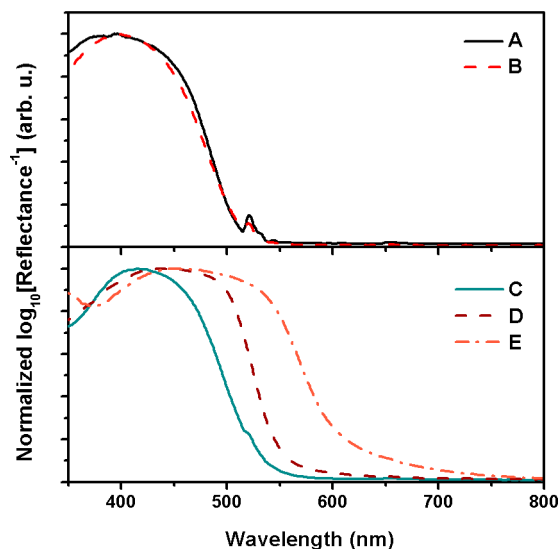


Figure 3. Inverted reflectance spectra of solid $CsErL_4$ complexes.

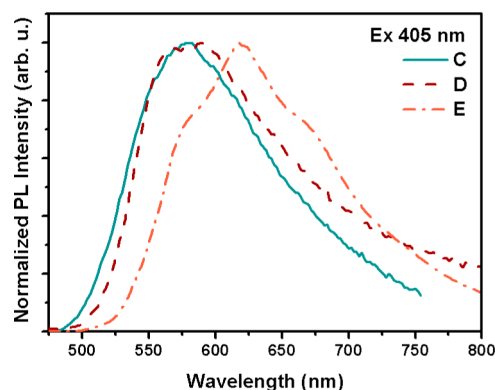


Figure 4. Photoluminescence emission spectra of solid CsErL₄ complexes excited at 405 nm.

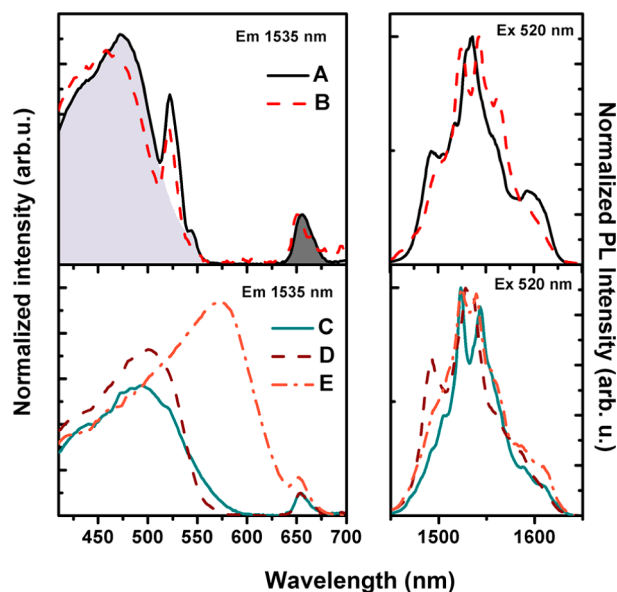


Figure 5. (left) Excitation spectra of CsErL₄ solids. The intensity of the excitation spectra is normalized to the intensity of the 650 nm (erbium) peak. (right) NIR emission spectra of CsErL₄ complexes in the solid.

the intended purpose of sensitization is to broaden and increase the excitation window of erbium species, the indirect excitation pathway intensity is compared to that of the direct excitation. Using the direct excitation peak as an internal standard, we give *relative sensitization* in this Letter to quantify the contribution by chromophores. The same method was employed in ref 3.

For complex A, for instance, the sensitized excitation, integrated across the whole band, is ~19 times the direct excitation at ~660 nm (ratio of light gray to dark gray area in Figure 5; see the SI). Moreover, the excitation through the ligand is more than six times broader than the direct excitation of the ion, enormously increasing the sensitization range and facilitating broad excitation sources such as white light.

The tricyclic ligands show greatly improved and red-shifted sensitization. Indirect excitation reaches over 50 times the direct excitation for complex D, whereas for complex E, it is even higher (the overlap of the bands due to the red shift of the ligand absorption in E precludes a more precise estimate). The comparison of the excitation and the absorption spectra suggests in all cases that sensitization occurs through lower-lying levels in the organic antennae.⁷

The nonexponential PL decay curves of the Er³⁺ ⁴I_{13/2} → ⁴I_{15/2} transition (Figure 6) were fitted to give effective photoluminescence decay times in the range of 7–16 μs (Table 1 and the SI).

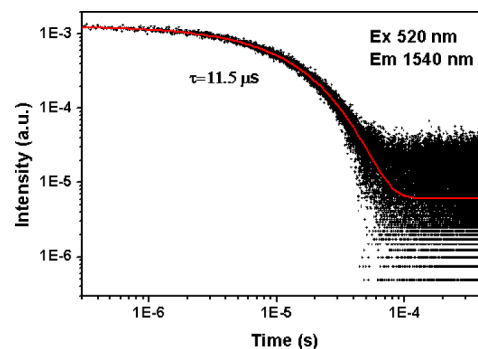


Figure 6. Photoluminescence decay of CsEr(L_E)₄ powder at 1540 nm. The line represents the fitted stretched exponential with a decay constant of 11.5 μs.

Table 1. Luminescence Decay Times^a for Erbium Complexes^b

complex	A	B	C	D	E
$\langle\tau\rangle/\mu\text{s}$	11.1	7.3	15.6	11.3	11.5

^aThe experimental uncertainty in the reported lifetimes is ~±15%.

^bPowder, excitation is at 520 nm, and emission is at 1540 nm; see the SI. Lifetimes measured for excitation at the excitation maxima of the complexes do not differ significantly from the above values.

These values are nearly 10 times higher than those for ¹H-containing hexafluoroacetylacetonates⁵ and similar to the 15.7 μs reported for a fully fluorinated pyrazolone derivative.¹⁵ However, the lifetimes are still much shorter than the hundreds of microseconds observed for perfluorinated erbium complexes in which the coordinating ligand oxygen atoms derive only from P=O groups, rather than C=O (carbonyl) groups.^{9–13} This suggests that carbonyl groups may contribute to vibrational quenching and that future ligand design should focus on combining P=O groups to bind the erbium ion with fully fluorinated fused ring aromatic systems to provide effective sensitization. Importantly, it has recently been demonstrated that the corresponding values of the radiative lifetimes are expected to be reduced due to the combined effect of aromaticity and fluorination.¹⁷ Therefore, the reported decay times represent a considerable increase (more than an order of magnitude) in the IR emission efficiency, with respect to analogous erbium tetrakis diketonates.

In summary, we have synthesized a novel series of fully fluorinated 2-acylphenoxide ligands and characterized, structurally and spectroscopically, their tetrakis erbium(III) complexes. Our ligands function as photosensitizers for the near-infrared emission at 1540 nm. Broad sensitization is obtained that covers most of the visible spectrum up to 650 nm, and luminescence lifetimes exceeding 10 μs have been achieved. Thus, the perfluorinated ligands may be of interest for the broader context of metal complexation,¹⁹ and the erbium compounds are particularly attractive for photonic applications with low-energy, broad-band excitation sources or OLEDs.

■ ASSOCIATED CONTENT

■ Supporting Information

Detailed syntheses, spectroscopic data, examples of relative sensitization and photoluminescence lifetime calculations, crystal structures, and description of the method for measuring excitation spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: p.b.wyatt@qmul.ac.uk (P.B.W.).

*E-mail: w.gillin@qmul.ac.uk (W.P.G.).

*E-mail: ignacio.hernandez@unican.es (I.H.).

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Eliseeva, S. V.; Bünzli, J.-C. G. Lanthanide Luminescence for Functional Materials and Bio-sciences. *Chem. Soc. Rev.* **2010**, *39*, 189–227.
- (2) Curry, R. J.; Gillin, W. P. 1.54 μm Electroluminescence from Erbium(III) Tris(8-hydroxyquinoline) (ErQ)-Based Organic Light-Emitting Diodes. *Appl. Phys. Lett.* **1999**, *75*, 1380–1382.
- (3) Ye, H.; Li, Z.; Peng, Y.; Wang, C. C.; Li, T. Y.; Zheng, Y. X.; Sapelkin, A.; Adamopoulos, G.; Hernández, I.; Wyatt, P. B.; et al. 1.5 μm Optical Gain from a Waveguide Fabricated from an Efficient, Sensitized Organic Lanthanide System. *Nat. Mater.* **2014**, *13*, 382–386.
- (4) Bünzli, J.-C. G. Lanthanide Luminescence for Biomedical Analyses and Imaging. *Chem. Rev.* **2010**, *110*, 2729–2755.
- (5) Tan, R. H. C.; Motevalli, M.; Abrahams, I.; Wyatt, P. B.; Gillin, W. P. Quenching of IR Luminescence of Erbium, Neodymium, and Ytterbium β -Diketonate Complexes by Ligand C–H and C–D Bonds. *J. Phys. Chem. B* **2006**, *110*, 24476–24479.
- (6) Winkless, L.; Tan, R. H. C.; Zheng, Y.; Motevalli, M.; Wyatt, P. B.; Gillin, W. P. Quenching of Er(III) Luminescence by Ligand C–H Vibrations: Implications for the Use of Erbium Complexes in Telecommunications. *Appl. Phys. Lett.* **2006**, *89*, 111115.
- (7) Hernández, I.; Zheng, Y.-X.; Motevalli, M.; Tan, R. H. C.; Gillin, W. P.; Wyatt, P. B. Efficient Sensitized Emission in Yb(III) Pentachlorotropolonate Complexes. *Chem. Commun.* **2013**, *49*, 1933–1935.
- (8) Crosby, G. A.; Whan, R. E.; Alire, R. M. Intramolecular Energy Transfer in Rare Earth Chelates. Role of the Triplet State. *J. Chem. Phys.* **1961**, *34*, 743.
- (9) Mancino, G.; Ferguson, A. J.; Beeby, A.; Long, N. J.; Jones, T. S. Dramatic Increases in the Lifetime of the Er^{3+} Ion in a Molecular Complex Using a Perfluorinated Imidodiphosphinate Sensitizing Ligand. *J. Am. Chem. Soc.* **2005**, *127*, 524–525.
- (10) Glover, P. B.; Bassett, A. P.; Nockemann, P.; Kariuki, B. M.; Van Deun, R.; Pikramenou, Z. Fully Fluorinated Imidodiphosphinate Shells for Visible- and NIR-Emitting Lanthanides: Hitherto Unexpected Effects of Sensitizer Fluorination on Lanthanide Emission Properties. *Chem.—Eur. J.* **2007**, *13*, 6308–6320.
- (11) Song, L.; Hu, J.; Wang, J.; Liu, X.; Zhen, Z. Novel Perfluorodiphenylphosphinic Acid Lanthanide (Er or Er–Yb) Complex with High NIR Photoluminescence Quantum Yield. *Photochem. Photobiol. Sci.* **2008**, *7*, 689–693.
- (12) Tan, R. H. C.; Pearson, J. M.; Zheng, Y.; Wyatt, P. B.; Gillin, W. P. Evidence for Erbium–Erbium Energy Migration in Erbium(III) bis(perfluoro-*p*-tolyl)phosphinate. *Appl. Phys. Lett.* **2008**, *92*, 103303.
- (13) Hernández, I.; Tan, R. H. C.; Pearson, J. M.; Wyatt, P. B.; Gillin, W. P. Nonradiative De-excitation Mechanisms in Long-Lived Erbium(III) Organic Compounds $\text{Er}_x\text{Y}_{1-x}[(p\text{-CF}_3\text{-C}_6\text{F}_4)_2\text{PO}_2]_3$. *J. Phys. Chem. B* **2009**, *113*, 7474–7481.
- (14) Zheng, Y.; Motevalli, M.; Tan, R. H. C.; Abrahams, I.; Gillin, W. P.; Wyatt, P. B. Near IR Luminescent Rare Earth 3,4,5,6-Tetrafluoro-2-nitrophenoxide Complexes: Synthesis, X-ray Crystallography and Spectroscopy. *Polyhedron* **2008**, *27*, 1503–1510.
- (15) Beverina, L.; Crippa, M.; Sassi, M.; Monguzzi, A.; Meinardi, F.; Tubino, R.; Pagani, G. A. Perfluorinated Nitrosopyrazolone-Based Erbium Chelates: A New Efficient Solution Processable NIR Emitter. *Chem. Commun.* **2009**, 5103–5105.
- (16) Binnemans, K. Rare-Earth β -Diketonates. In *Handbook on the Physics and Chemistry of Rare Earths*; Gschneider, K. A., Jr., Bünzli, J.-C. G., Pecharsky, V. K., Eds.; Elsevier: Amsterdam, The Netherlands, 2005; Vol. 35, Chapter 225, p 107.
- (17) Ye, H. Q.; Peng, Y.; Li, Z.; Wang, C. C.; Zheng, Y. X.; Motevalli, M.; Wyatt, P. B.; Gillin, W. P.; Hernández, I. Effect of Fluorination on the Radiative Properties of Er^{3+} Organic Complexes: An Opto-Structural Correlation Study. *J. Phys. Chem. C* **2013**, *117*, 23970–23975.
- (18) Non-fluorinated 2-hydroxybenzophenone ligands are used as photosensitizers for lanthanide ions; see: Zhang, B.; Xiao, T.; Liu, C.; Li, Q.; Zhu, Y.; Tang, M.; Du, C.; Song, M. Systematic Study of the Luminescent Europium-Based Nonanuclear Clusters with Modified 2-Hydroxybenzophenone Ligands. *Inorg. Chem.* **2013**, *52*, 13332–13340.
- (19) For further discussion of the effects of ligand fluorination on the properties of metallo-organic materials, see: Li, Z.; Dellali, A.; Malik, J.; Motevalli, M.; Nix, R. M.; Olukoya, T.; Peng, Y.; Ye, H.; Gillin, W. P.; Hernández, I.; et al. Luminescent Zinc(II) Complexes of Fluorinated Benzothiazol-2-yl Substituted Phenoxide and Enolate Ligands. *Inorg. Chem.* **2013**, *52*, 1379–1387.