

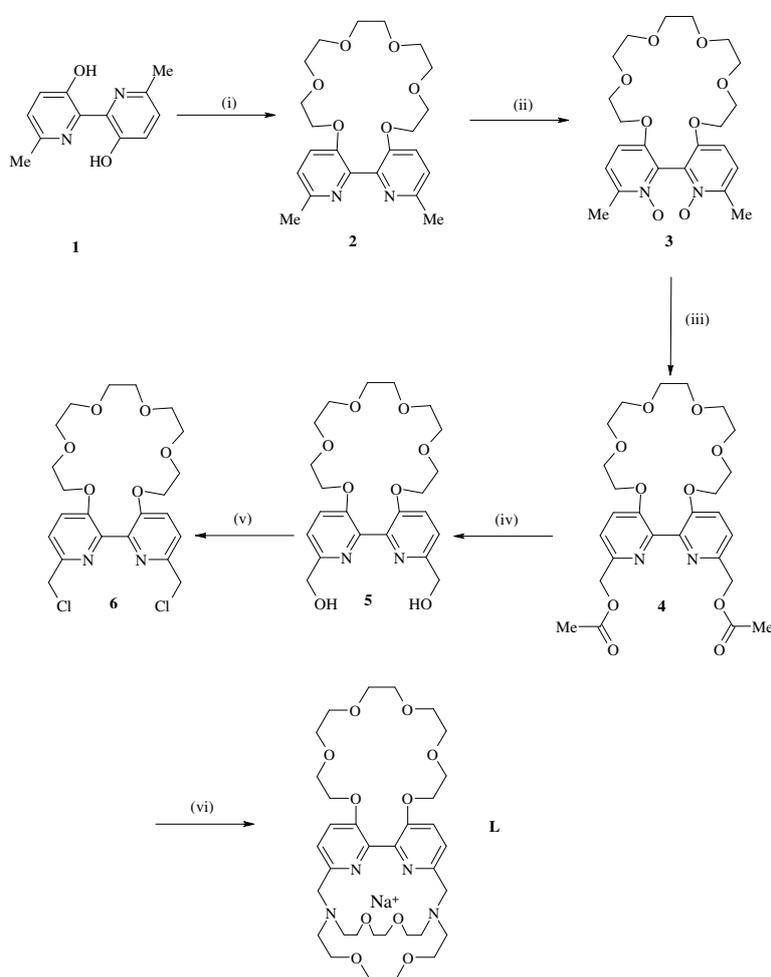
Electronic Supplementary Data

Barium induced modulation of NIR emission in a Neodymium cryptate complex

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Synthetic Details

The synthesis of the ditopic ligand **L** was achieved by an 6 step convergent route starting from 6,6'-dimethyl-2,2'-bipyridine-3,3'-diol **1**.



Scheme 1. Synthesis of ligand **L** from 6,6'-dimethyl-2,2'-bipyridine-3,3'-diol (**1**). Reagents and conditions: (i) NaH, penta-(ethylene glycol)-di-*p*-tosylate, anhydrous DMF, N₂, 60°C, (ii) *m*CPBA, DCM, RT, (iii) acetic anhydride, N₂, 120°C, (iv) K₂CO₃, anhydrous methanol, RT, (v) thionyl chloride, DCM, reflux, (vi) Diaza-18-crown-6, NaI, Na₂CO₃, MeCN, reflux.

Experimental.

Chemicals were purchased and used without further purification. ^1H NMR spectra were recorded on a 400MHz Bruker Avance DPX400 for the organic species and the ^1H NMR for the complexes was recorded on a 500MHz Bruker Avance 500. Mass spectra were obtained on a Bruker MicroTOF LC. Full synthetic details of the precursors **1-6** will be reported elsewhere.

Synthesis of [LNa]Cl

To a solution of the 6,6-chloromethyl derivative **6** (0.17 g, 0.35 mmol) in MeCN (50 ml) was added diaza-18-crown-6 (0.09 g, 0.34 mmol), Na_2CO_3 (0.10 g, 0.90 mmol) and a catalytic amount of NaI (0.01 g, 0.07 mmol) and the reaction refluxed under N_2 for 72hrs. After this time the solvent was removed by evaporation and the resulting white solid suspended in CH_2Cl_2 (100 ml). Filtration and evaporation gave the crude ligand which was purified by column chromatography (CH_2Cl_2 :MeOH 9:1, SiO_2) giving the ditopic ligand [LNa]Cl as a pale yellow oil which slowly solidified. (0.15 g, 58 % yield). ^1H NMR (500MHz, CDCl_3) δ 7.37 (2H, d, $J = 8.4$), 7.30 (2H, d, $J = 8.4$), 4.26 (m, 2H), 4.16 (m, 2H), 4.07 (d, $J = 13$, 2H), 3.90 – 3.46 (m overlapping, 26H), 3.42 (m, 2H), 3.33 (d, $J = 13\text{Hz}$, 2H), 3.00 (m, 2H), 2.85 (m, 4H), 2.69 (m, 2H), 2.61 (m, 4H). ESI-MS: m/z 699 $\{\text{NaL}\}^+$

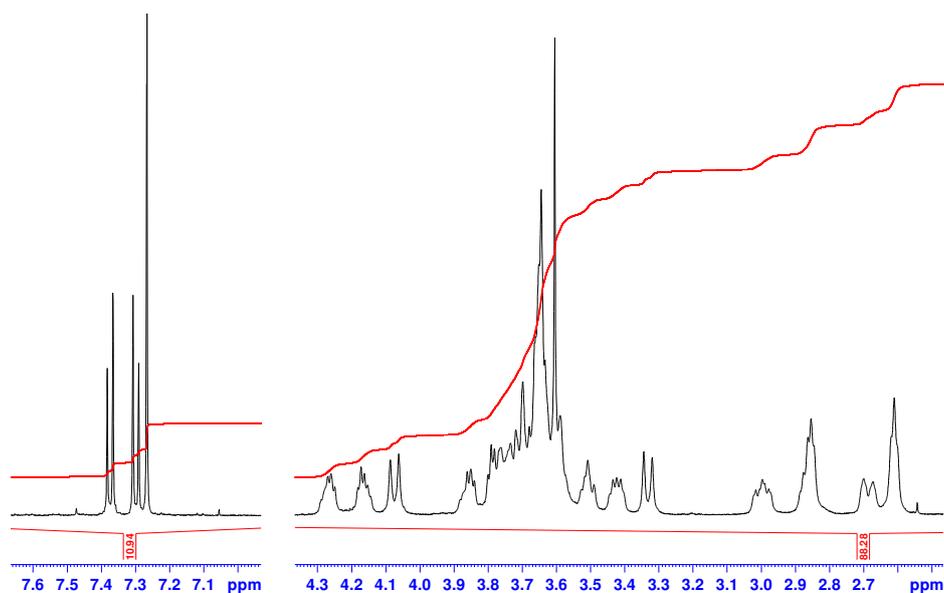


Fig. 1 Selected regions of the ^1H NMR spectra (CDCl_3) of $[\text{NaL}]^+$.

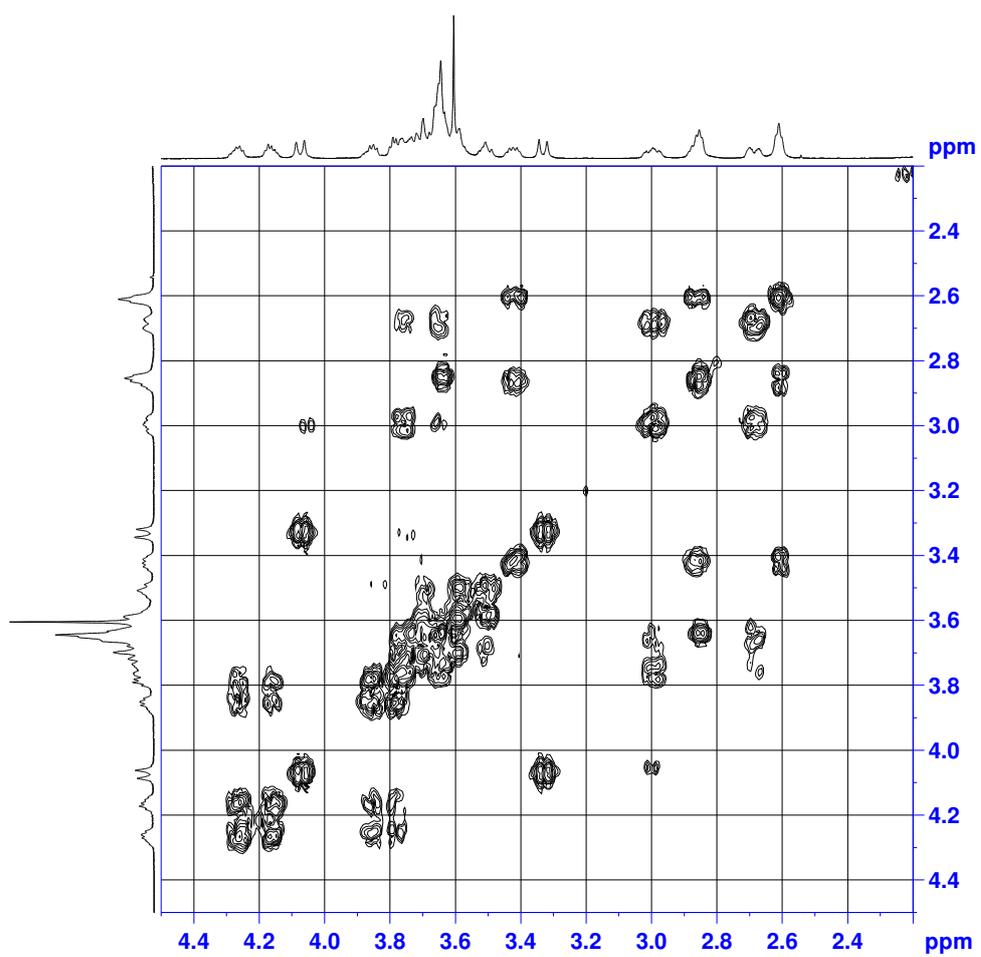


Fig. 2 $^1\text{H}/^1\text{H}$ COSY NMR of the aliphatic region of for $[\text{NaL}]^+$.

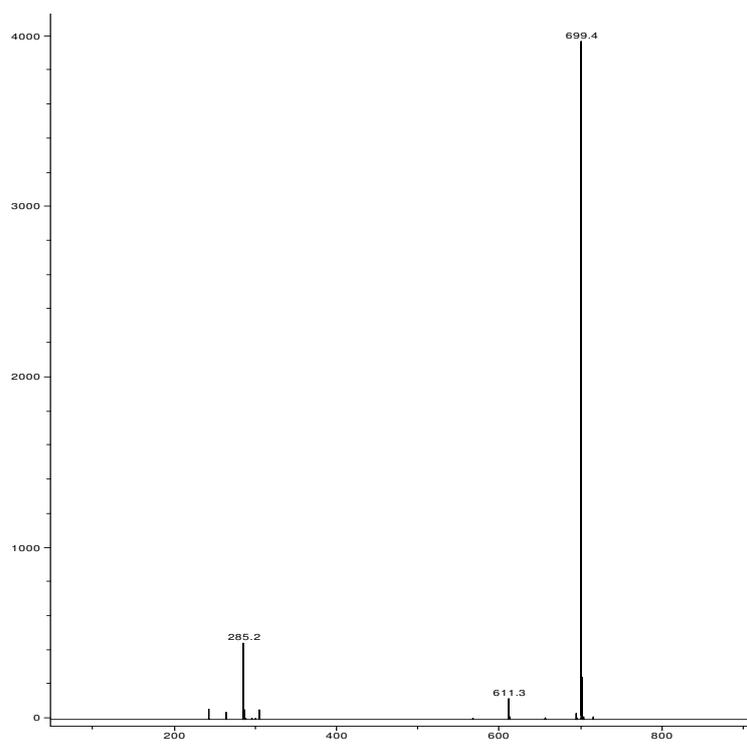


Fig. 3 ESI-MS of $[\text{NaL}]^+$.

Synthesis of $[\text{NdL}](\text{CF}_3\text{SO}_3)_3$

A solution of $[\text{NaL}]\text{Cl}$ (0.014 g, 0.019 mmol) and $\text{Nd}(\text{CF}_3\text{SO}_3)_3$ (0.011 g, 0.019 mmol) in MeCN (5 ml) was refluxed under N_2 and the reaction monitored by tlc ($\text{CH}_2\text{Cl}_2:\text{MeOH}$ 9:1, SiO_2). Upon complete consumption of the starting material (≈ 24 hrs) the MeCN was evaporated and the resulting oil dissolved in acetone and filtered. Slow addition of diethyl ether at 0°C gave the complex as a colourless solid which was isolated by filtration. (0.018 mg, 75% yield). ESI-MS: m/z 1118 $\{[\text{NdL}](\text{CF}_3\text{SO}_3)_2\}^+$.

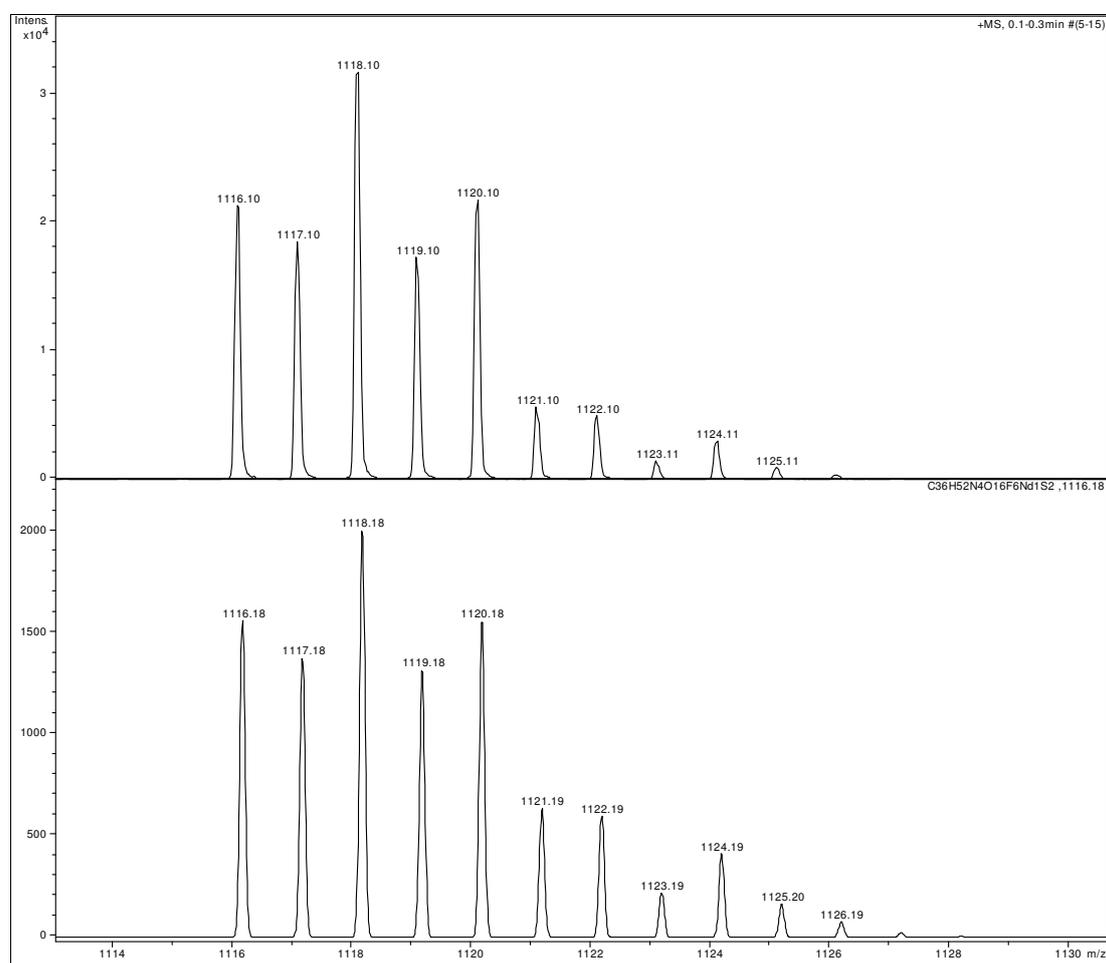


Fig. 4 The observed (top) and calculated (bottom) isotopic distribution pattern of $\{[\text{NdL}](\text{CF}_3\text{SO}_3)_2\}^+$.

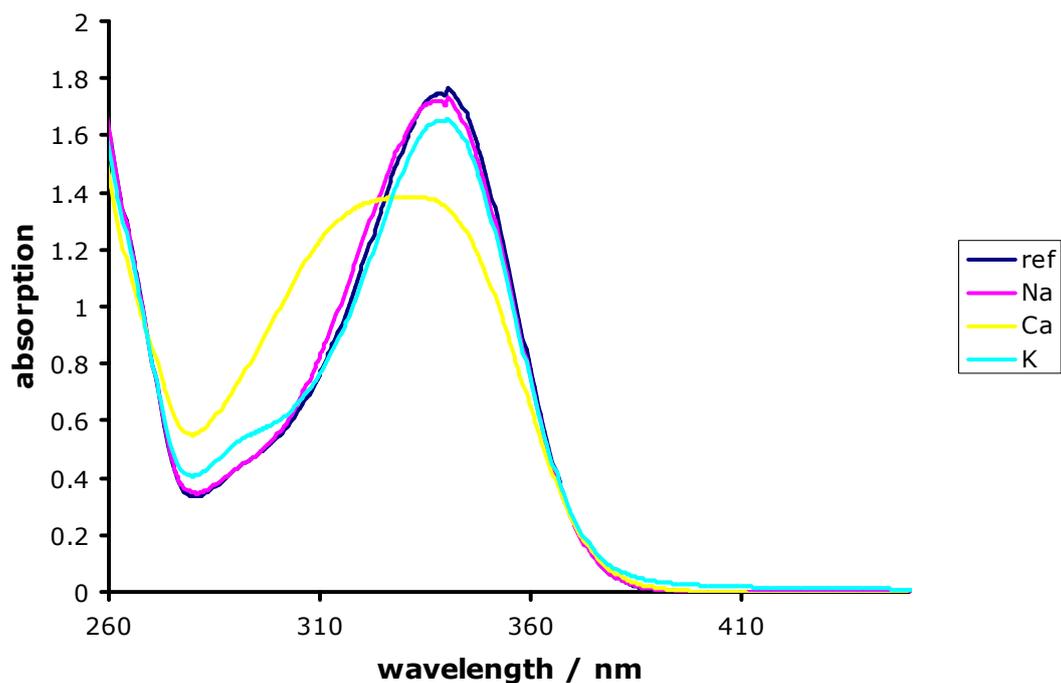


Fig. 5 Absorption spectra of [NdL]^{III} in MeCN. The blue reference spectrum is the free Nd^{III} complex.

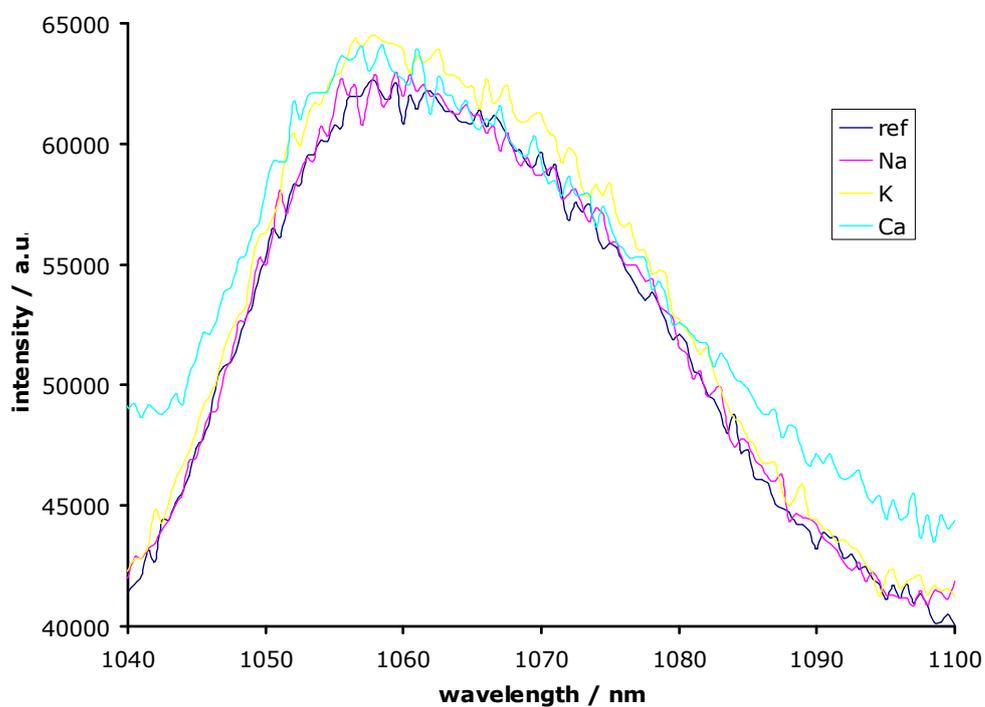


Fig. 6 Steady state NIR emission spectra of [NdL]^{III} in MeCN. The blue reference spectrum is the free Nd^{III} complex. Addition of the cationic alkali metals results in little change in emission intensity following excitation at 335 nm.

Photophysical Measurements

All photophysical data were obtained on a JobinYvon-Horiba Fluorolog spectrometer fitted with a JY TBX picosecond photodetection module and a Hamamatsu R5509-73 detector (cooled to $-80\text{ }^{\circ}\text{C}$ using a C9940 housing). The pulsed laser source was a Continuum Minilite Nd:YAG configured for 355 nm output and operating at 15 Hz. Lifetimes were obtained using the JY-Horiba FluorHub single photon counting module.

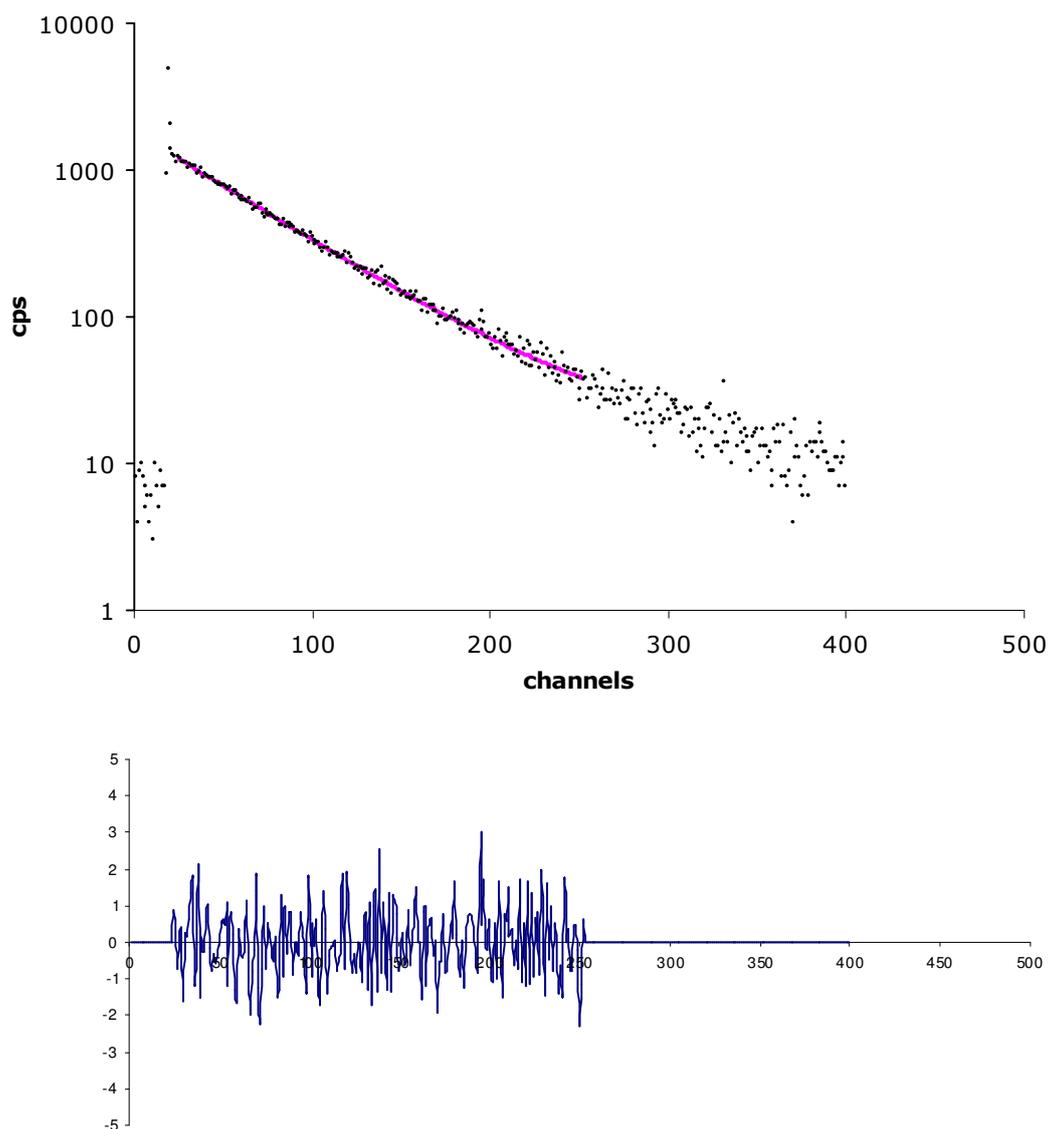


Fig. 7 Top: Lifetime decay of $[\text{NdL}]^{\text{III}}$ at 1055 nm following excitation at 355 nm in CD_3OD . Bottom: Residual errors.