

Supplementary Information for:

First Example of a Supramolecular Lanthanoid Tecton: Stepwise Assembly of a Highly Ordered Molecular Network

*Philip C. Andrews, William J. Gee, Harald Krautscheid, Jonathan G. MacLellan
and Peter C. Junk**

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S1. Synthetic Protocols:

S1.1. General: All chemicals were purchased from Sigma-Aldrich and were used as received. Anhydrous solvents were obtained from a MBRAUN MB SPS-800 solvent purification system. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity Nova 500 spectrometer. Chemical shifts were recorded on the δ scale and referenced against the solvent. Electrospray ionization spectra were recorded on a *Micromass* Platform II QMS spectrometer. Solid-state IR spectra were recorded on a Bruker Equinox 55 Infrared Spectrometer fitted with a Specac Diamond ATR source. Melting points were measured on a Stuart Scientific Melting Point Apparatus SMP3 in an open capillary and were uncalibrated. Elemental Analyses were performed by Institut für Anorganische Chemie, University of Leipzig, Germany.

S1.2. Methodology for synthesis of Hcpb¹: Hcpb was synthesised by reaction of the corresponding acid chloride with lithium propen-2-olate as per a modified literature method [R1]. To an anhydrous THF (10 mL) solution of acetone (0.58 mL, 6.8 mmol) cooled to $-78\text{ }^\circ\text{C}$ was added LiHMDS (1.6 M in hexanes, 4.5 mL, 6.8 mmol). One equivalent of *p*-cyanobenzoyl chloride (1g, 6.8 mmol) was next added with rapid stirring and the solution allowed to warm to room temperature. The reaction was quenched with water (~30 mL) and acidified to pH 5 with 1M HCl. The solution was extracted with ethyl acetate (3x 50 mL) and the organic extracts dried (MgSO_4) and concentrated to dryness under reduced pressure. The crude product was then purified by column chromatography yielding the β -diketone.

S1.3. Synthesis of 1-(4-cyanophenyl)-1,3-butanedione (Hcpb): Yield: 0.70 g (55%). Mp $75.4\text{--}77.8\text{ }^\circ\text{C}$. Elemental analysis (%) Found (calc for $\text{C}_{11}\text{H}_9\text{NO}_2$): C, 70.64 (70.58); H, 4.91 (4.85); N, 7.20 (7.48). ^1H NMR (CDCl_3 , 400 MHz): δ 2.25 (s, 3H, CH_3); 6.20 (s, 1H, COCHCOH); 7.75 (d, 2H, $J = 8.4\text{ Hz}$, PhH); 7.76 (d, 2H, $J = 8.4\text{ Hz}$, PhH); 15.92 (s, 1H, OH). ^{13}C NMR (CDCl_3 , 100 MHz): δ 26.36; 97.66; 115.37; 117.92; 127.39; 132.22, 138.73, 179.76, 195.80. IR (KBr): ν/cm^{-1} 3446 (m), 2228 (s), 1718 (s), 1691 (s), 1653 (s), 1616 (s), 1559 (m), 1540 (m), 1522 (m), 1506 (m), 1457 (m), 1436 (m), 1404 (m), 1384 (m), 1362 (w), 1293 (s), 1262 (s), 1212 (s), 1182 (w), 1118 (m), 1078 (w), 1018 (m), 998 (w), 848 (s), 802 (s), 685 (w), 592w, 556 (m), 538 (m). MS (ESI): calc. for $[\text{M} - \text{H}]^-$: 186.2 Found $[\text{M} - \text{H}]^-$: 185.9.

S1.5. Synthesis of $[\text{Nd}(\text{cpb})_3(\text{H}_2\text{O})(\text{DMF})]\cdot\text{DMF}$ (1): To a solution of ligand (0.3 mmol) and lanthanoid trichloride (0.1 mmol) in methanol was slowly added triethylamine (0.35 mmol) in a dropwise fashion. The reaction mixture was then stirred for 12 hours. After this time the solvent was removed and the residue stirred in toluene (~2 mL) for 1 hour. The solution was then filtered to remove any salts and the filtrate dried in vacuo. Single crystals were obtained by dissolving the crude product in DMF (1 mL) and slowly allowing the solution to concentrate. Yield: 45 mg (53%), Mp $\sim 260\text{ }^\circ\text{C}$ (dec). Elemental analysis (%) Found (calc for $\text{C}_{39}\text{H}_{40}\text{N}_5\text{NdO}_9$): C, 54.19 (54.03); H, 4.56 (4.65); N, 7.80 (8.08). IR (KBr): ν/cm^{-1} 3417 (brs), 2983 (m), 2228 (m), 1599 (s), 1550 (m), 1520 (s), 1493 (s), 1414 (s), 1387 (s), 1291 (m), 1272 (m), 1115 (w), 1017 (w), 956 (w), 851 (m), 773 (m), 695 (w), 594 (w), 545 (w). MS (ES):

¹ This method of diketone synthesis was not optimised. The authors suggest greater yields could be achieved by more traditional Claisen condensation methodologies (see: F. W. Bergstrom, Fernelius, W. C. *Chem. Rev.* **1933**, *12*, 43-179)

calc. for $\{[\text{Nd}(\text{cpb})_2(\text{H}_2\text{O})(\text{DMF}) + \text{H}]\cdot\text{DMF}, \text{H}_2\text{O}, \text{MeOH}\}^{2+}$: 365.6 Found: 365.9; for $[\mathbf{1-cpb}]^+$: 680.1 Found: 679.8.

S1.6. $[\text{Tb}(\text{cpb})_3(\text{H}_2\text{O})(\text{DMF})]\cdot\text{DMF}$ (2): Synthesis as per **1**. Single crystals were obtained by slow evaporation of a concentrated DMF solution. Yield: 51 mg (63%). Mp ~ 240 °C (dec). Elemental analysis (%) Found (calc for $\text{C}_{39}\text{H}_{40}\text{N}_5\text{O}_9\text{Tb}$): C, 54.03 (53.13); H, 4.68 (4.57); N, 8.31 (7.94). IR (KBr): ν/cm^{-1} 3446 (brs), 2229 (m), 1601 (s), 1558 (m), 1520 (s), 1494 (s), 1417 (s), 1389 (s), 1291 (m), 1213 (m), 1115 (w), 1018 (w), 1002 (w), 954 (w), 852 (m), 772 (m), 695 (w), 595 (w), 545 (w), 468 (m). MS (ESI): calc. for $\{[\text{Tb}(\text{cpb})_4(\text{OH})]\cdot\text{MeCN}\}^{2-}$: 480.6 Found: 480.9; for $\{[\text{Tb}(\text{cpb})_2(\text{OH})_2]\cdot\text{MeCN}\}^-$: 606.1 Found: 606.8; for $\{[\text{Tb}(\text{cpb})_2(\text{OH})_2]\cdot\text{MeCN}, \text{H}_2\text{O}\}^-$: 624.1 Found: 624.8.

S1.7. Methodology for solution IR experiment:

A 0.10 M solution of $[\text{Nd}(\text{cpb})_3(\text{H}_2\text{O})_2]$ in DMF was generated and the Mettler Toledo ReactIR probe immersed in the solution. The probe was removed leaving a droplet of the solution at the tip of the probe. Scanning began at intervals of 2 minutes and the droplet left undisturbed to evaporate. The experiment was halted when it was determined that the solution have concentrated to dryness and the concentrations of observable species remained static for 6 hours.

S1.8. References:

[R1]: S. T. Heller, S. R. Natarajan. *Org. Lett.* **2006**, *8(13)*, 2675.

S2. Further description of dipole-dipole network

Table 1. Observed bond dipole-bond dipole interactions for **1**.

Assym. Unit –Symmetry Interaction	Intermolecular symmetry transformation	Interatomic distance (Å)	Alignment
N(1)-C(20)	(x-1, y, z)	3.505	Sheared parallel
N(1)-C(20)	(-x-1, 1-y, -z)	4.090	Sheared parallel
C(9)-N(3)	(x-1, y, z)	4.052	Sheared parallel
N(1)-C(9)	(-x-1, 1-y, -z)	3.616	Antiparallel
N(2)-C(9)	(-x-1, 1-y, -z)	4.638	Sheared antiparallel
N(2)-C(20)	(-x, 1-y, -z)	4.506	Antiparallel
N(2)-C(31)	(x, 1+y, z)	3.852	Sheared parallel
C(20)-N(1)	(1+x, y, z)	3.505	Sheared parallel
C(31)-N(2)	(-x, 1-y, -z)	4.897	Sheared antiparallel
N(3)-C(9)	(1+x, y, z)	4.052	Sheared parallel
N(3)-C(31)	(1-x, -y, -z)	4.069	Antiparallel

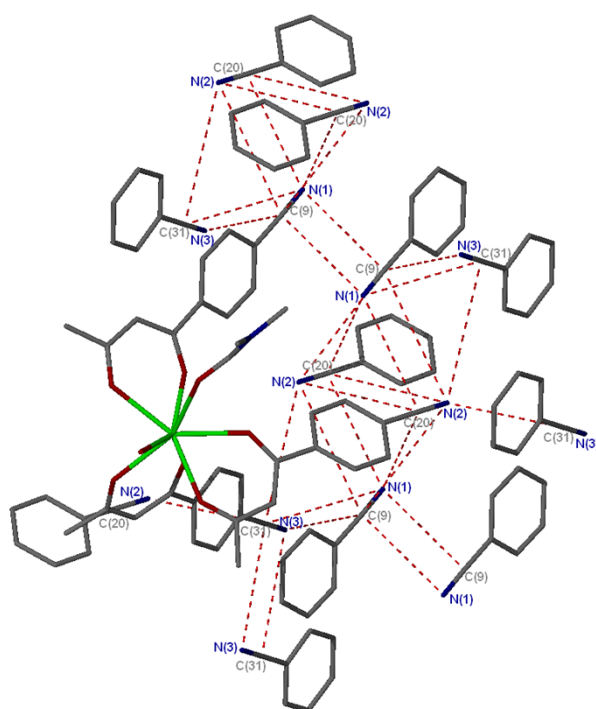


Figure 5. Complete network of bond dipole-bond dipole interactions within 5 Å observed for **1**. Broken red lines represent nitrile bond dipole interactions.

The strongest interaction occurs at a distance of 3.616 Å between N(1), C(9) of the asymmetric unit and C(9), N(1) at $-x-1, 1-y, -z$. The symmetry-generated complex undergoes π - π stacked chain propagation to a second complex at $-x, 1-y, -z$, which in turn exhibits antiparallel bond dipole-bond dipole interaction between N(2), C(20) of the asymmetric unit and at C(20), N(2) with a distance of 4.506 Å.

S2. Crystallographic Data

S2.1 Table 1 Crystallographic data for **1** and **2**

Complex	1	2
Empirical formula	C ₃₉ H ₄₀ N ₅ NdO ₉	C ₃₉ H ₄₀ N ₅ O ₉ Tb
Formula weight	867.00	881.68
Crystal system	Triclinic	Triclinic
Space group	<i>P</i> -1	<i>P</i> -1
<i>a</i> /Å	9.8275(6)	9.774(2)
<i>b</i> /Å	10.7284(7)	10.682(2)
<i>c</i> /Å	19.2871(12)	19.281(4)
α /°	91.021(5)	91.16(3)
β /°	102.172(5)	101.99(3)
γ /°	95.652(5)	95.68(3)
<i>V</i> /Å ³	1976.6(2)	1957.7(7)
<i>Z</i>	2	2
<i>D</i> _c /g cm ⁻³	1.46	1.49
μ /mm ⁻¹	1.372	1.866
<i>F</i> (000)	882	892
θ range/°	1.91 to 25.00	2.16 to 23.85
<i>R</i> _{int}	0.0275	0.0371
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0275, <i>wR</i> ₂ = 0.0613	<i>R</i> ₁ = 0.0275, <i>wR</i> ₂ = 0.0966
GOF	1.005	1.064

S2.2 Selected Bond Lengths and Angles for **1**:

Table 2 Selected bond lengths for **1**

1	
Nd(1)-O(1)	2.455(2)
Nd(1)-O(2)	2.383(2)
Nd(1)-O(3)	2.428(2)
Nd(1)-O(4)	2.391(2)
Nd(1)-O(5)	2.4340(19)
Nd(1)-O(6)	2.370(2)
Nd(1)-O(7)	2.505(2)
Nd(1)-O(9)	2.505(2)

Table 3 Selected bond angles for **1**

1	
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O(6)-Nd(1)-O(2)	76.62(7)	O(6)-Nd(1)-O(9)	142.15(7)
O(2)-Nd(1)-O(4)	77.88(8)	O(2)-Nd(1)-O(9)	138.04(8)
O(2)-Nd(1)-O(3)	146.14(7)	O(4)-Nd(1)-O(9)	117.64(8)
O(6)-Nd(1)-O(5)	70.54(7)	O(3)-Nd1-O(9)	70.83(8)
O(4)-Nd(1)-O(3)	70.87(7)	O(5)-Nd1-O(9)	77.46(7)
O(2)-Nd(1)-O(5)	117.60(8)	O(1)-Nd1-O(9)	75.75(8)
O(4)-Nd(1)-O(5)	139.12(7)	O(6)-Nd1-O(7)	144.29(6)
O(3)-Nd(1)-O(5)	80.60(7)	O(2)-Nd1-O(7)	77.18(7)
O(6)-Nd(1)-O(1)	115.25(8)	O(4)-Nd1-O(7)	73.24(7)
O(2)-Nd(1)-O(1)	70.52(7)	O(3)-Nd1-O(7)	105.15(8)
O(4)-Nd(1)-O(1)	140.81(7)	O(5)-Nd1-O(7)	144.33(7)
O(3)-Nd(1)-O(1)	143.33(6)	O(1)-Nd1-O(7)	77.57(7)
O(5)-Nd(1)-O(1)	77.81(7)	O(9)-Nd1-O(7)	71.73(7)

S2.3 Selected Bond Lengths and Angles for 2:

Table 2 Selected bond lengths for 2

2	
Tb(1)-O(6)	2.317(3)
Tb(1)-O(4)	2.339(3)
Tb(1)-O(2)	2.342(3)
Tb(1)-O(1)	2.367(3)
Tb(1)-O(5)	2.379(3)
Tb(1)-O(3)	2.387(3)
Tb(1)-O(7)	2.442(3)
Tb(1)-O(9)	2.447(3)

Table 3 Selected bond angles for 2

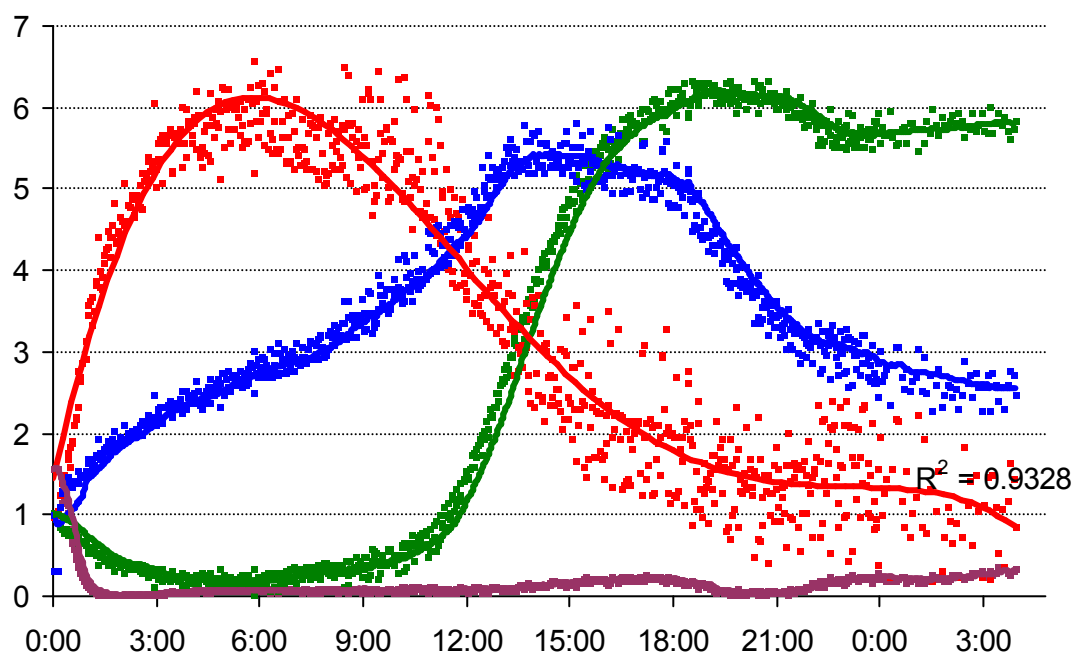
2			
O(6)-Tb(1)-O(4)	75.71(10)	O(1)-Tb(1)-O(3)	141.70(9)
O(6)-Tb(1)-O(2)	76.99(11)	O(5)-Tb(1)-O(3)	76.98(10)
O(4)-Tb(1)-O(2)	76.99(11)	O(6)-Tb(1)-O(7)	143.95(9)
O(6)-Tb(1)-O(1)	83.94(10)	O(4)-Tb(1)-O(7)	78.02(10)
O(4)-Tb(1)-O(1)	145.93(10)	O(2)-Tb(1)-O(7)	73.23(10)
O(2)-Tb(1)-O(1)	72.29(10)	O(1)-Tb(1)-O(7)	105.45(10)
O(6)-Tb(1)-O(5)	72.28(10)	O(5)-Tb(1)-O(7)	143.13(9)
O(4)-Tb(1)-O(5)	118.49(10)	O(3)-Tb(1)-O(7)	77.79(10)
O(2)-Tb(1)-O(5)	139.95(10)	O(6)-Tb(1)-O(9)	142.70(9)
O(1)-Tb(1)-O(5)	79.43(10)	O(4)-Tb(1)-O(9)	139.05(10)
O(6)-Tb(1)-O(3)	116.28(10)	O(2)-Tb(1)-O(9)	117.50(11)
O(4)-Tb(1)-O(3)	72.36(10)	O(1)-Tb(1)-O(9)	70.19(10)
O(2)-Tb(1)-O(3)	141.09(10)	O(5)-Tb(1)-O(9)	76.79(10)

S3. *In situ* FTIR analyses

S3.1. General

Solution RTIR scanning measurements were recorded using a Mettler Toledo ReactIR 10 spectrometer fitted with a DiComp probe and connected to an MCT detector by a K6 Conduit. Scanning was performed in the region of 4000 to 650 wavenumbers at 4 wavenumber resolution. Elucidation of reaction components was performed using ConcIRT™ software.

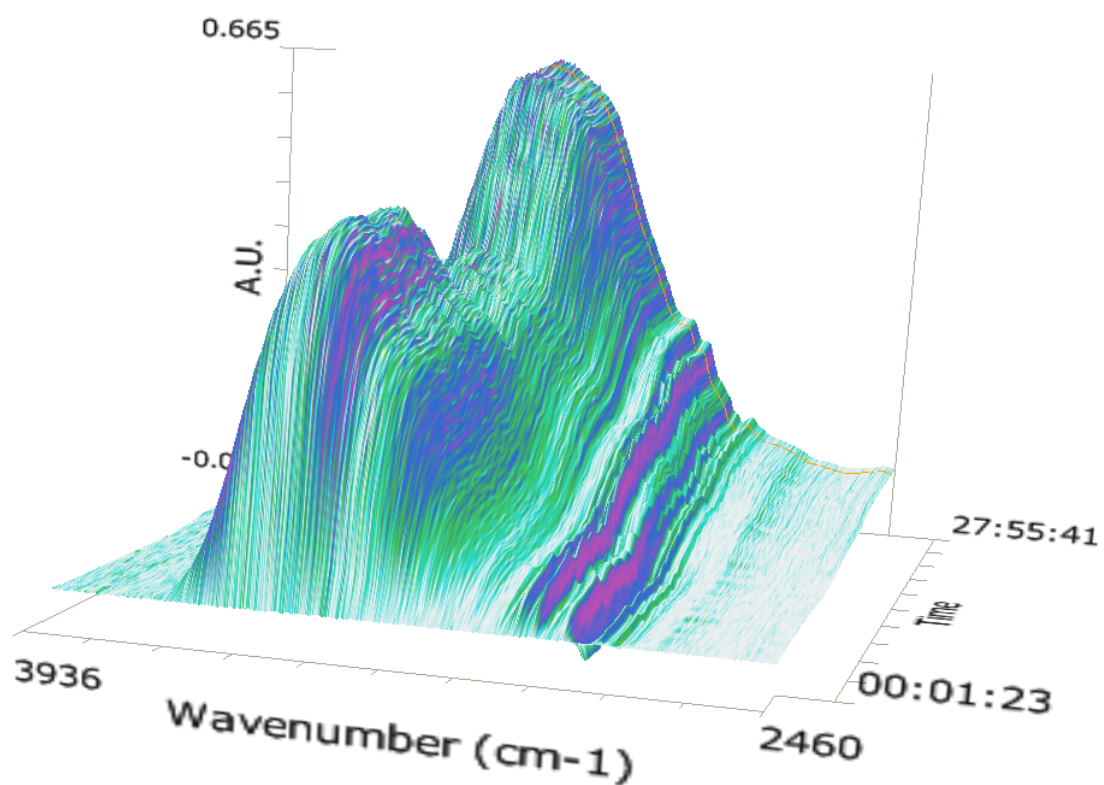
S3.2. Figure 4 data point precursors to trend lines



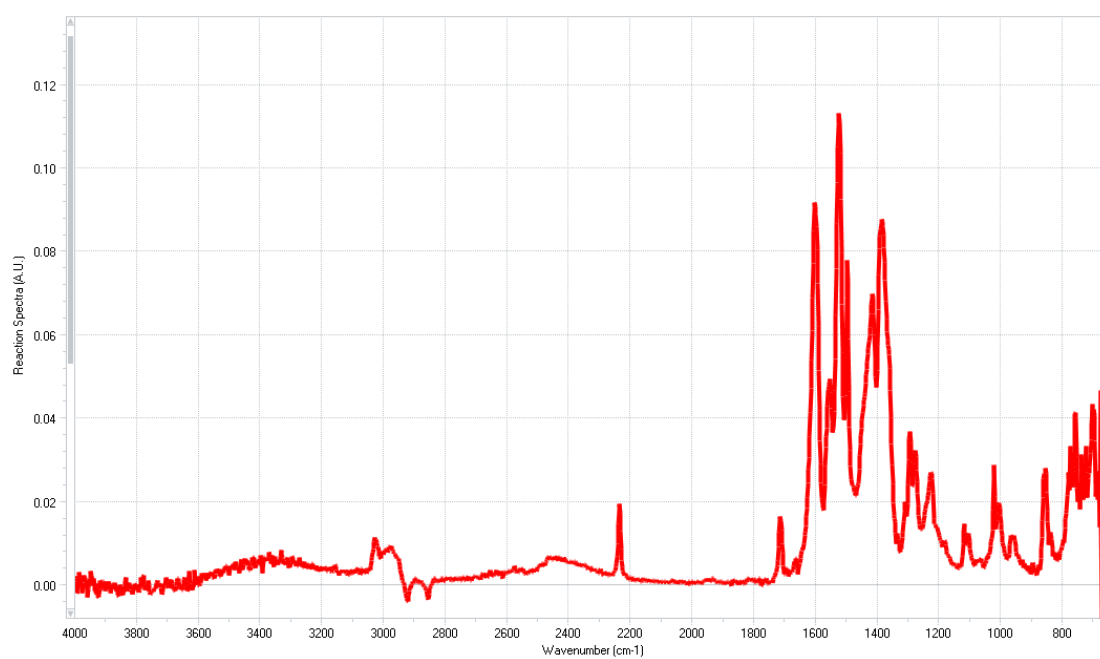
Trend lines are moving averages with the exception of the red series, which is described by a polynomial equation. The R^2 value is given. No data was trimmed from the experiment.

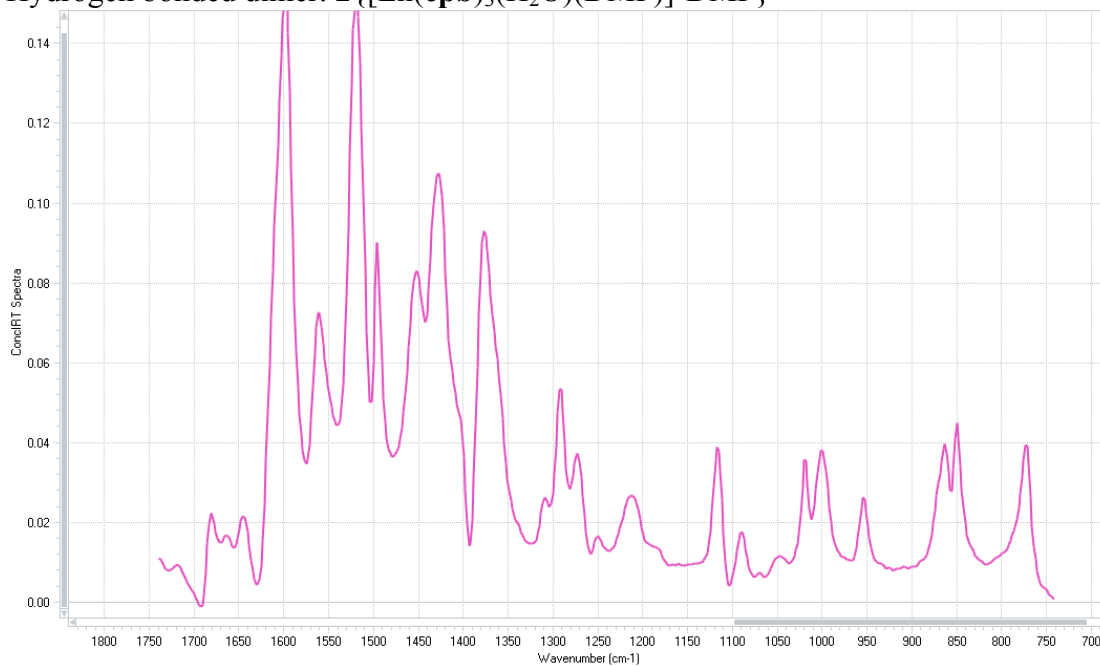
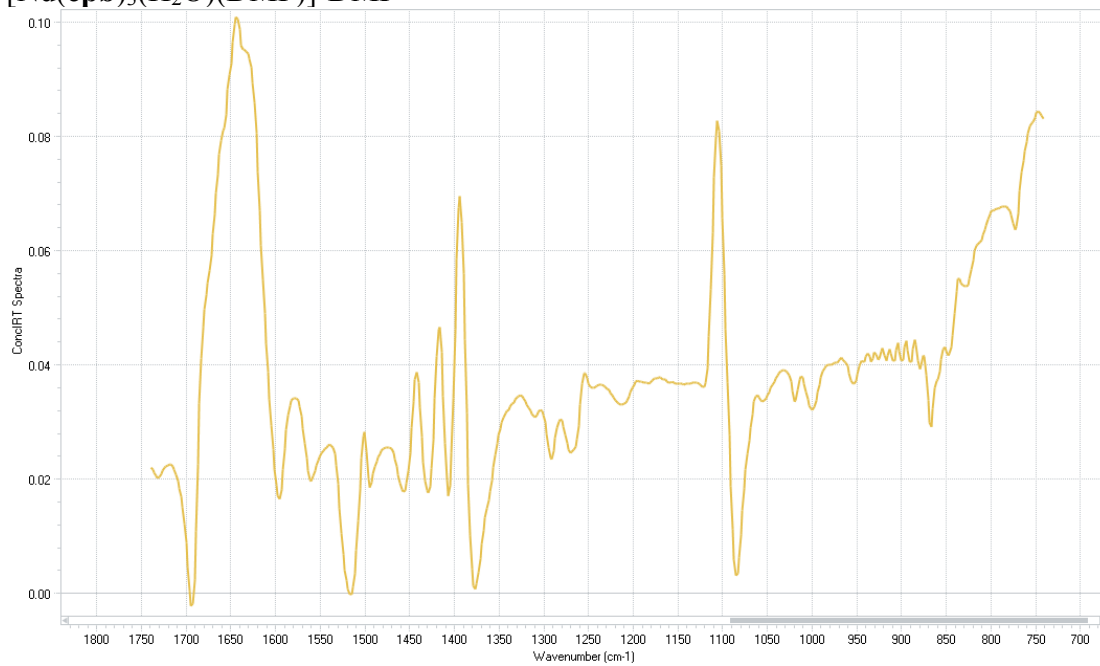
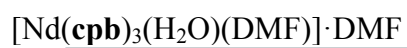
The intensities of the trend lines reported are based on changes in absolute peak intensities with respect to time. Changes in dipole strength affecting the intensity of the IR bands between species prevent a highly accurate correlation between concentration of the starting material $[\text{Ln}(\text{cpb})_3(\text{H}_2\text{O})_2]$ with the subsequent species.

S3.3. Waterfall diagram displaying change in O-H bands with time

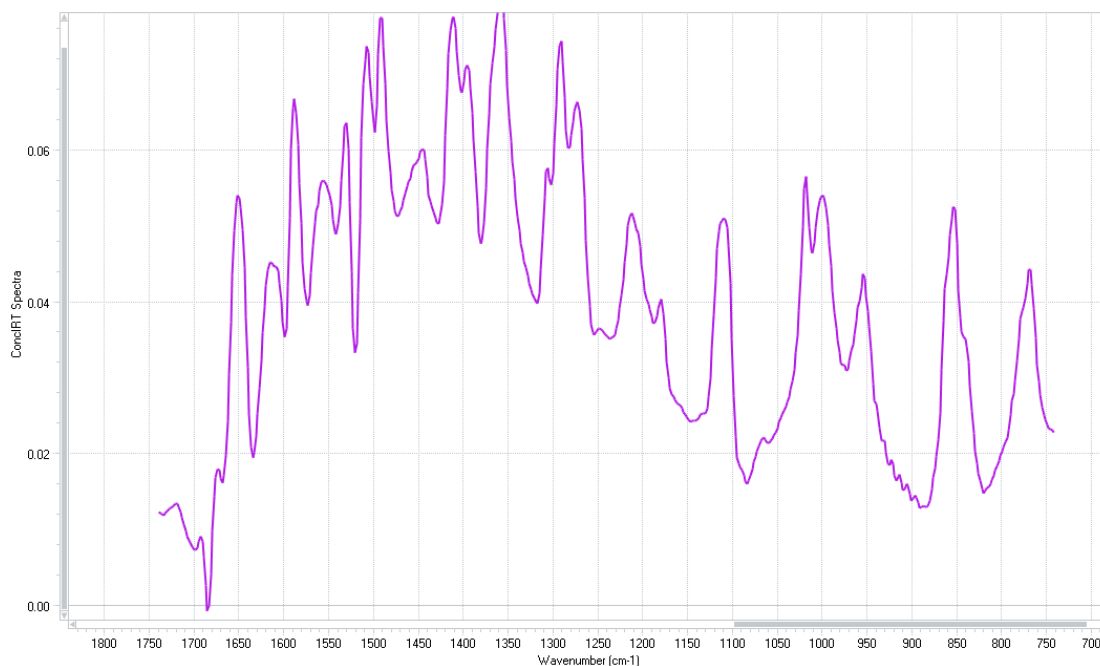


S3.2. Chloroform spectrum of $[\text{Nd}(\text{cpb})_3(\text{H}_2\text{O})_2]$

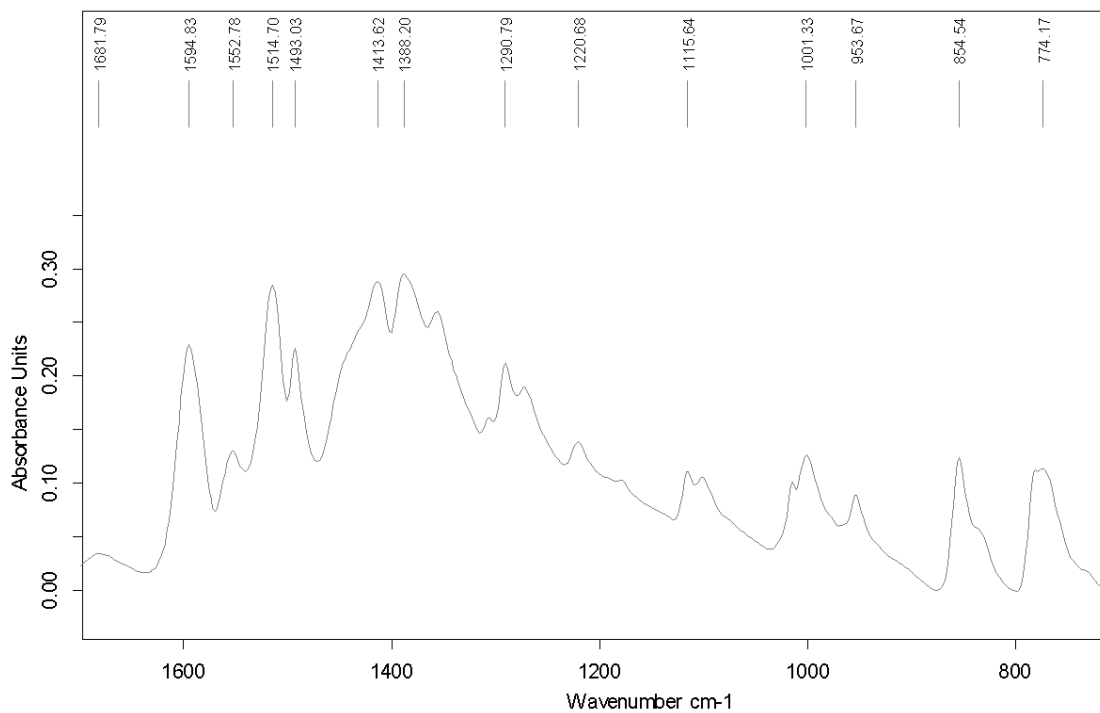




S3.2. Comparison of solution and solid state IR for molecular network



Solution state molecular network obtained by crystallisation on *in situ* probe tip



Reference solid-state molecular network obtained with a pure crystalline sample using a Bruker Equinox 55 Infrared Spectrometer fitted with a Specac Diamond ATR source.