

SUPPORTING INFORMATION

Dual Visible and Near-Infrared Luminescence in Mononuclear Macrocyclic Erbium(III) Complexes via Ligand and Metal Centred Excitation

Yolimar Gil^{1*}, Ricardo Costa de Santana^{2*}, Andréa Simone Stucchi de Camargo³, Leonnam Gotardo Merízio³, Patricia Farías Carreño¹, Pablo Fuentealba¹, Jorge Manzur¹ and Evgenia Spodine¹.

¹*Facultad de Ciencias Químicas y Farmacéuticas, Universidad de Chile, Olivos 1007, 8380544, Santiago, Chile.*

²*Instituto de Física, Universidade Federal de Goiás, Campus Samambaia, 74690-900, Goiânia (GO), Brazil.*

³*Instituto de Física de São Carlos, Universidade de São Paulo, Avenida Trabalhador São-Carlense, n° 400 Parque Arnold Schimidt, CEP 13566-590, São Carlos, SP, Brazil.*

Synthesis of macrocyclic Er^{III} complexes (1-3)

A solution of Er(CF₃SO₃)₃ (0.5 mmol, 307 mg) in anhydrous ethanol (30 ml) was added to a solution of 2,6-piridinedicarboxaldehyde (1 mmol, 135 mg) in acetonitrile (50 ml) under stirring. Then, a solution of the corresponding diamine (1 mmol, ethylenediamine (**1**), *o*-phenylenediamine (**2**), or 1,3-diaminepropane (**3**)) in acetonitrile (50 ml) was added dropwise. Subsequently, a solution of Bu₄N SCN (1.5 mmol, 450.8 mg) in anhydrous ethanol (20 ml) was added and the mixture was stirred at room temperature for 4 hours. Single crystals suitable for X-Ray diffraction were obtained by slow evaporation of the solutions at room temperature after 20 days.

For **1**, pale red block crystals in 72.74% (0.24 g) yield were obtained. Anal. calc. for C₂₁H₁₈ErN₉S₃: C, 38.22; H, 2.75; N, 19.10%. Found C, 38.19; H, 2.99; N, 18.76%. IR (cm⁻¹): 2933, 2847 (m, C–H), 2040 (s, C=N, NCS), 1651(m, C=N, imine), 1591(m, C=N, py), 1463 (m, CH₂). For **2**, yellow rods with 0.22 g (55.27 %) yields were obtained. IR (cm⁻¹): 3028, 2963, 2872 (m, C-H), 2040 (s, C=N, NCS), 1630 (m, C=N, imine), 1589 (m, C=N, py), 1490, 739 (m, CH₂). Anal. calc. for C₂₉H₁₈ErN₉S₃: C, 46.08; H, 2.40; N, 16.68 %. Found C, 45.49; H, 3.09; N, 16.35 %. For **3**, pale amber block crystals with a yield of 0.23 g (67.45 %) were obtained. Anal. calc. for C₂₃H₂₂ErN₉S₃: C, 40.16; H, 3.22; N, 18.32 %. Found C, 40.32; H, 2.83; N, 17.97 %. IR (cm⁻¹): 2939, 2872 (m, C-H), 2043 (s, C=N, NCS), 1649 (m, C=N, imine), 1590 (m, C=N, py), 1463 (m, CH₂).

Diffuse Reflectance Spectra

Figures S1a and S1b shows the diffuse reflectance spectra (DRS) of **1** – **3** in the range of 250 to 1800 nm and from 250 to 700 nm, and Figure S1c show DRS for Y^{III} complexes **4**–**6**. The optical absorption edges lie at 400 ± 5 nm for **1** and **3**, and 456 ± 5 nm for **2**. A number of sharp peaks corresponding to several transitions between the $^4I_{15/2}$ ground state and the excited states of the $4f^{11}$ configuration of the Er^{III} ion can also be observed in the spectra; these bands have been assigned following previously reported data^{1,2}, being $^4I_{15/2} \rightarrow ^4F_{5/2,3/2}$ for 450 nm, (1), $^4I_{15/2} \rightarrow ^4F_{7/2}$ for 487 nm (2), $^4I_{15/2} \rightarrow ^2H_{11/2}$ for 519 nm (3), $^4I_{15/2} \rightarrow ^4S_{3/2}$ for 539 nm (4), $^4I_{15/2} \rightarrow ^4F_{9/2}$ for 652 nm (5) and 665 nm (6), $^4I_{15/2} \rightarrow ^4I_{9/2}$ for 785 nm (7), $^4I_{15/2} \rightarrow ^4I_{11/2}$ for 968 nm (8) and $^4I_{15/2} \rightarrow ^4I_{13/2}$ for 1522 nm (12). In addition, the spectra present some bands due to the absorptions of the ligands: 1090–1230 nm (peaks (9) and (10)) and 1600–1850 nm (peaks (13) and (14)) assigned to the third and second overtones of the aromatic C–H vibrations, respectively, and the third band at 1300–1470 nm region, due to overtones of the O–H stretching vibrations. These are also observed in the spectra of the Y^{III} complexes **4**–**6**, (Figure S1c)¹.

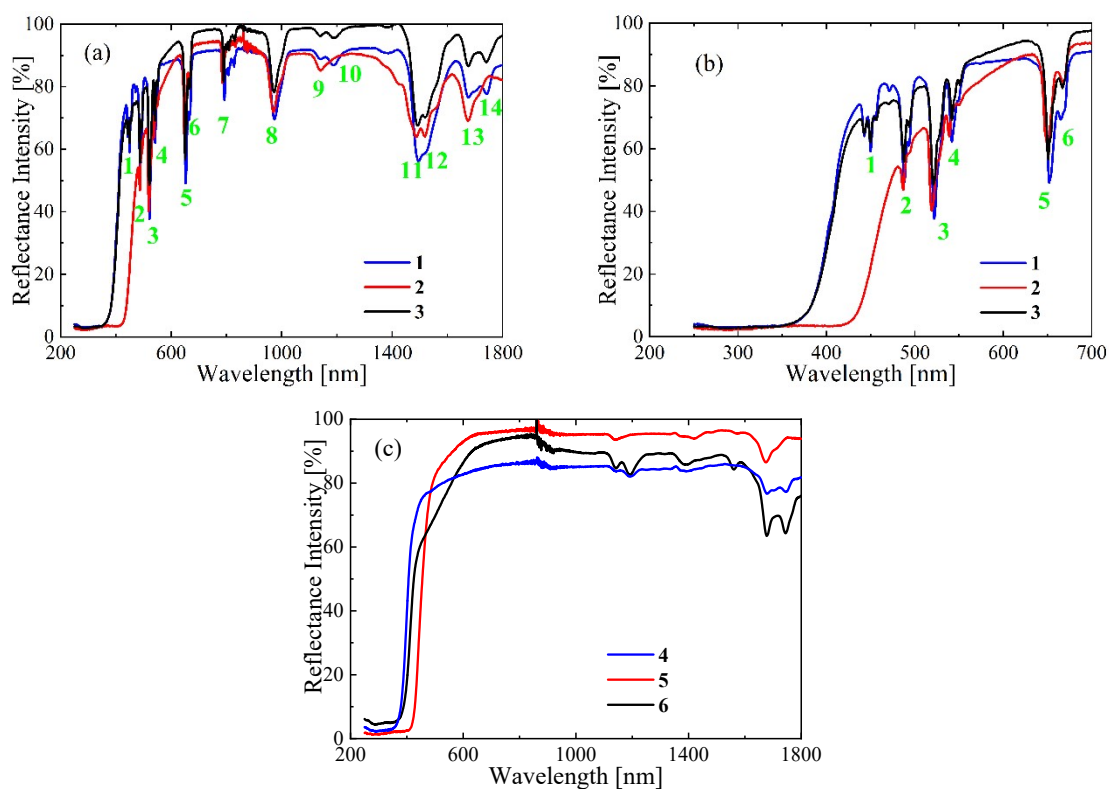


Figure S1. Diffuse reflectance spectra for the Er^{III} (a and b) and Y^{III} (c) complexes.

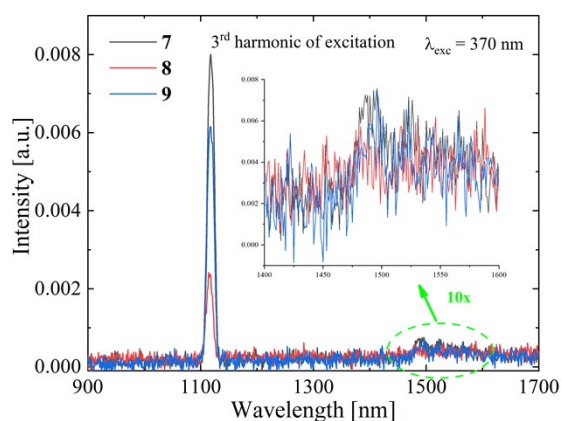


Figure S2. NIR emission spectra of **1-3** under excitation of 370 nm.

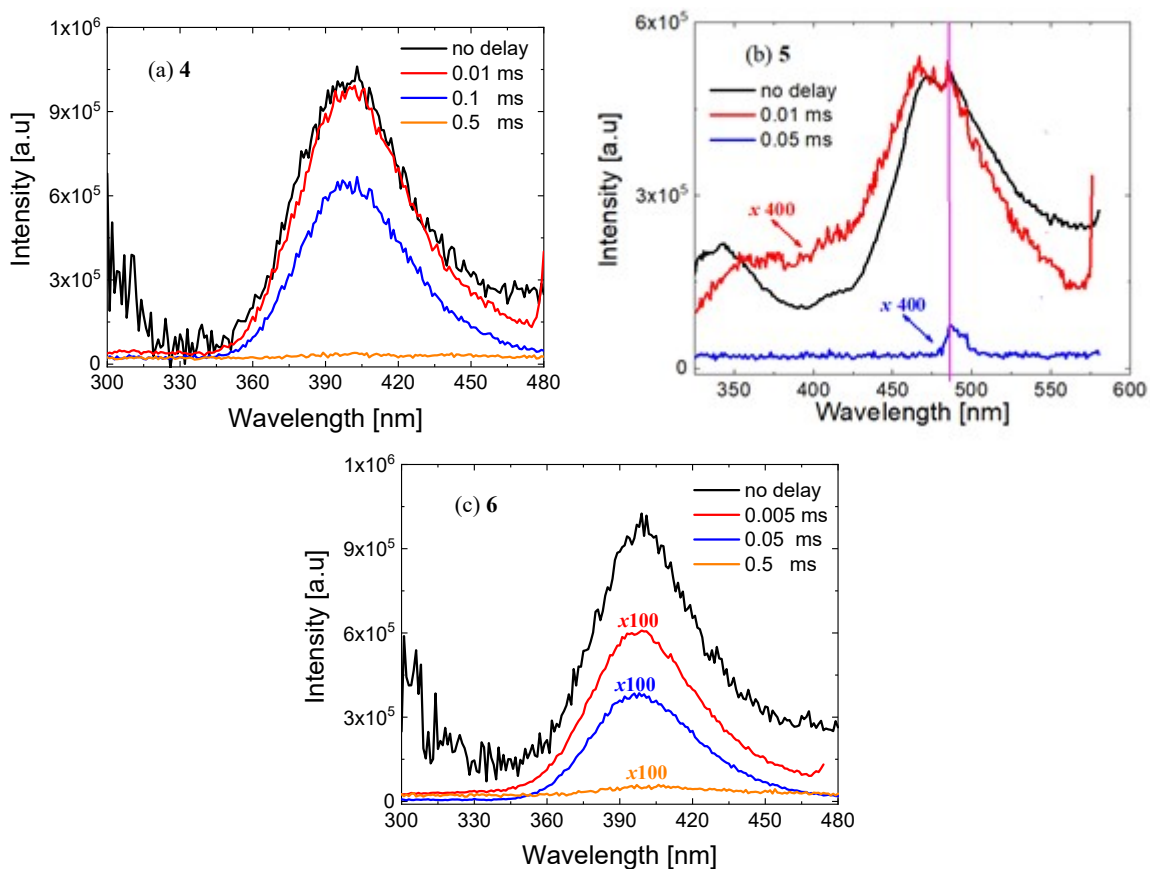


Figure S3. Phosphorescence spectra at 20 K with and without delay for yttrium(III) complexes, **4(a)**, **5(b)** and **6(c)**. ($\lambda_{\text{exc}} = 250$ nm for **4** and **6**, $\lambda_{\text{exc}} = 300$ nm for **4**).

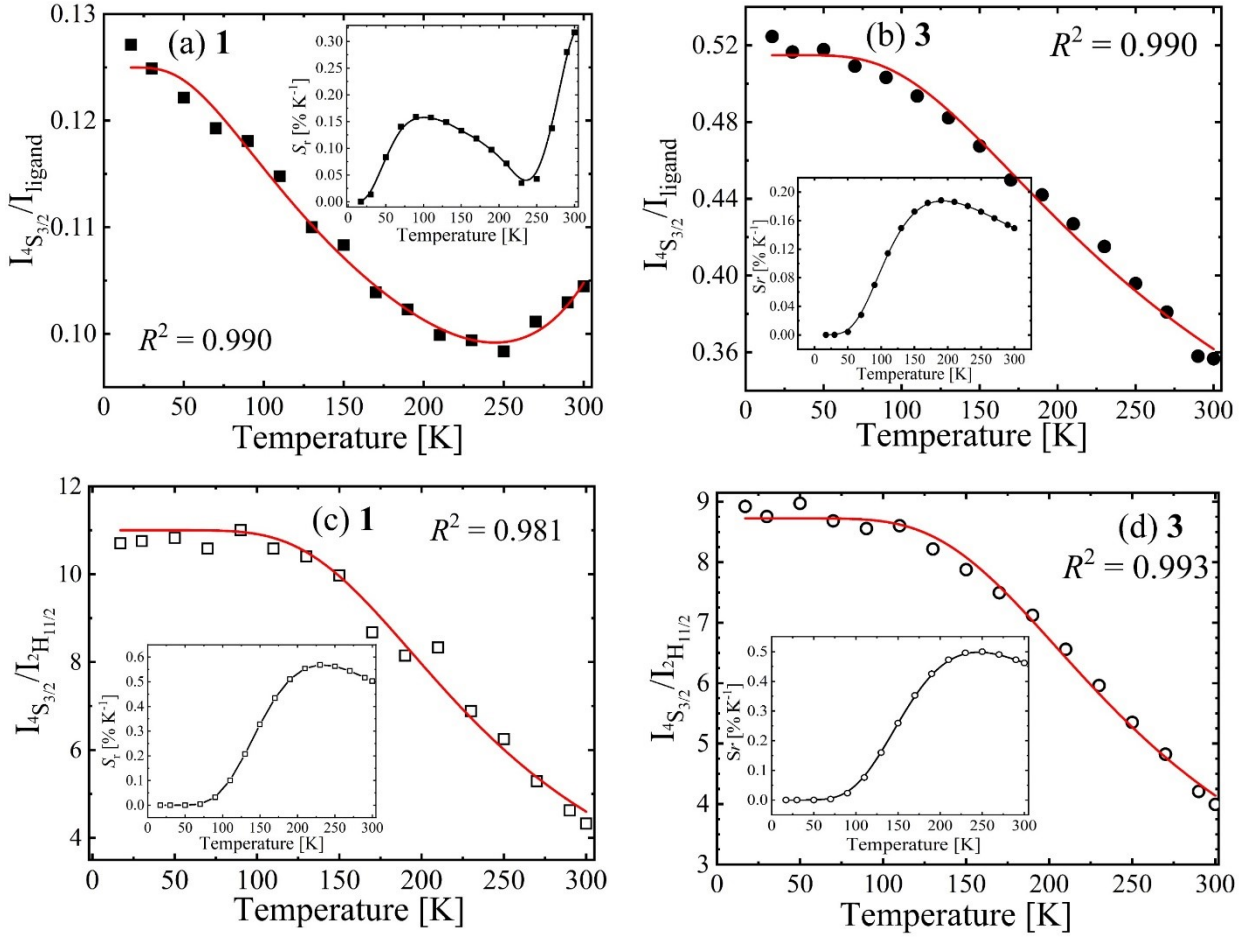


Figure S4. (a), (b) Thermal dependence of the ratio between the integrated areas $I_{4S_{3/2}}/I_{ligand}$ for **1** and **3**, after spectra deconvolution. (c), (d) Thermal dependence of $I_{4S_{3/2}}/I_{2H_{11/2}}$ for **1** and **3**. The points are the experimental data and the red solid lines represent the best fit from equations (1) and (2), as explained in the experimental section. The insets are the relative sensitivity S_r for **1** and **3**, where the solid lines are guides for the eyes.

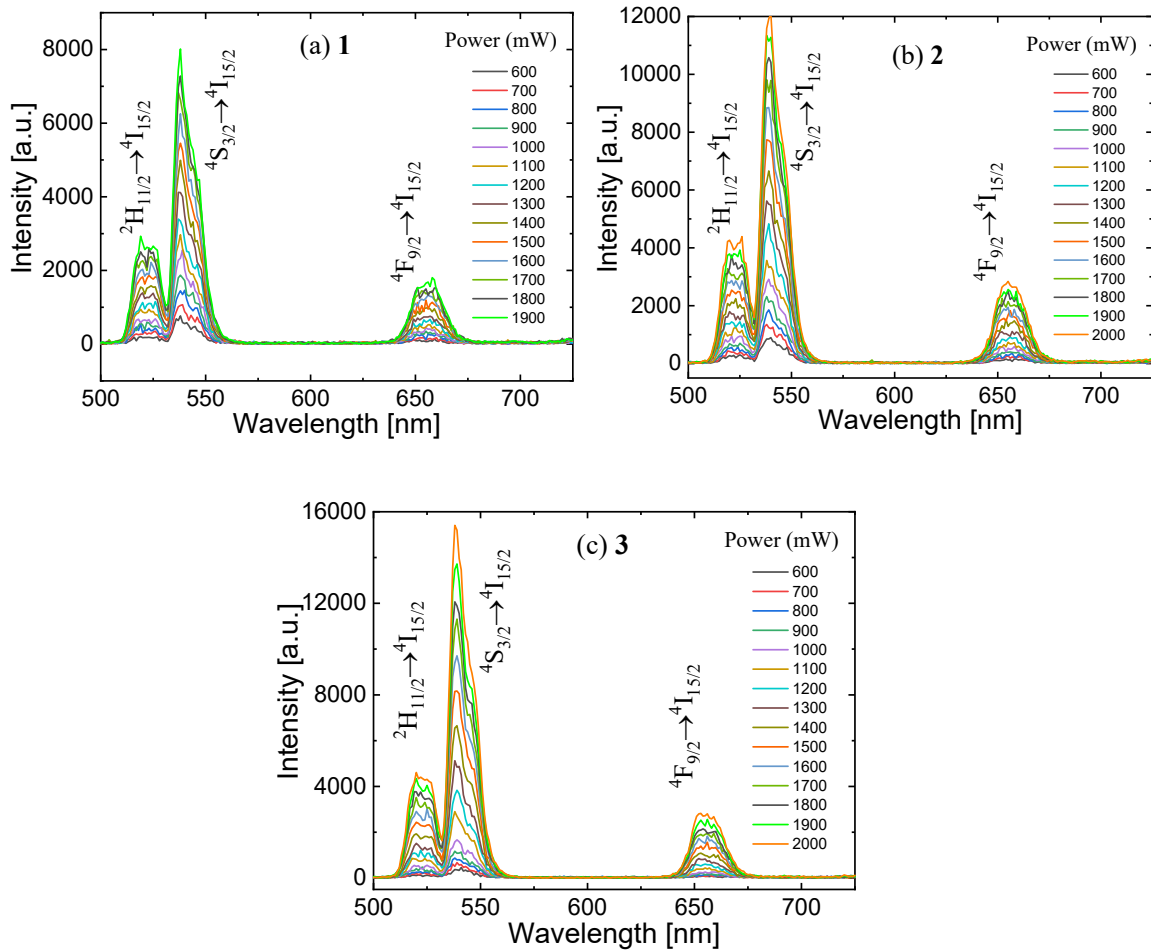


Figure S5. Up-conversion emission spectra of **1-3** in the wavelength range of 500–750 nm, at different pump powers of the 980 nm laser excitation.

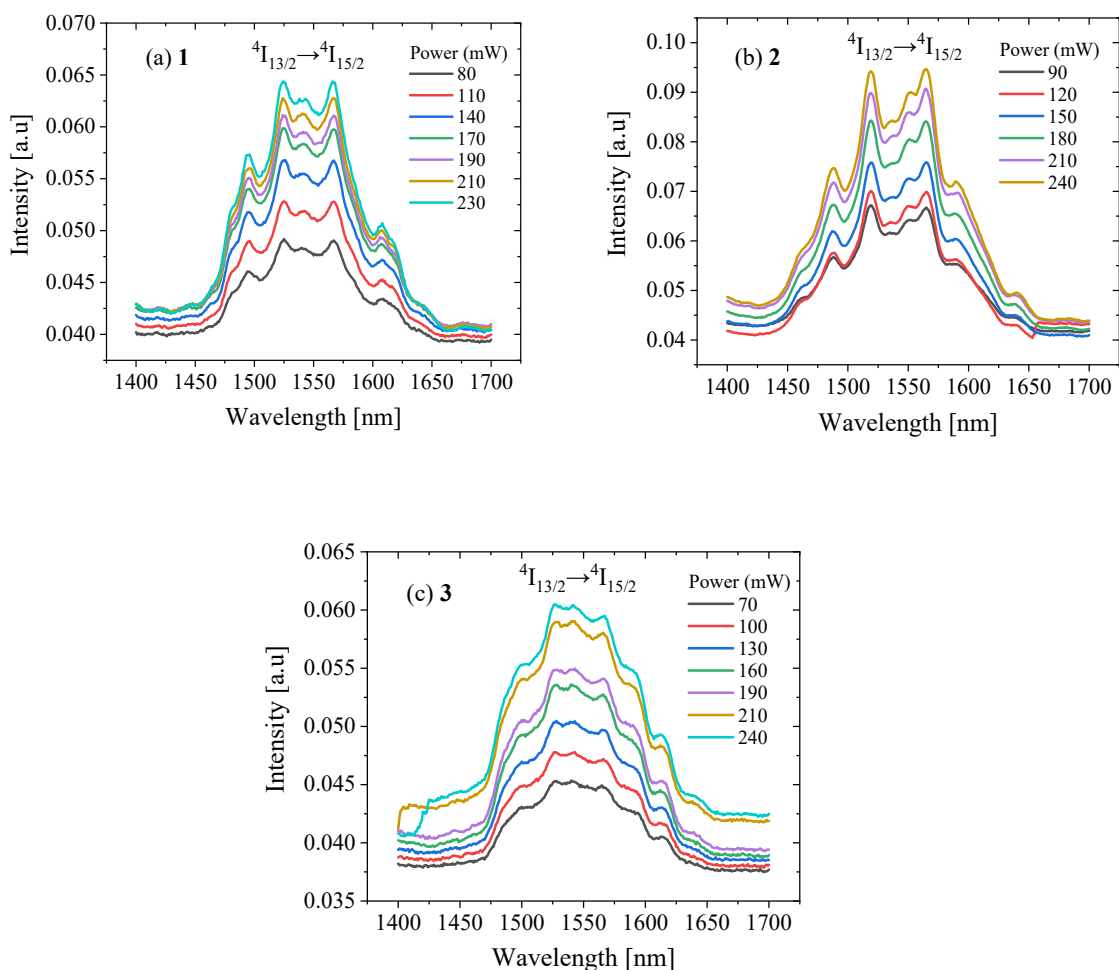


Figure S6. Near-infrared downshifted emission spectra for **1-3** in the wavelength range of 1400–1700 nm, at different pump powers of the 980 nm laser excitation.

Table S1. Thermometric parameters ΔE_A and S_r for **1** and **3**, obtained after the spectra deconvolution.

complex	$I_{4S_{3/2}}/I_{ligand}$			$I_{4S_{3/2}}/I_{2H_{11/2}}$		
	ΔE_A (cm ⁻¹)	S_r (%K ⁻¹) (max)	S_r (%K ⁻¹) (300K)	ΔE_A (cm ⁻¹)	S_r (%K ⁻¹) max	S_r (%K ⁻¹) (300K)
1	148** 1509**	0.32 (300 K)	0.32	539*	0.57 (230 K)	0.50
3	313*	0.19 (190 K)	0.15	549*	0.50 (250 K)	0.46

* ΔE_A : fit with equation (1); ** ΔE_A : fit with equation (2).

References

- 1 P. Martín-Ramos, L. C. J. Pereira, J. T. Coutinho, F. Koprowiak, H. Bolvin, V. Lavín, I. R. Martín, J. Martín-Gil and M. R. Silva, Structure, Luminescence and Magnetic Properties of an Erbium(III) β -Diketonate Homodinuclear Complex, *New J. Chem.*, 2016, **40**, 8251–8261.
- 2 G. H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals*, Wiley-Interscience, New York, USA, 1968.