

Elucidation of naphthalene diimide metallomacrocycles and catenanes by solvent dependent excimer and exciplex emission

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Supplementary Information

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1. General experimental details

All starting materials, solvents and reagents were purchased from Sigma-Aldrich, TCI, Merck or Alfa Aesar and used as received. H₂LeuNDI was synthesised according to a literature procedure.¹

Nuclear Magnetic Resonance (NMR) spectroscopy

Nuclear magnetic resonance spectra were collected using a Bruker DRX-400 spectrometer with signals (reported in ppm) references against TMS.

Mass Spectrometry

Mass spectrometry experiments using crystalline samples of **1**·2H₂O·DMF and **2**₂·2DMF·5H₂O, were performed on a hybrid linear quadrupole ion trap and orbitrap mass spectrometer (Thermo LTQ Orbitrap XL) that was equipped with a custom external nanoelectrospray ionisation (nESI) source. Theta (dual chamber) nESI emitters were prepared by pulling borosilicate capillaries (theta capillaries, Harvard Apparatus, 1.5 mm o.d) to an inner orifice diameter of < 1 μm (Narishige PN-3 Glass Micropipette Puller, Narishige Scientific Instrument Labs, Tokyo, Japan). The electrospray capillaries were sputter-coated with a thin layer of Au and Pd (1:1 molar ratio) for 20 s (Scancoat Six, Edwards) operated at a pressure of 0.1 mbar in an Ar(g) atmosphere (1.25 kV, 30 mA). ESI solutions containing the samples in chloroform were loaded into a chamber of the theta capillary, with the other chamber containing acetonitrile with 1% acetic acid. For ion formation, a voltage of 1.5 kV was applied to the ESI emitter relative to the capillary entrance of the mass spectrometer. The temperature of the capillary entrance to the mass spectrometer was 50°C.

Thermogravimetric Analysis

Thermogravimetric analysis (TGA) was conducted using a Mettler TGA/DSC 1 instrument. The temperature was ramped at 5 °C/min from room temperature to 400 °C under a dry N₂ supply of 10.0 mL/min. The data were analysed with the STARE program.

Microanalysis

Microanalyses were performed at the Science Centre, London Metropolitan University, UK.

Powder X-Ray Diffraction

Powder X-ray diffraction (PXRD) data were collected at room temperature using a Bruker D8 Focus diffractometer equipped with Cu-Kα ($\lambda = 1.5418 \text{ \AA}$) radiation. The sample was mounted on a zero background silicon single crystal stage. Data were collected in the angle interval $2\theta = 5 - 55^\circ$ with a step size of 0.02° . The data was collected at 298 K and compared to predicted patterns based on the single crystal data (collected at 100 K).

Absorbance and fluorescence emission

UV-Visible absorption measurements were taken with a Varian Cary 100 Bio UV-Visible spectrophotometer (Agilent) using solvent for baseline subtraction. Fluorescence excitation and emission spectra were recorded using a Varian Cary Eclipse fluorimeter (Agilent). All samples for steady state spectra were prepared in 1.0 cm path length quartz cuvettes. All solvents used for absorption and fluorescence measurements were of spectroscopic grade from Merck, TCI or Aldrich.

Fluorescence lifetimes

Fluorescence lifetimes were measured using the method of time correlated single photon counting (TCSPC) on a set-up described previously.² The excitation source was a 375 nm pulsed diode laser (Picoquant, LDH-P-C-375) with a repetition rate of 5 or 10 MHz. The laser light was passed through a quarter waveplate (Thor labs) to ensure linear polarisation before being directed onto the sample. Emission was collected at 90° and passed through a polariser set to the magic angle (54.7°) to eliminate any photoselection bias. Detection wavelength selection was achieved using a monochromator (CVI, dk480) after which emission photons were focused onto a microchannel plate (Hamamatsu, R3809U-50) for detection. Photon emission times from the START (laser sync) and STOP (microchannel plate) signals were recorded using a photon timing device (PicoQuant, PicoHarp 300) and histogrammed to create a fluorescence decay profile. An instrument response function (IRF) was obtained by recording the decay profile of a scattering solution of dilute milk powder in water. Fluorescence lifetimes were determined by fitting the sample decay profile, by a sum of exponential functions convolved with the IRF, using a least-squares method based on the Levenberg-Marquardt algorithm (TRFA Global Analysis version 1.0, Scientific Software Technologies Centre). Goodness-of-fit was determined by the χ^2 parameter (values of $\sim 1.0 < \chi^2 < 1.2$ signifying a good fit) and inspection of the residuals (data minus fitted function) which should be randomly distributed about zero.

2. Synthesis

Synthesis of $[\text{Cd}_2(1,10\text{-phen})_2(\text{LeuNDI})_2(\text{OH}_2)_2] \cdot 2\text{H}_2\text{O} \cdot \text{DMF}, 1 \cdot 2\text{H}_2\text{O} \cdot \text{DMF}$

(*S*)- H_2LeuNDI (20 mg, 40.4 μmol), 1,10-phenanthroline (8.0 mg, 20.2 μmol) and $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (25 mg, 80.8 μmol) were added to a solvent mixture of DMF (2 mL), methanol (1 mL) and water (1 mL) in a glass vial and sonicated to dissolve. The solution was heated at 85 °C in a dry block incubator overnight, during which time yellow crystals of $1 \cdot 2\text{H}_2\text{O} \cdot \text{DMF}$ were formed, which were recovered by vacuum filtration. Yield 21.3 mg, 63%. Found C, 55.65; H, 4.26, N, 6.97%; $\text{C}_{76}\text{H}_{67}\text{N}_8\text{O}_{18}\text{Cd}_2 \cdot 2\text{H}_2\text{O} \cdot \text{DMF}$, $[\text{Cd}_2(\text{phen})_2(\text{LeuNDI})_2(\text{OH}_2)_2] \cdot 2\text{H}_2\text{O} \cdot \text{DMF}$ requires C, 55.35; H, 4.59; N, 7.35%. $\nu_{\text{max}}/\text{cm}^{-1}$ 3070w, 2953w, 2116w, 1705m, 1660s, 1574s, 1515m, 1450m, 1376m, 1329s, 1246s, 1192m, 1145m, 1097m, 987m, 891w, 849m, 780s, 725s, 679m. m/z (ES^+) 787.13 $[\text{Cd}(\text{LeuNDI})(\text{phen})+\text{H}]^+$, (calculated for $\text{C}_{38}\text{H}_{33}\text{CdN}_4\text{O}_8^+$, 787.13), 823.11 $[\text{Cd}(\text{LeuNDI})(\text{phen})(\text{H}_2\text{O})+\text{H}]^+$, (calculated for $\text{C}_{38}\text{H}_{37}\text{CdN}_4\text{O}_{10}^+$, 823.15), 1607.23 $[\text{Cd}_2(\text{LeuNDI})_2(\text{phen})_2(\text{H}_2\text{O})_2+\text{H}]^+$, (calculated for $\text{C}_{76}\text{H}_{69}\text{Cd}_2\text{N}_8\text{O}_{18}^+$, 1607.28). TGA: On-set, 60 °C, mass loss = 4.5% (calculated 4.2% for loss of one DMF and two water molecules, and two coordinated water molecules), decomp. 300 °C. Bulk phase purity was confirmed by PXRD (see below, Figure S7).

The data was processed with the SQUEEZE routine of PLATON,³ showing solvent accessible voids of 166 Å³ containing 52 e⁻ per asymmetric unit, which is accounted for by the solvent not modelled in the crystal structure, one DMF and two water molecules, which are also present in the microanalysis and TGA.

Synthesis of $[\text{Cd}_2(\text{LeuNDI})_2(2,2'\text{-bipy})_2(\text{OH}_2)_2] \cdot 2\text{DMF} \cdot 5\text{H}_2\text{O}, 2 \cdot 2\text{DMF} \cdot 5\text{H}_2\text{O}$

(*S*)- H_2LeuNDI (10 mg, 20.2 μmol), $\text{Cd}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (12.5 mg, 40.4 μmol) and 2,2'-bipyridine (3.0 mg, 20.2 μmol) were added to DMF (2 mL) and water (1 mL) in a glass vial and sonicated to dissolve. The solution was heated at 85 °C in a dry block incubator for 2 nights, during which time yellow block crystals of $2 \cdot 2\text{DMF} \cdot 5\text{H}_2\text{O}$ were formed which were recovered by vacuum filtration. Yield 5.1 mg, 16%. Found C, 55.34; H, 4.47, N, 7.27%; $\text{C}_{144}\text{H}_{136}\text{N}_{16}\text{O}_{36}\text{Cd}_4$, $[\text{Cd}_2(\text{LeuNDI})_2(2,2'\text{-bipy})_2(\text{OH}_2)_2]_2$ requires C, 55.49; H, 4.40; N, 7.19%. $\nu_{\text{max}}/\text{cm}^{-1}$ 31.05w, 2953w, 2868w, 1705m, 1663s, 1591s, 1578s, 1491w, 1474w, 1438m, 1380m, 1328s, 1245s, 1193m, 1175w, 1154w, 1105w, 1060w, 1018w, 988w, 924w, 879w, 850w, 811w, 762s, 737m. m/z (ES^+) 1621.88 $[\text{Cd}_4(\text{LeuNDI})_4(2,2'\text{-bipy})_4(\text{OH}_2)(\text{CHCl}_3)(\text{CH}_3\text{COOH})+2\text{H}]^{2+}$ (calculated for $\text{C}_{147}\text{H}_{137}\text{Cd}_4\text{Cl}_3\text{N}_{16}\text{O}_{35}^{2+}$, 1621.73), 1631.42 $[\text{Cd}_2(\text{LeuNDI})_2(2,2'\text{-bipy})_2(\text{OH}_2)_2(\text{CH}_3\text{CN})+\text{H}]^+$, (calculated for $\text{C}_{74}\text{H}_{72}\text{Cd}_2\text{N}_9\text{O}_{20}^+$, 1631.30). TGA: On-set, 50 °C, mass loss = 16.1% (calculated 15.2% for loss of five water and two DMF molecules, and two coordinated water molecules per asymmetric unit), decomp. 350 °C. Bulk phase purity was confirmed by PXRD (see below, Figure S8).

The X-ray structure showed significant void space in which no solvent could be modelled, so the data were processed with the SQUEEZE routine of PLATON,³ to show total void space of 534 Å³ containing 131 e⁻ per asymmetric unit. This void may contain five water and two DMF molecules, accounting for 130 e⁻, which could not be modelled in the structure. The TGA and SQUEEZE results show the same composition of non-coordinated solvent, and the microanalysis shows less solvent, as all but the coordinated solvent was lost before the microanalysis could be conducted.

3. H₂LeuNDI ¹H-NMR studies

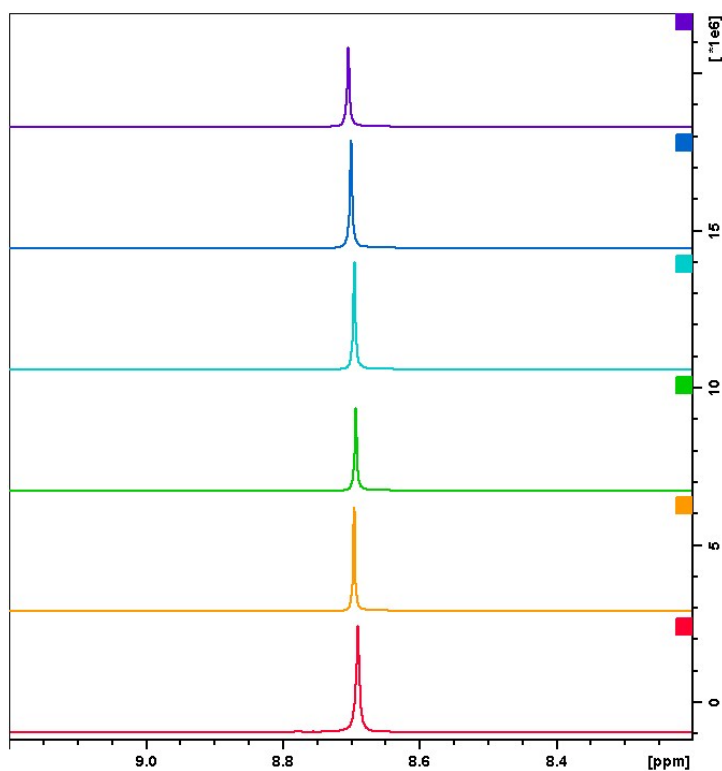


Figure S1. The ¹H-NMR signal for the NDI core of H₂LeuNDI in chloroform at concentrations of 10 mmol/L (red), 20 mmol/L (orange), 30 mmol/L (green), 40 mmol/L (light blue), 60 mmol/L (dark blue) and 80 mmol/L (purple) (right), showing that increased concentration does not shift the ¹H-NMR signal for the NDI core, suggesting that the H₂LeuNDI molecules do not aggregate in solution, despite elevated concentration.

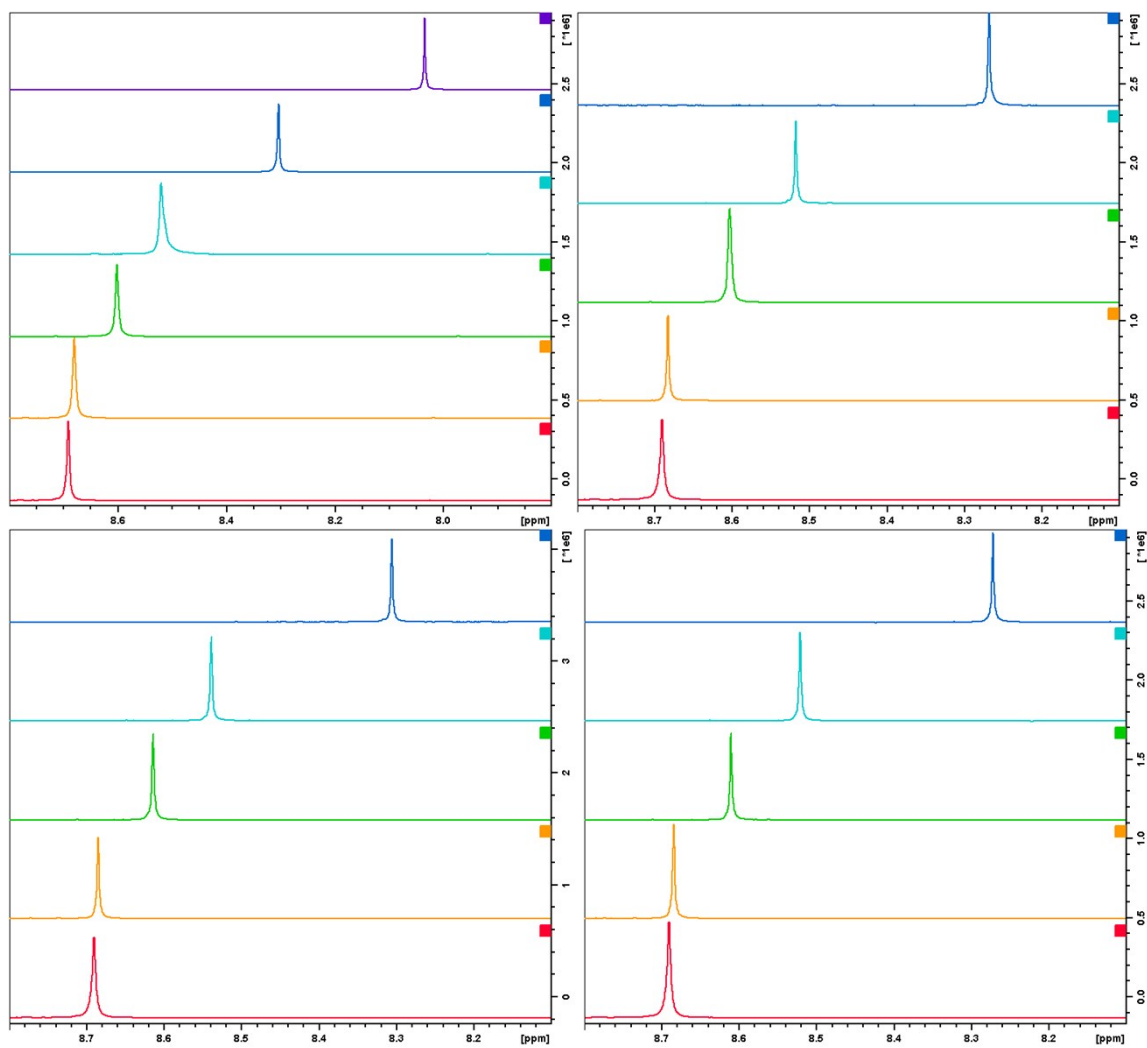


Figure S2. The ^1H -NMR titrations of H_2LeuNDI in chloroform ($30\ \mu\text{mol/L}$) with toluene (top left), *o*-xylene (top right), *m*-xylene (bottom left) and *p*-xylene (bottom right) proportions of 0% (red), 1% (orange), 10% (green), 20% (light blue), 50% (dark blue) and 100% (purple).

4. Fluorescence lifetimes

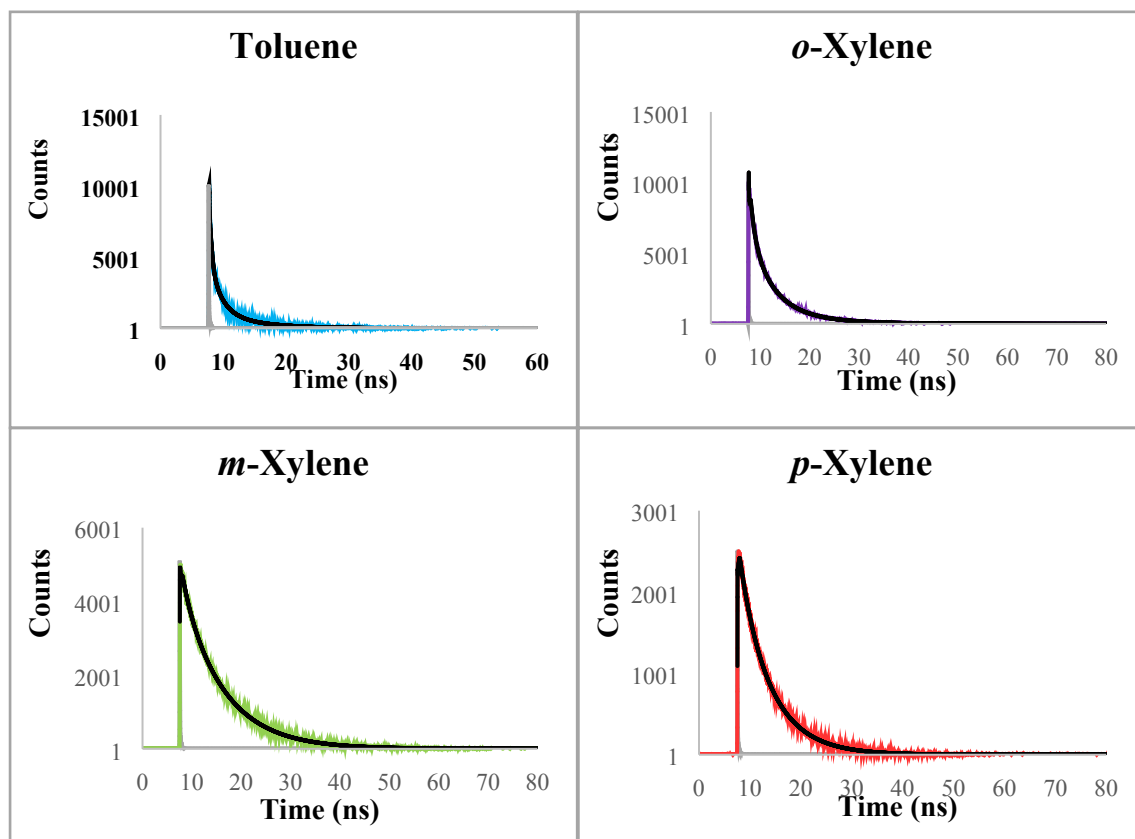


Figure S3. Time correlated single photon counting decay histograms and fitted exponentials decay functions (black) of H₂LeuNDI in toluene (blue), o-xylene (purple), m-xylene (green) and p-xylene (red). IRF (grey) is instrument response function.

5. Fluorescence emission solvent titrations

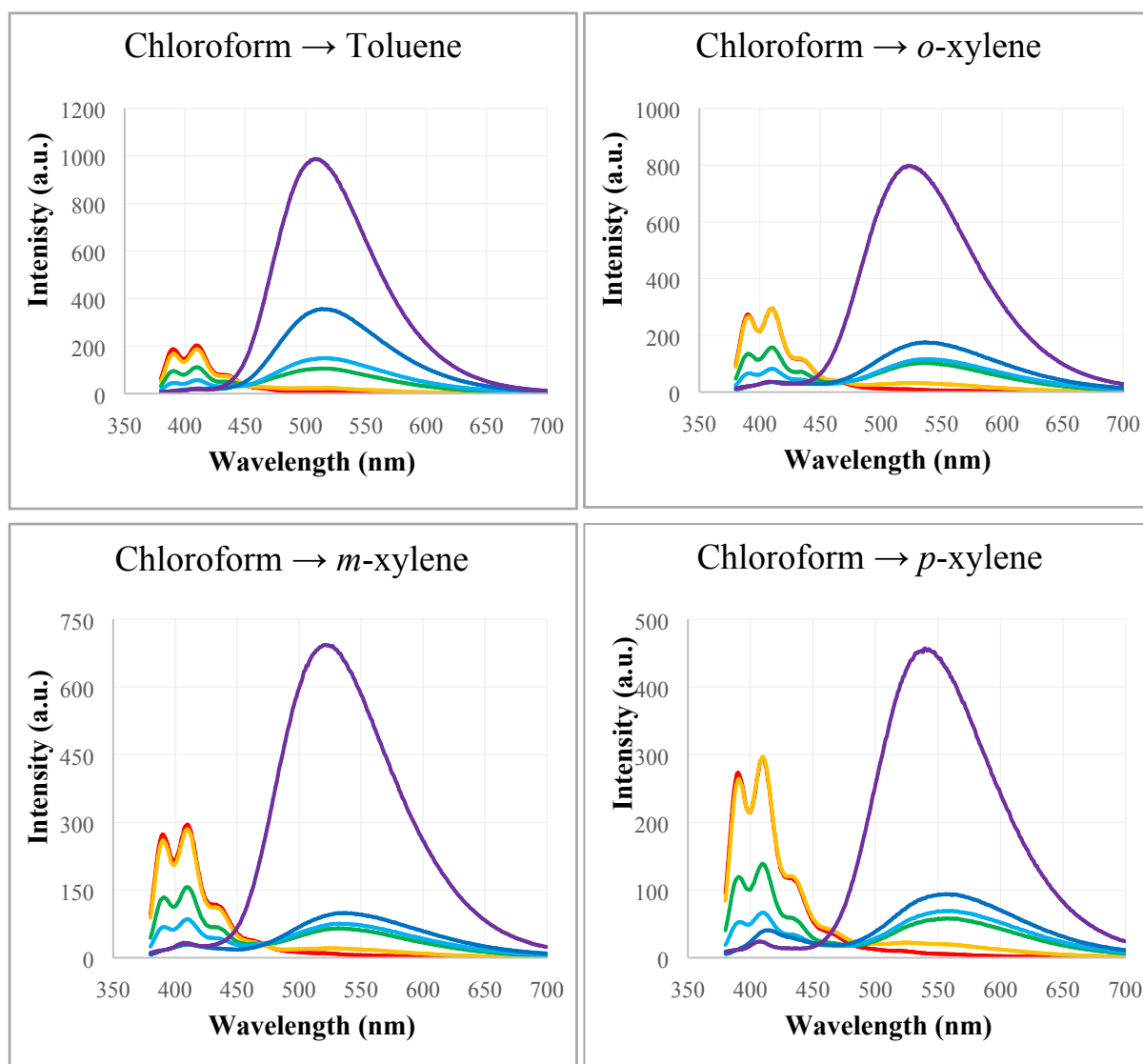


Figure S4. Emission spectra of H₂LeuNDI at 30 μmol/L in chloroform with aromatic solvent proportions of 0% (red), 1% (orange), 10% (green), 20% (light blue), 50% (dark blue) and 100% (purple) upon excitation at 360 nm.

6. Absorbance/Emission Spectra of 1 and 2₂

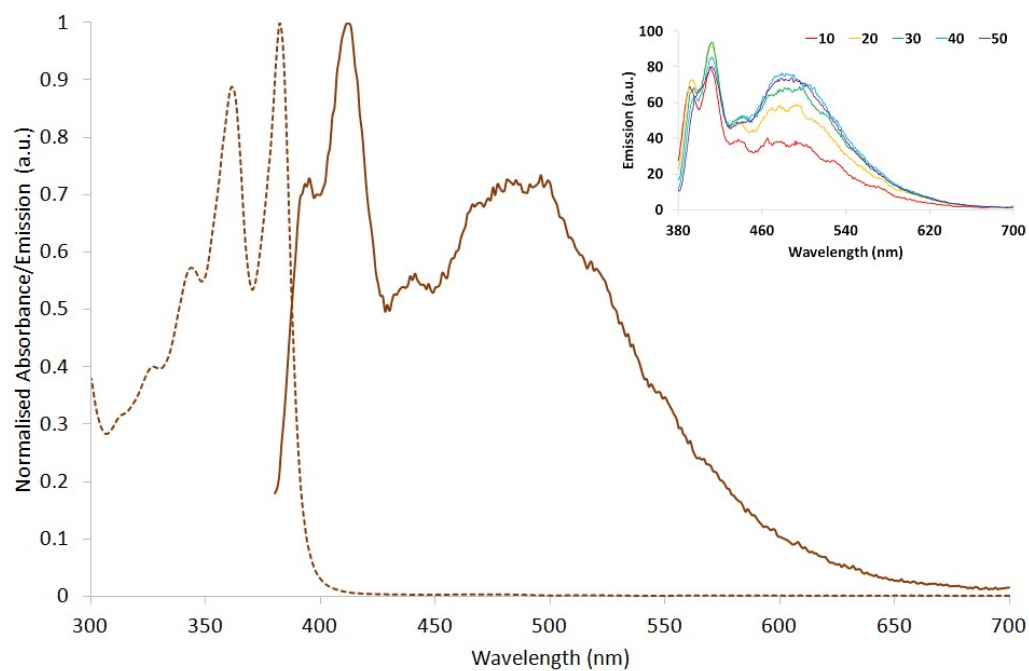


Figure S5. The absorbance (dashed) and emission (solid) spectra of **1** in CHCl₃ (25 μmol/L) upon excitation at 360 nm and (inset) concentration dependence of the emission (10-50 μmol/L).

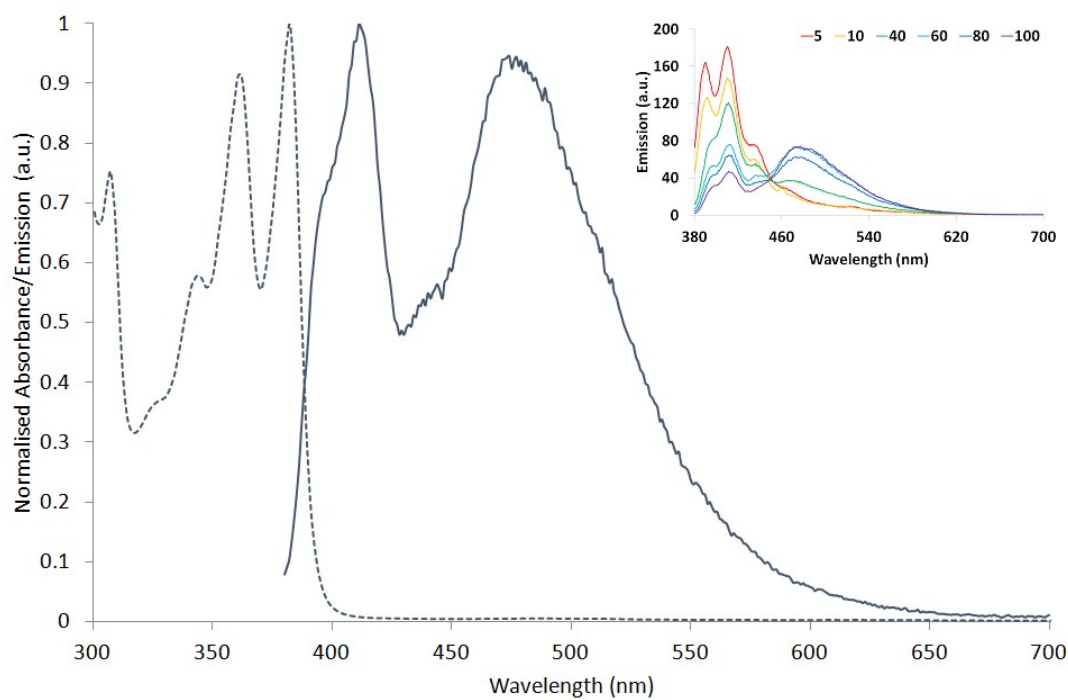


Figure S6. The absorbance (dashed) and emission spectra (solid) of **2** in CHCl₃ (70 μmol/L) upon excitation at 360 nm and (inset) concentration dependence of the emission (5-100 μmol/L).

7. X-ray crystallography details

Data for $1 \cdot 2\text{H}_2\text{O} \cdot \text{DMF}$ was collected on an OXFORD Gemini Ultra diffractometer at 123 K. data were processed, including an empirical absorption correction, using proprietary software CrysAlisPro.⁴ Data for $2_2 \cdot 2\text{DMF} \cdot 5\text{H}_2\text{O}$ was collected using the MX1 or MX2 beamlines at the Australian Synchrotron. Data was collected at 100 K using an energy equivalent to Mo-K α radiation (17.4 keV, $\lambda = 0.7108 \text{ \AA}$). All structures were solved with SHELXT⁵ using the dual-space method or SHELXS⁶ using direct methods, and refined by least-squares methods using SHELXL-2016⁶ within OLEX-2.⁷ Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were placed in calculated positions and refined using a riding model with isotropic displacement parameters 1.2 or 1.5 times the isotropic equivalent of their carrier atoms. O-H hydrogen atoms were placed in calculated positions and refined using SHELX DFIX and DANG restraints to maintain their positions. The structures both contained solvent accessible voids, and were processed with the SQUEEZE routine of PLATON.³

[Cd₂(1,10-phen)₂(LeuNDI)₂(OH₂)₂]·DMF·2H₂O, 1·DMF·2H₂O

All four of the LeuNDI isobutyl side chains showed signs of disorder which could not be modelled, so were refined using SHELX DFIX, DANG, DELU and ISOR restraints to give a chemically sensible model. The hydrogen atoms of all water molecules were placed in calculated positions and refined using SHELX DFIX restraints. One of the coordinated water molecules is disordered over two positions (free occupancy 57:43) and was refined with SHELX ISOR restraints. The non-coordinated water molecule is hydrogen bonding with one of the LeuNDI carbonyl groups and a coordinated water molecule. The data was processed with the SQUEEZE routine of PLATON,³ showing solvent accessible voids of 166 \AA^3 containing 52 e⁻ per asymmetric unit.

[Cd₂(2,2'-bipy)₂(LeuNDI)₂(OH₂)₂]₂·2DMF·5H₂O, 2₂·2DMF·5H₂O

The crystals were not of high quality, and no crystals of higher quality could be formed. The poor crystal quality led to poor diffraction quality, which caused a high R_{int} for the data, and large displacement ellipsoids in the model. The SHEL command was used to cut off the poor data past 0.8 \AA . The 2,2'-bipy ligands showed signs of disorder which could not be modelled, so were refined with SHELX DFIX, DELU, ISOR and DELU restraints. Both rings of one of the 2,2'-bipy ligands were constrained with AFIX 66 to give appropriate aromatic geometry. All four leucine isobutyl side chains showed signs of disorder which could not be modelled, so were refined with SHELX DFIX, DANG, ISOR, DELU and RIGU restraints. The structure showed void space in which no solvent could be modelled. Therefore the data were processed with the SQUEEZE routine of PLATON,³ showing total voids of 534 \AA^3 containing 131 e⁻ per asymmetric unit.

Table S1. Crystallographic parameters.

Compound reference	1·2H₂O·DMF	2₂·2DMF·5H₂O
Empirical formula	C ₇₆ H ₆₉ Cd ₂ N ₈ O ₁₉	C ₇₂ H ₆₈ Cd ₂ N ₈ O ₁₈
Formula weight	1623.19	1558.14
Crystal system	Monoclinic	Orthorhombic
a/Å	27.9956(5)	17.463(4)
b/Å	14.8843(2)	30.555(6)
c/Å	18.7743(2)	30.775(6)
α/°	90	90
β/°	107.1577(17)	90
γ/°	90	90
Volume/Å ³	7475.0(2)	16421(6)
Temperature /K	123.00(10)	100(2)
Space group	C2	C222 ₁
Z	4	8
Reflections measured	89995	176547
Reflections observed	11774	11910
Independent reflections	13273	16752
R _{int}	0.0597	0.1271
Final R1 values (I>=2σ (I))	0.0543	0.0865
Final wR(F2) values (I>=2σ (I))	0.0616	0.1119
Final R1 values (all data)	0.1380	0.2371
Final wR(F2) values (all data)	0.1431	0.2682
Flack parameter	0.040(5)	0.062(9)
CCDC Number	1828740	1828741

8. Powder X-ray diffraction

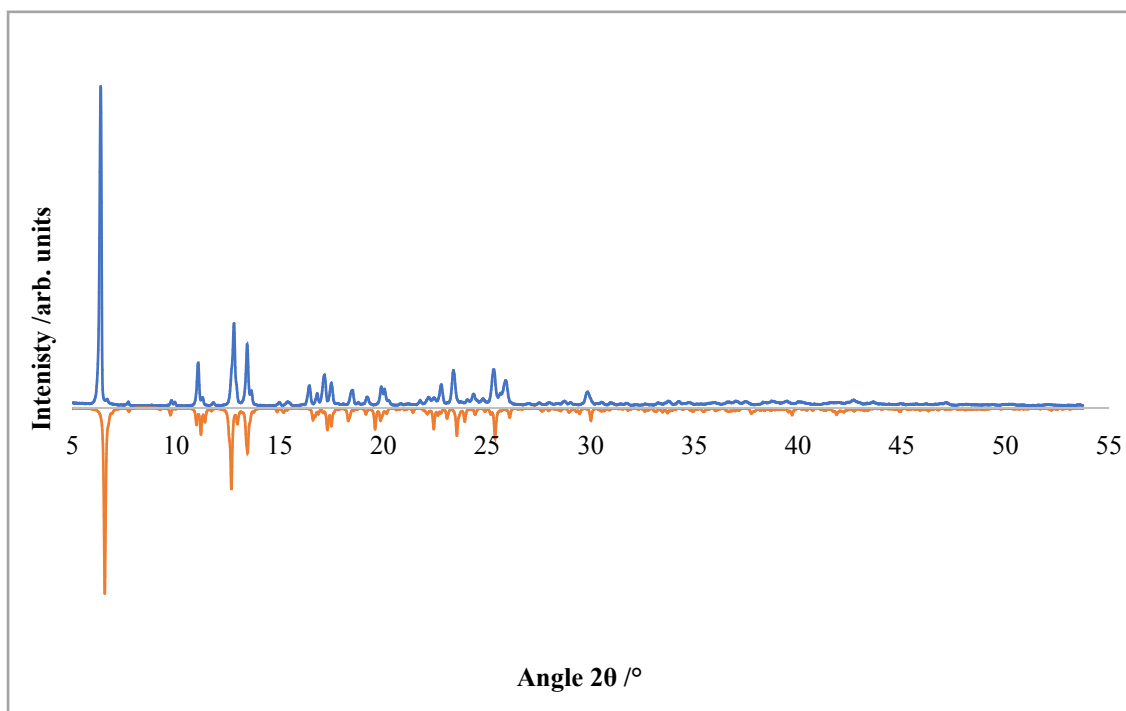


Figure S7: Comparison of experimental (298 K, blue) and calculated (100 K, orange) PXRD of $[\text{Cd}_2(1,10\text{-phen})_2(\text{LeuNDI})_2(\text{OH}_2)_2] \cdot \text{DMF} \cdot 2\text{H}_2\text{O}$, **1**·DMF·2H₂O.

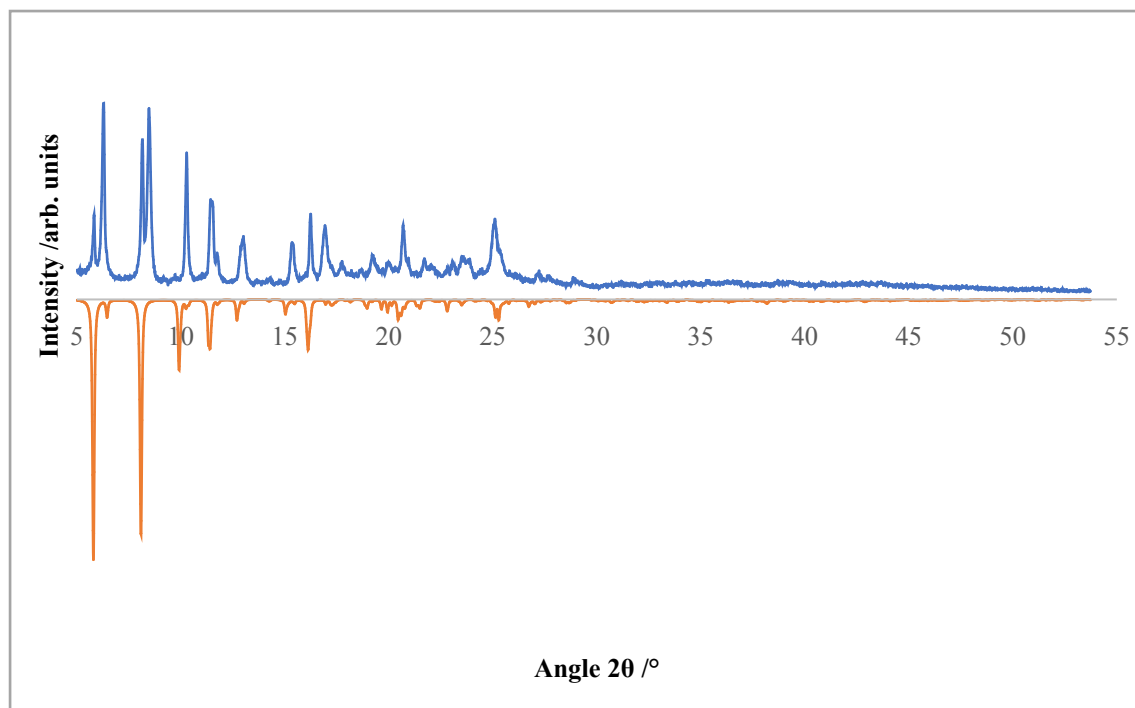


Figure S8: Comparison of experimental (298 K, blue) and calculated (100 K, orange) powder X-ray diffraction patterns of $[\text{Cd}_2(\text{LeuNDI})_2(2,2'\text{-bipy})_2(\text{OH}_2)_2]_2 \cdot 2 \cdot 2\text{DMF} \cdot 5\text{H}_2\text{O}$, **2**₂·2DMF·5H₂O.

9. Thermogravimetric analysis

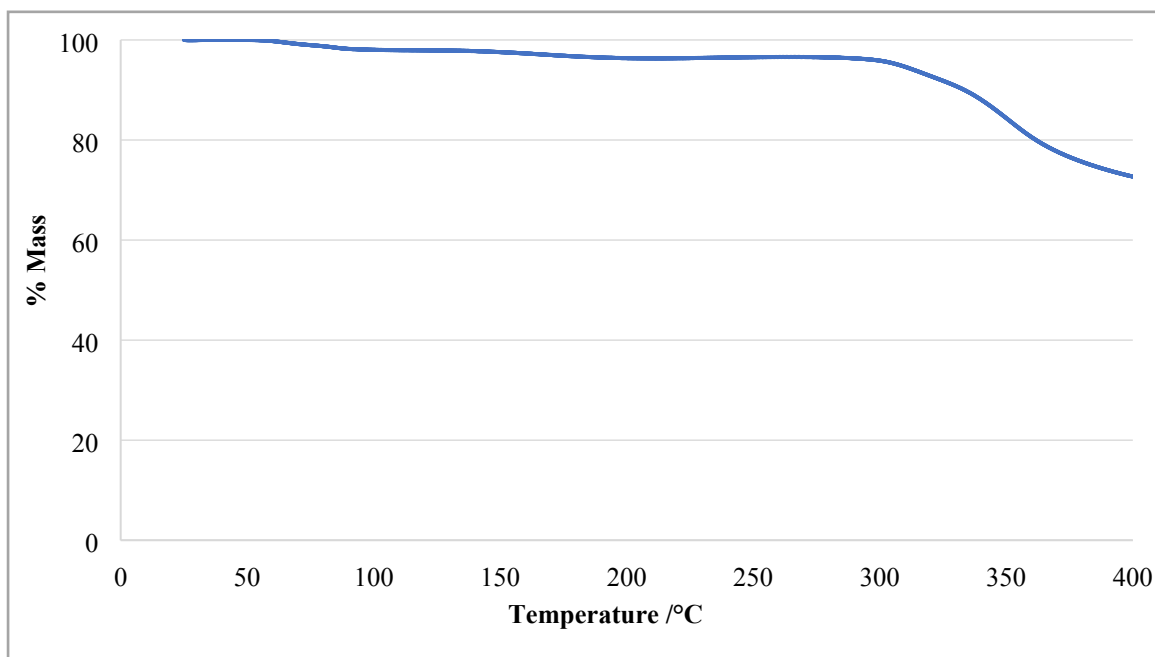


Figure S9: Thermogravimetric analysis trace for $[\text{Cd}_2(1,10\text{-phen})_2(\text{LeuNDI})_2(\text{OH}_2)_2] \cdot 2\text{H}_2\text{O} \cdot \text{DMF}, 1 \cdot \text{DMF} \cdot 2\text{H}_2\text{O}$

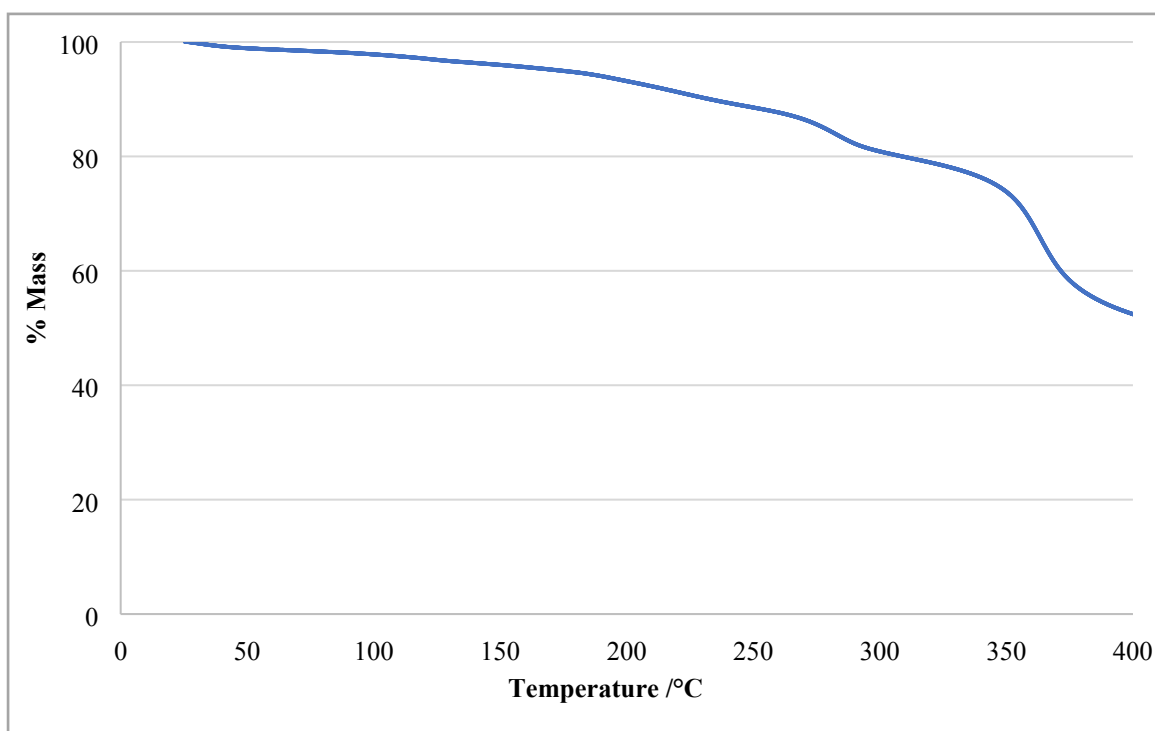


Figure S10: The thermogravimetric analysis trace for $[\text{Cd}_2(\text{LeuNDI})_2(2,2'\text{-bipy})_2(\text{OH}_2)_2]_2 \cdot 2\text{DMF} \cdot 5\text{H}_2\text{O}$

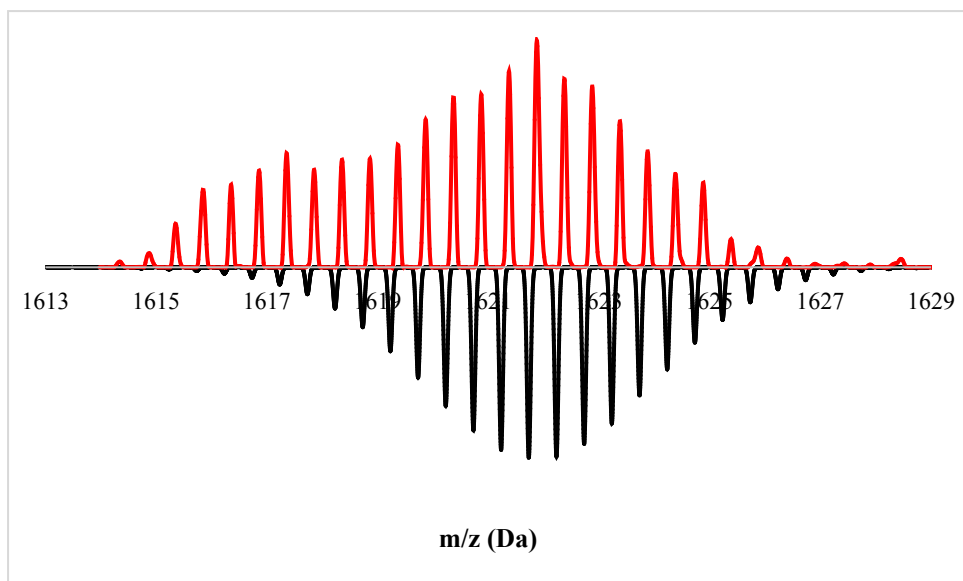


Figure S15: Magnified section of the mass spectrum of **2** showing the signal corresponding to the catenane $[\mathbf{2}_2(\text{CHCl}_3)(\text{CH}_3\text{COOH})+2\text{H}]^{2+}$, calculated 1621.73 (black), measured 1621.88 (red).

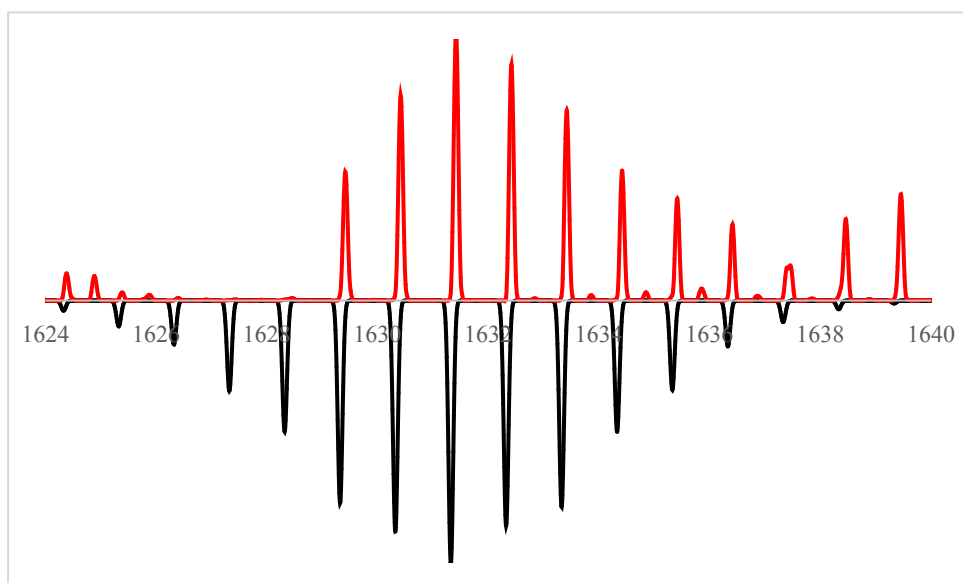


Figure S16: Magnified section of the mass spectrum of **2** showing the signal corresponding to $[\text{Cd}_2(2,2'\text{-bipy})_2(\text{LeuNDI})_2(\text{H}_2\text{O})_6 + \text{H}]^+$, calculated 1631.2480 (black), measured 1631.4279 (red).

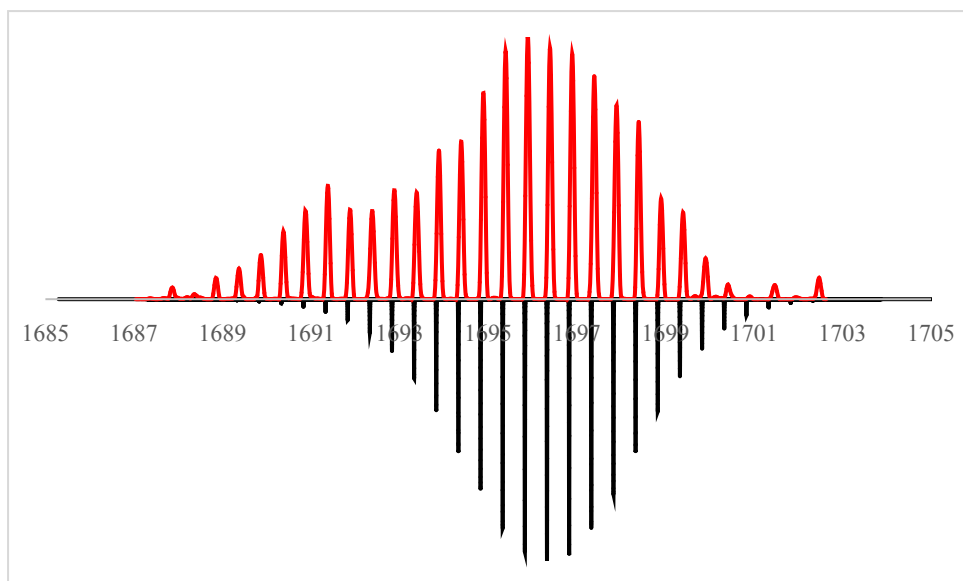


Figure S17: Magnified section of the mass spectrum of **2** showing the signal corresponding to $[2_2(\text{DMF})_2(\text{CH}_3\text{COOH})_2+2\text{Na}]^{2+}$, calculated 1695.8256 (black), measured 1695.8896 (red).

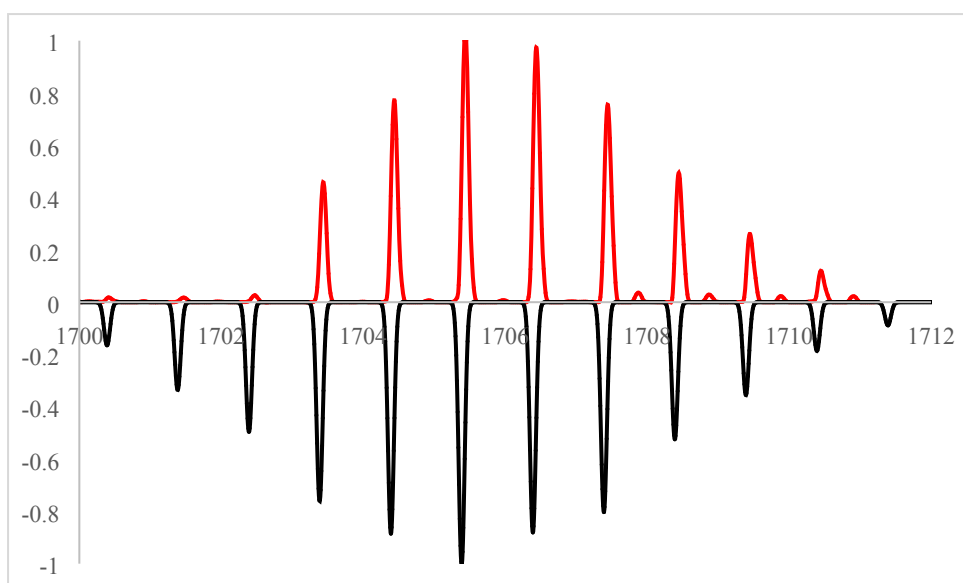


Figure S18: Magnified section of the mass spectrum of **2** showing the signal corresponding to $[\text{Cd}_2(2,2'\text{-bipy})_2(\text{LeuNDI})_2(\text{DMF})_2(\text{H}_2\text{O})(\text{H}_3\text{O})]^{+}$, calculated 1705.3747 (black), measured 1705.4247 (red).

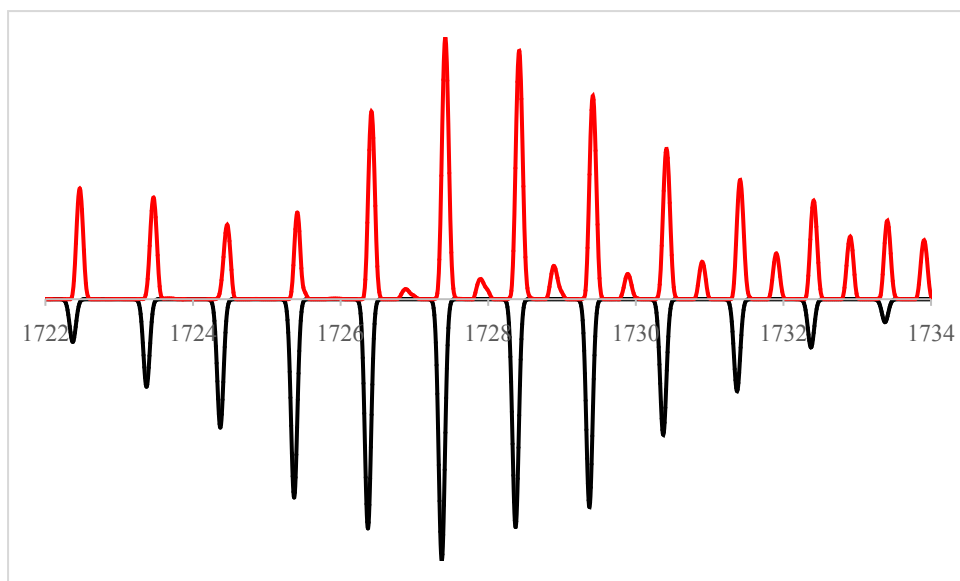


Figure S19: Magnified section of the mass spectrum of **2** showing the signal corresponding to $[\text{Cd}_2(2,2'\text{-bipy})_2(\text{LeuNDI})_2(\text{DMF})_2(\text{H}_2\text{O})_2+\text{Na}]^+$, calculated 1727.3565 (black), measured 1727.4187 (red).

11. References

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