Supporting Information for

Shape-conserving enhancement of Vibrational Circular Dichroism in Lanthanide Complexes

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Instrumentation and measurements

VCD spectra were acquired with a JASCO FVS-4000 instrument using BaF_2 cells and were baseline subtracted with the spectra of the cell filled with blank solvent using the same acquisition parameters and recorded immediately after and/or immediately before the sample. In all cases 6000 or 8000 scans were accumulated for the Ln complexes with a background (50 accumulations) – blank solvent (2000 accumulations) – sample (6000 / 8000 accumulations) methodology in the 2000-900 cm^{-1} (Ln DOTMA) or 2000-1300 cm^{-1} (Ln Lasalocid) spectral range.

The Ln DOTMA spectra (2000-900 cm^{-1}) were acquired as 50 mM D_2O solutions in 50 μm BaF_2 cells.

The Ln Lasalocid spectra (2000-1300 cm^{-1}) were acquired as ca. 30 mM CD_3CN solutions in 150 μm BaF_2 cells. The spectra were normalized, due to some uncertainty on the concentrations, toward the Er Lasalocid IR-absorption spectrum, using the absorbance of five maxima (1681, 1592, 1461, 1428 and 1394 cm^{-1}) of the solvent-subtracted spectra. These averaged normalization constants differ from 1 (Er Lasalocid reference) by less than 20% (see later on for details). In addition, the spectra were referred to the total concentration of the Lasalocid ligand (60 mM), which is the reason for using Δε' instead of Δε. In addition, the contribution of the free Lasalocid ligand (scarcely soluble in CD_3CN) to the VCD spectrum is generally small and negligible at the chosen wavenumbers. ^1H NMR (Agilent Inova 600 operating at 14.1 T, and 25° C, in D_2O and CD_3CN) were collected for all compounds prepared with the exception of Gd-complexes, to check the identity of the products.

Synthesis

Lanthanides salts were used as received from Aldrich and stored in a desiccators with P_2O_5; the ligand H_4-DOTMA was a gift from Bracco; Lasalocid sodium salt was used as received from Aldrich. All the solvents were reagent or HPLC grade.

Preparation of Na[Ln(DOTMA)]

Na[Ln(DOTMA)] were synthetized according to a described procedure.[1] A stoichiometric amount of 0.1 M lanthanide chloride, or triflate (La, Sm), or nitrate (Pr), aqueous solution was added to solid H_4-DOTMA. The resulting mixtures were heated up to 80°C and kept stirring for 24 h. Diluted NaOH solution was then added in each case to pH 6.5 and finally water was removed by

evaporation. The NMR characterization can be found elsewhere.[2]

Preparation of Ln Lasalocid (Ln=Tb-Lu)

In 1 mL of ethanol, 5.4 mg of Lasalocid sodium salt ($9 \cdot 10^{-6}$ mol, $C_{34}H_{53}NaO_8$, MW = 612.79 g / mol) and the equimolar amount of lanthanide chloride (Ln=Tb-Lu), was suspended and stirred for 24 h, resulting in a clear colourless solution. Ethanol was evaporated and the white solid obtained was dried under vacuum (0.1 mm Hg) and not further purified. The ^{1}H NMR spectra confirmed the presence of the Ln Lasalocid complex, together with a variable but small quantity of the free ligand.

Lu Lasalocid, ^{1}H NMR CD_3CN (ppm): 7.08, 6.56, 4.6, 3.85, 3.66, 3.59, 3.47, 3.26, 3.21, 2.31, 2.25, 2.12, 2.07, 2.03, 2.02, 1.93, 1.74, 1.56, 1.55, 1.54, 1.53, 1.5, 1.49, 1.42, 1.33, 1.26, 1.08, 1.08, 1.05, 1.02, 0.99, 0.9, 0.77, 0.42.

Yb Lasalocid, ^{1}H NMR CD_3CN (ppm): 55.9, 41, 31.3, 26.6, 24.5, 23.1, 17.6, 11.3, 11, 8.5, 6.3, 2.67, 1.7, -1.03, -1.24, -1.32, -1.58, -3.36, -3.6, -3.72, -3.82, -4.7, -6.4, -6.94, -7.04, -7.47, -7.7, -8.2, -11.4, -11.9, -12.5, -13.4, -32.7.

Er Lasalocid, ^{1}H NMR CD_3CN (ppm): 134, 74.82, 61.25, 51.74, 34.06, 25.37, 24.8, 20.43, 11.15, 9.99, 8.81, 8.48, -0.98, -2.54, -3.15, -4.42, -6.71, -7.19, -9.96, -10.19, -10.87, -11.72, -12.49, -12.94, -18.86, -19.31, -20.71, -23.31, -27.65, -32.04, -41.95, -70.66.

Dy Lasalocid, ^{1}H NMR CD_3CN (ppm): 148.64, 79.02, 75.26, 72.06, 52.26, 44.29, 36.45, 26.23, 24.01, 21.95, 13.51, 10.67, 9.03, 8.51, 7.32, 5.01, 3.67, 2.67, 2.14, 0.8, -14.47, -18.26, -33.12, -36.7, -47.37, -49.08, -63.44, -65.49, -75.19, -103.21, -135.04, -147.23.

Tb Lasalocid, ^{1}H NMR CD_3CN (ppm): 152.86, 129.39, 104.67, 92.44, 70.14, 57.16, 54.98, 37.73, 32.49, 28.5, 23.44, 16.97, -4.77, -7.37, -13.08, -20.58, -35.32, -37.7, -41.99, -67.52, -96.46, -132.92, -147.19.

Ho Lasalocid, ^{1}H NMR CD_3CN (ppm): 109.37, 75.15, 57.97, 47.93, 46.67, 44.87, 34.27, 32.73, 31.75, 21.68, 20.34, 16.74, 14.49, 13.38, 11.55, 10.74, 8.29, 6.98, 5.94, 3, -2.82, -7.44, -16.33, -21.8, -35.86, -42.88, -60.71, -73.92, -79.99, -111.35.

Tm Lasalocid, ^{1}H NMR CD_3CN (ppm): 143.55, 126.18, 74.99, 66.56, 47.61, 37.4, 30.16, 13.23, 11.88, -14.1, -14.69, -22.13, -23.27, -29.99, -30.92, -33.6, -36.92, -38.72, -45.29, -46.15, -46.77, -59.97, -84.88, -102.08, -107.15, -145.3, -154.89.

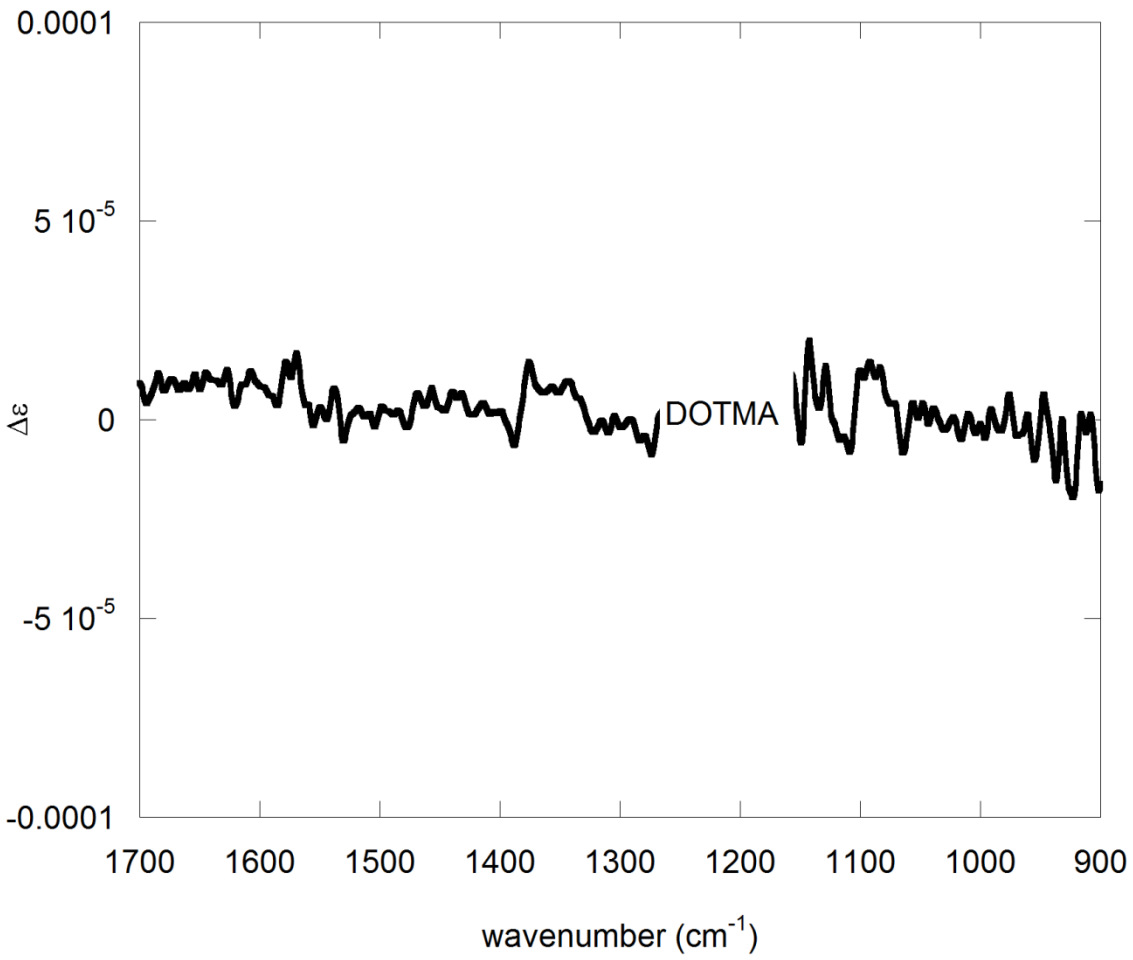

Figure S1. VCD spectrum of DOTMA free ligand (D_2O).

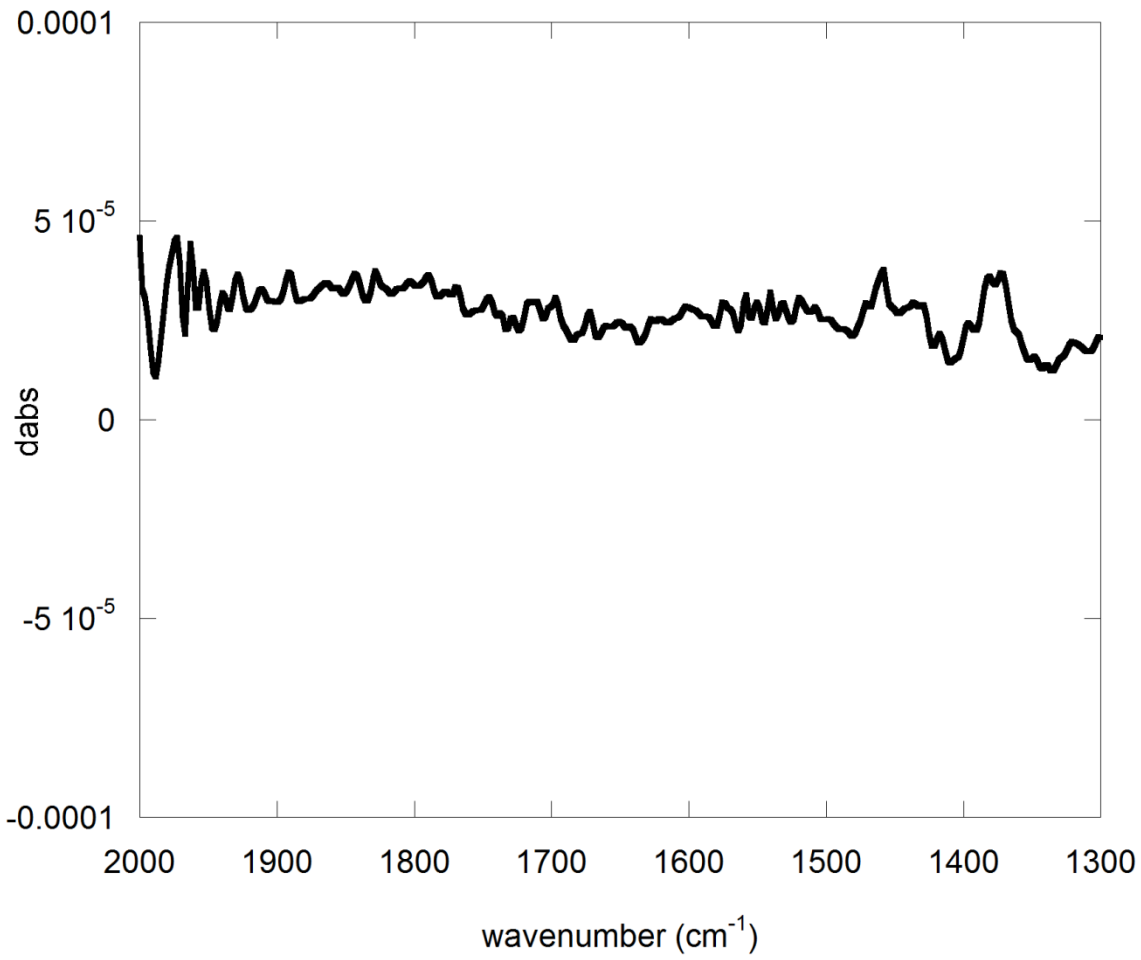

Figure S2. VCD spectrum of Lasalocid sodium salt (saturated solution CD_3CN).

Normalization of Ln Lasalocid spectra

The normalization procedure consists in taking different absorption values of five IR bands in Ln Lasalocid spectra and refer each of them to a Er Lasalocid (chosen as reference). The normalization factors* obtained were averaged and used to normalize both VA and VCD spectra. The values of Δε' refer to the total Lasalocid concentration of the samples (60 mM).

* $K_n = \frac{Abs^{\bar{\nu}_n}_{Er}}{Abs^{\bar{\nu}_n}_{Ln}}$

Table S1. Absorption values of Ln Lasalocid (CD_3CN, ca. 30 mM) at different frequencies (corresponding to IR bands).

	Abs @ different frequencies (in cm^{-1})				
Ln	$\bar{\nu}_1$ **(1461.8)**	$\bar{\nu}_2$ **(1591)**	$\bar{\nu}_3$ **(1681.6)**	$\bar{\nu}_4$ **(1429)**	$\bar{\nu}_4$ **(1394.3)**
Er	0.34	0.205	0.189	0.21	0.257
Ho	0.3	0.188	0.18	0.188	0.243
Dy	0.26	0.165	0.16	0.159	0.224
Lu	0.257	0.188	0.195	0.185	0.185
Tb	0.241	0.199	0.171	0.179	0.214
Yb	0.314	0.214	0.245	0.213	0.24
Tm	0.255	0.184	0.197	0.183	0.194

Table S2. Normalization factors for Ln Lasalocid.

	Normalization factor					
Ln	K_1	K_2	K_3	K_4	K_5	**Average**
Er	1.000	1.000	1.000	1.000	1.000	**1**
Ho	1.133	1.090	1.050	1.117	1.058	**1.090**
Dy	1.308	1.242	1.181	1.321	1.147	**1.240**
Lu	1.323	1.090	0.969	1.135	1.389	**1.181**
Tb	1.411	1.030	1.105	1.173	1.201	**1.184**
Yb	1.083	0.958	0.771	0.986	1.071	**0.974**
Tm	1.333	1.114	0.959	1.148	1.325	**1.176**

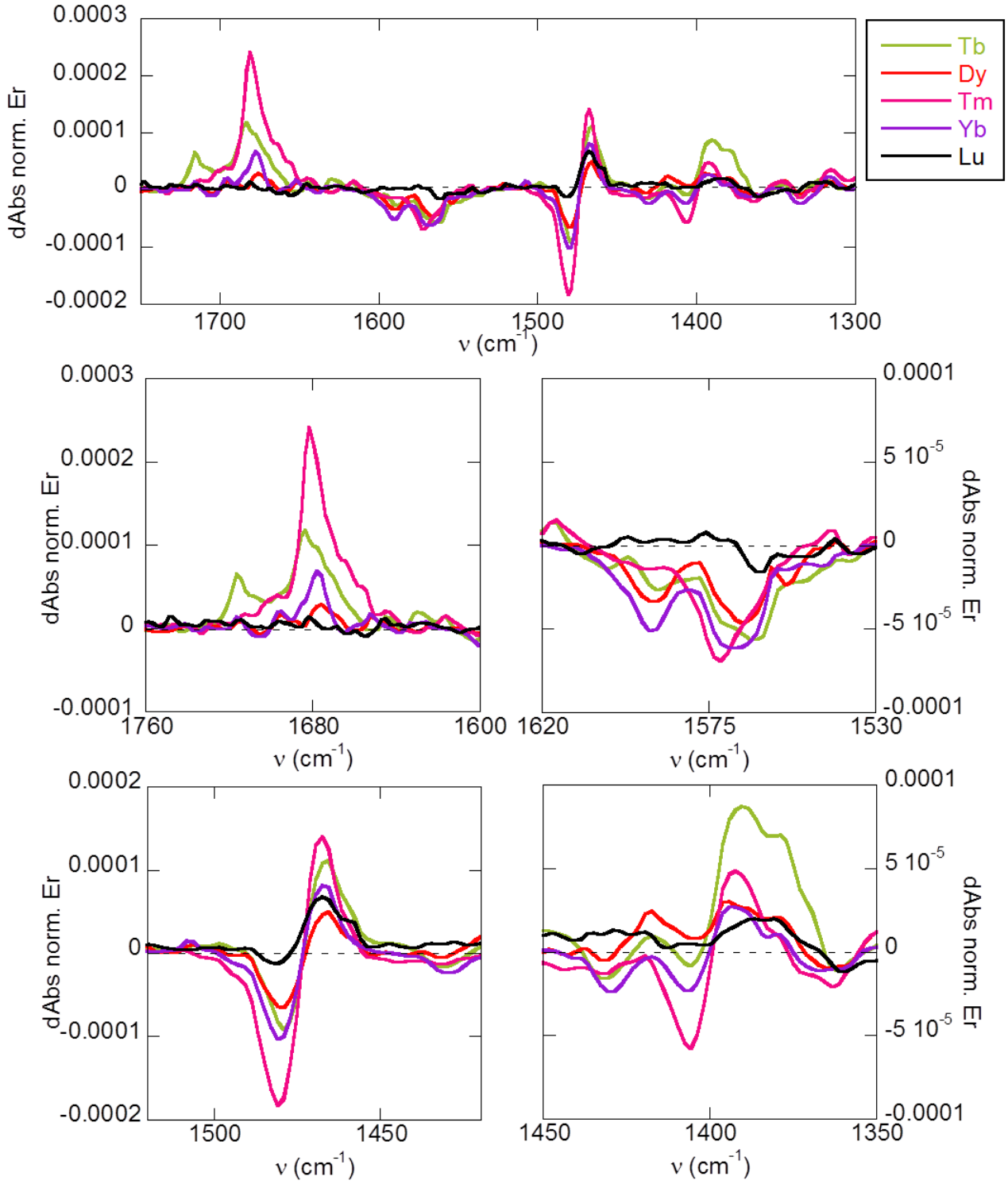

Figure S3. VCD spectra of Ln Lasalocid (CD_3CN) for Tb, Dy, Tm, Yb and Lu.

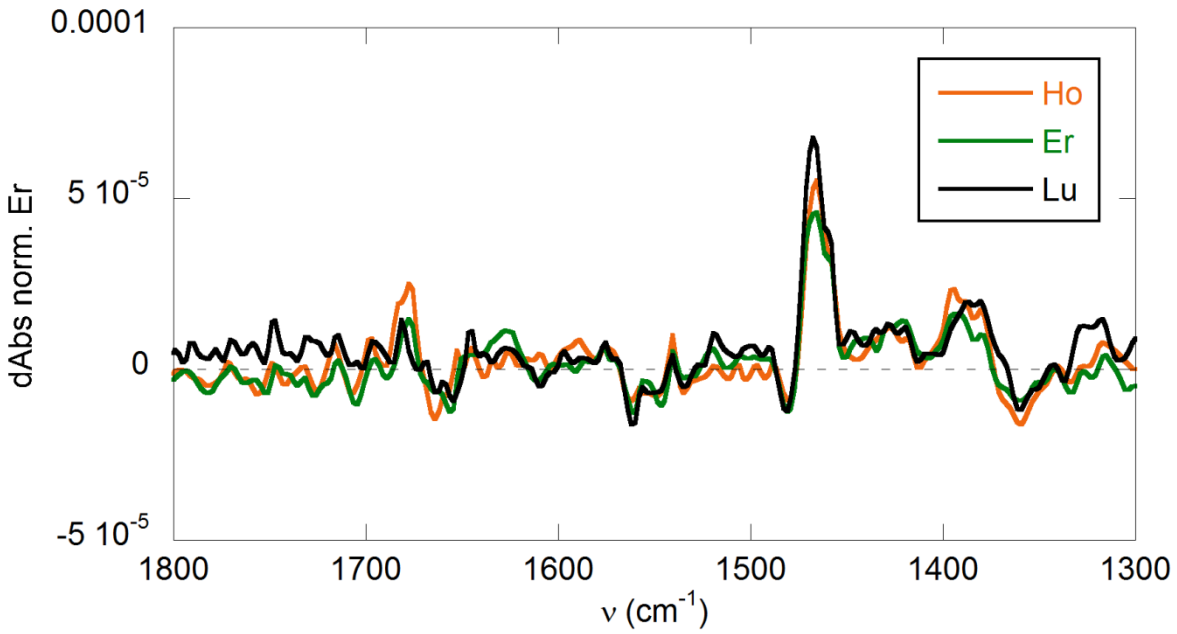

Figure S4. VCD spectra of Ln Lasalocid (CD_3CN) for Ho, Er and Lu.

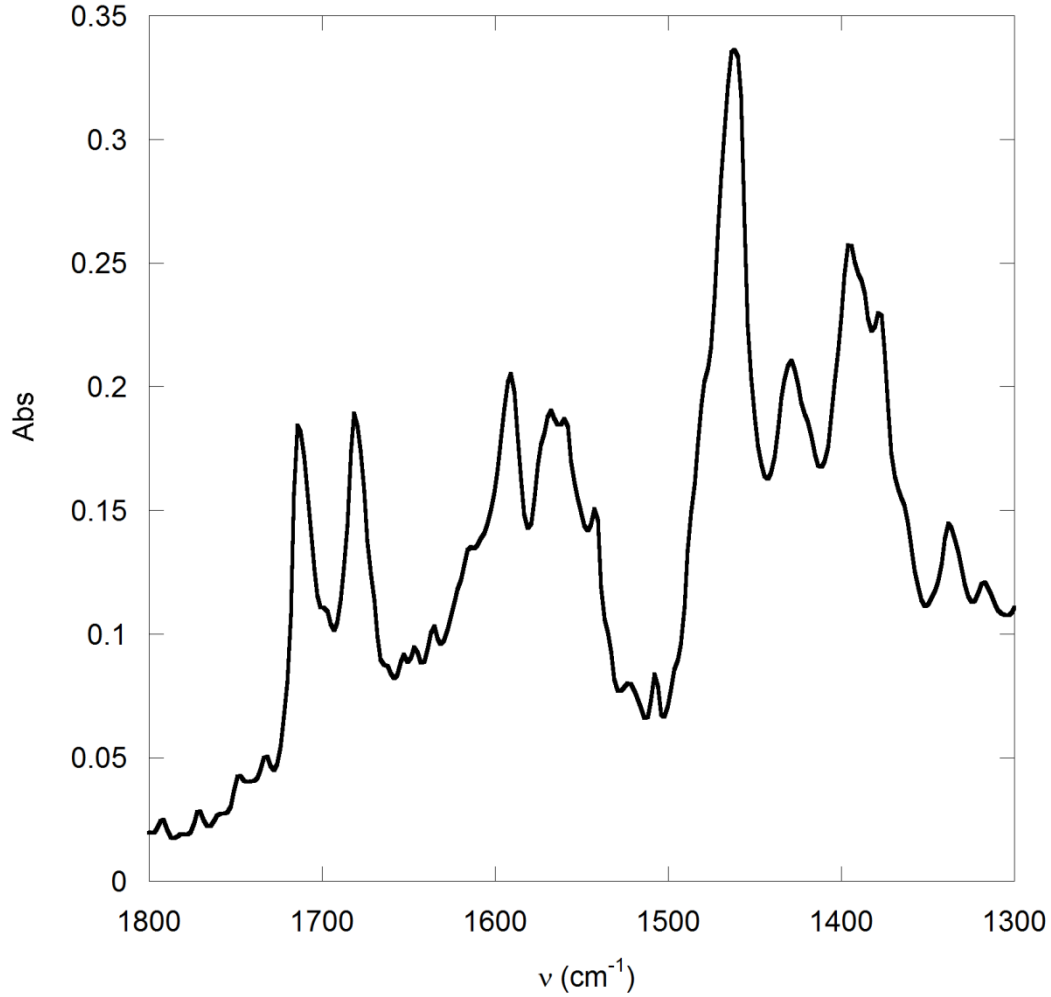

Figure S5. Absorption spectrum of Er Lasalocid (CD_3CN) [30 mM CD_3CN solutions in 150 µm BaF2 cells]. This compound was used to normalize all the other spectra, as explained above.

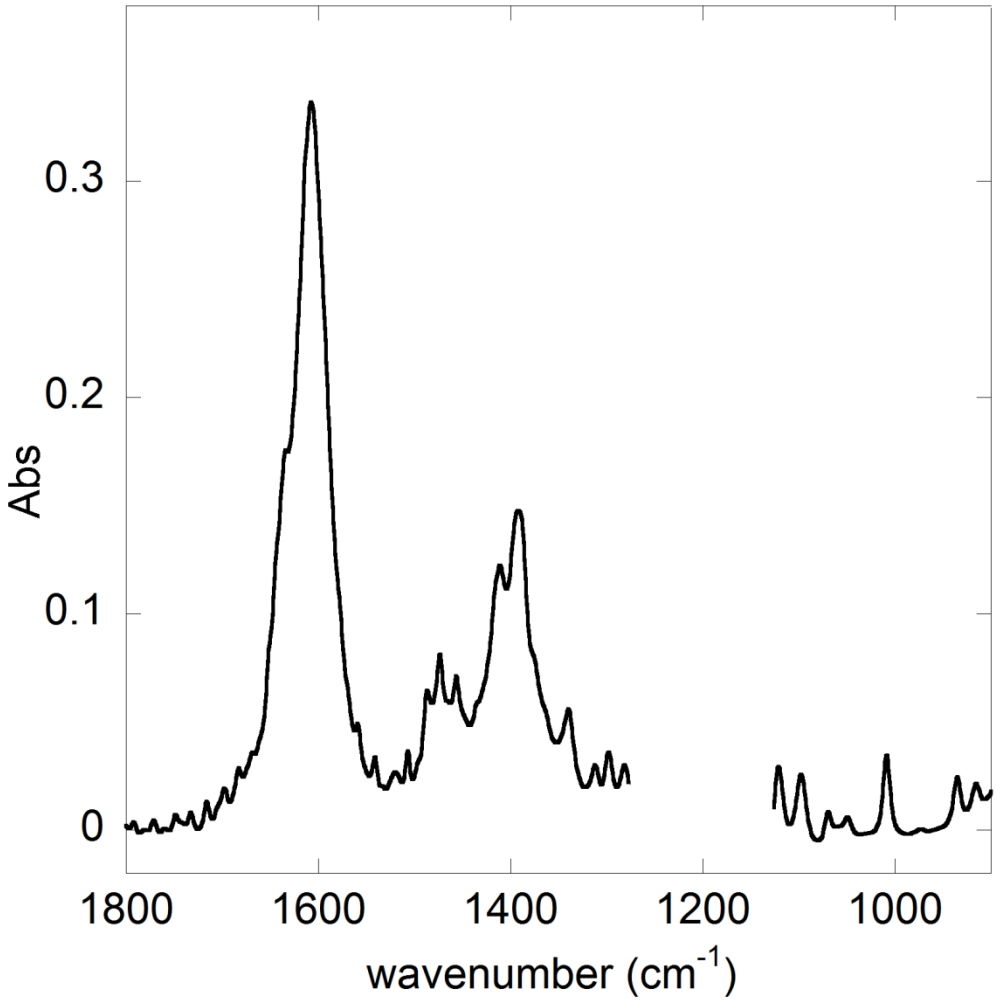

Figure S6. Absorption spectrum of Lu DOTMA (D_2O) [50 mM D_2O solutions in 50 µm BaF2 cells.]. The region between 1280 and 1160 cm^{-1} was erased because obscured by the D_2O signal

References

1. H. G. Brittain and J. F. Desreux, *Inorg. Chem.*, 1984, 23, 4459-4466.
2. S. Di Pietro, S. Lo Piano and L. Di Bari, *Coord. Chem. Rev.*, 2011, 255, 2810-2820.