ESI

Hierarchical lanthanide based self-assembly complexes that undergo reversible luminescent response to both temperature changes and chemical reactions within competitive media

Tumpa Gorai,*[a,d] June I Lovitt,[a,b] Brendan Twamley,[a] Ena T Luis,[a] and Thorfinnur Gunnlaugsson*[a,b,c]

[a]School of Chemistry and Trinity Biomedical Sciences Institute (TBSI), Trinity College Dublin, The University of Dublin, Dublin 2, Ireland. E-mail: gunnlaut@tcd.ie

[b]Advanced Materials and BioEngineering Research (AMBER) Centre, Trinity College Dublin, The University of Dublin, Dublin 2, Ireland.

[c]Synthesis and Solid State Pharmaceutical Centre (SSPC), Ireland

[d]Present address: Department of Polymers and Functional Materials, CSIR-Indian Institute of Chemical Technology, Hyderabad 500007, India

Contents

1 Materials and methods

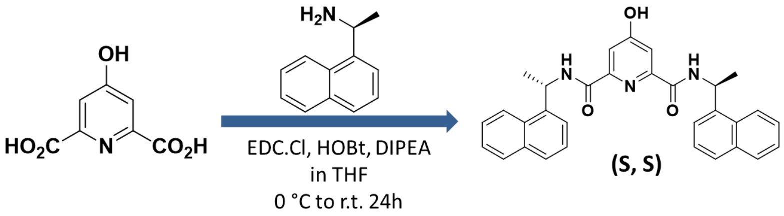
(S)-(+)-1-(1-Naphthyl)ethylamine and chelidamic acid monohydrate were purchased from TCI Europe. N,N-Diisopropylethylamine (DIPEA), 1-hydroxybenzotriazole hydrate (HOBt), N-(3-dimethylaminopropyl)-N′-ethylcarbodiimide hydrochloride (EDC.HCl) were purchased from Sigma Aldrich. Spectroscopic and HPLC grade solvents were used for all measurements. Water purified in Millipore Milli Q water purification system was used for all experiments. NMR spectra were recorded in a Bruker Spectrospin DPX-400 instrument operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C NMR or a Bruker AV-600 instrument operating at 600 MHz for ^{1}H NMR and 150 MHz for ^{13}C NMR. IR spectra were recorded in a PerkinElmer Spectrum One FTIR spectrometer within 4000-650 cm^{-1} range and mass spectra were recorded in Micro mass time of flight mass spectrometer (tof), interfaced to a waters 2690 HPLC. Exeter Analytical CE440 elemental analyser was used for elemental analysis at the microanalysis laboratory at School of Chemistry and Chemical Biology, University College Dublin. Absorption spectra were recorded in Cary 60 UV-Vis with 1 cm path length quartz cuvette. Emission spectra and lifetime were recorded in Cary eclipse fluorescence spectrophotometer with 1 cm path length quartz cuvette. Scanning Electron Microscopy (SEM) imaging was done on Carl Zeiss Ultra SEM. The samples were coated with a thin layer of gold-palladium using a sputtering procedure. Diffraction data were collected using a Bruker D8 Quest ECO instrument using graphite-monochromated Mo Kα (λ = 0.71073 Å) radiation.

2 Experimental for X-Ray Crystallography

Diffraction data were collected in a Bruker Apex Kappa Duo Imus CuKa instrument using microfocus Cu Kα (1.5405 Å) radiation as specified. Datasets were collected using ω and ϕ scans with the samples immersed in oil and maintained at a constant temperature of 100 K using a Cobra cryostream. The reflection data were reduced and processed using the Bruker APEX-3 suite of programs.[2a] Multi-scan absorption corrections were applied using SADABS.[2b, 2c] The diffraction data was solved using direct methods with SHELXT and refined by full matrix least-squares procedures with SHELXL-2015 within the OLEX-2 GUI.[2d-2g] All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon-bound hydrogen atoms were placed in calculated positions and refined with a riding model, with isotropic displacement parameters equal to either 1.2 or 1.5 times the isotropic equivalent of their carrier atoms. Where appropriate, the positions of the hydrogen atoms involved in hydrogen bonding interactions were refined to provide the best fit for the residual Fourier peaks and assigned a Uiso value equal to 1.5 times that of the nearest associated atom, with the appreciation that the exact positions of these atoms cannot be meaningfully inferred from X-ray diffraction data. Specific refinement strategies are outlined in the combined crystallographic information file. **CCDC 2427466-2427468**.

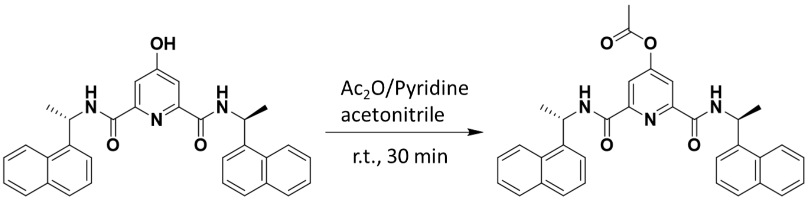
3 Synthetic scheme

3.1 Synthesis of 1-DPA (4-hydroxy-N^2,N^6-bis((S)-1-(naphthalen-1-yl)ethyl)pyridine-2,6-dicarboxamide) derivative



Scheme S 1: Synthesis of 1-DPA

3.2 Synthesis of 1-DPA-acetate (2,6-bis(((S)-1-(naphthalen-1-yl)ethyl)carbamoyl)pyridin-4-yl acetate)



Scheme S 2: Synthesis of 1-DPA acetate

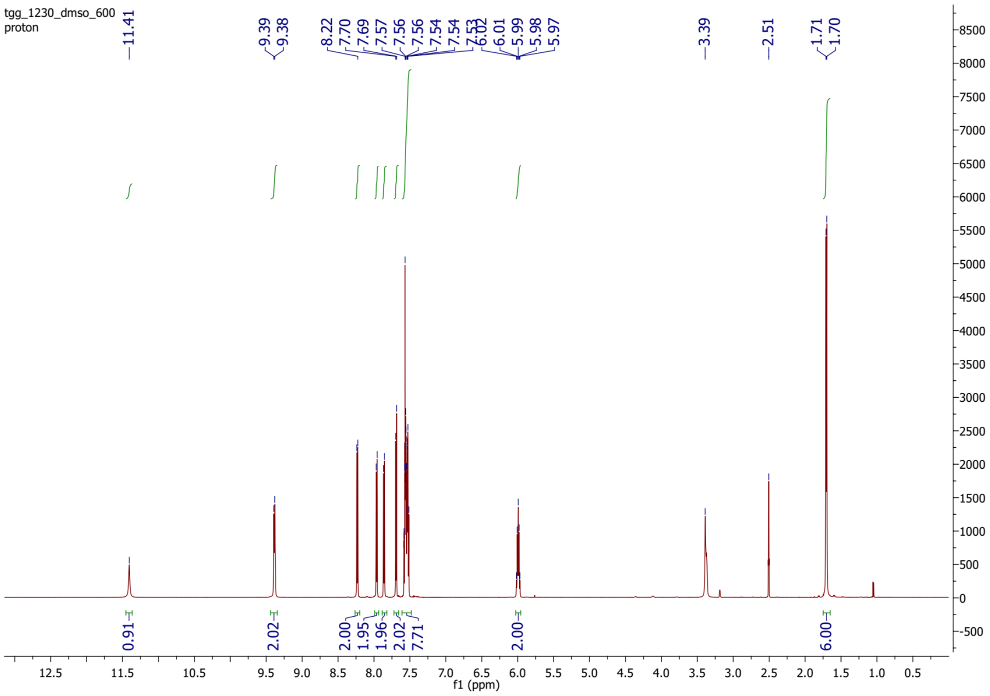


Figure S 1: ^{1}H NMR spectra of 1-DPA in DMSO-D_6 (600 MHz)

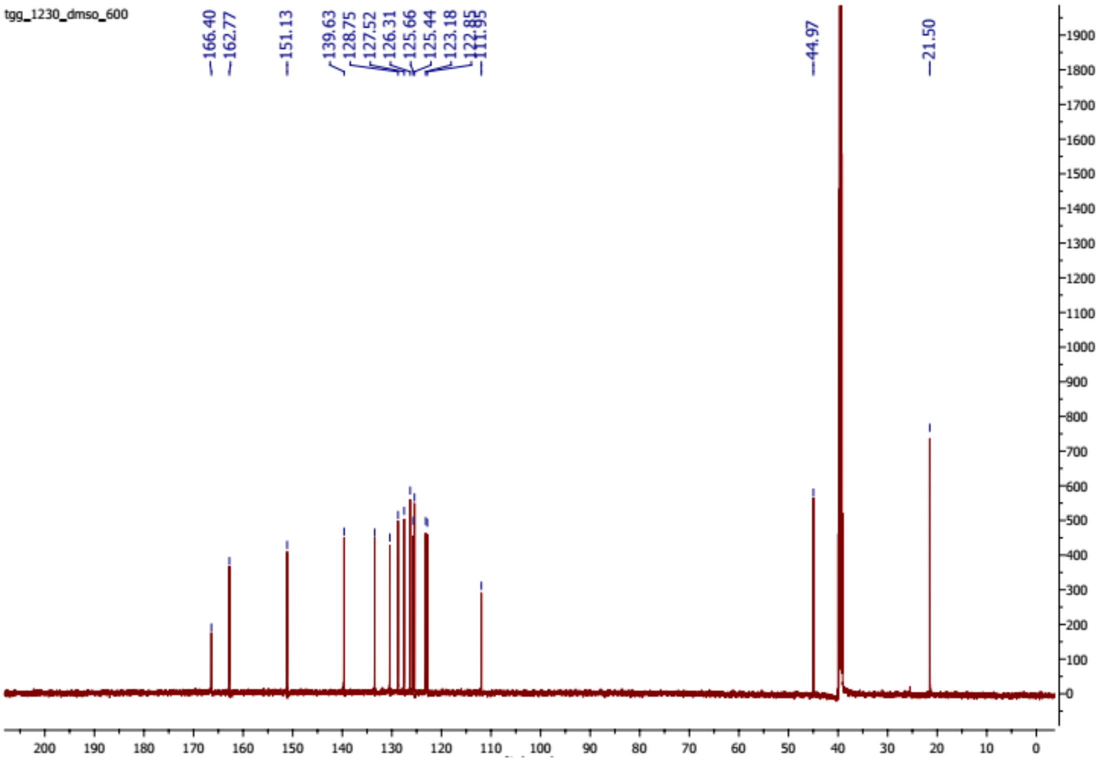
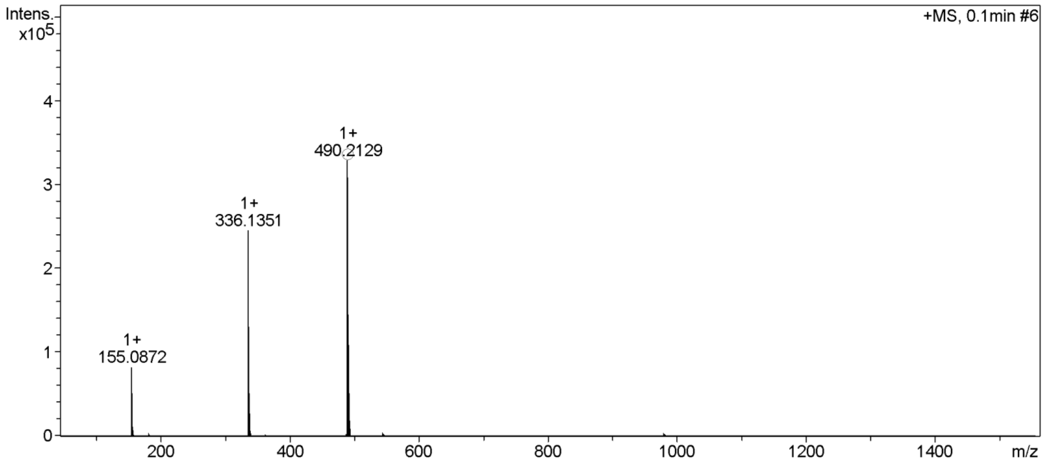


Figure S 2: ^{13}C NMR spectra of 1-DPA in DMSO-D$_6$ (600 MHz)



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
490.212919	1	C31H28N3O3	490.212518	0.4	0.8	19.5	ok	even	3.7

Figure S 3: HRMS spectrum of 1-DPA

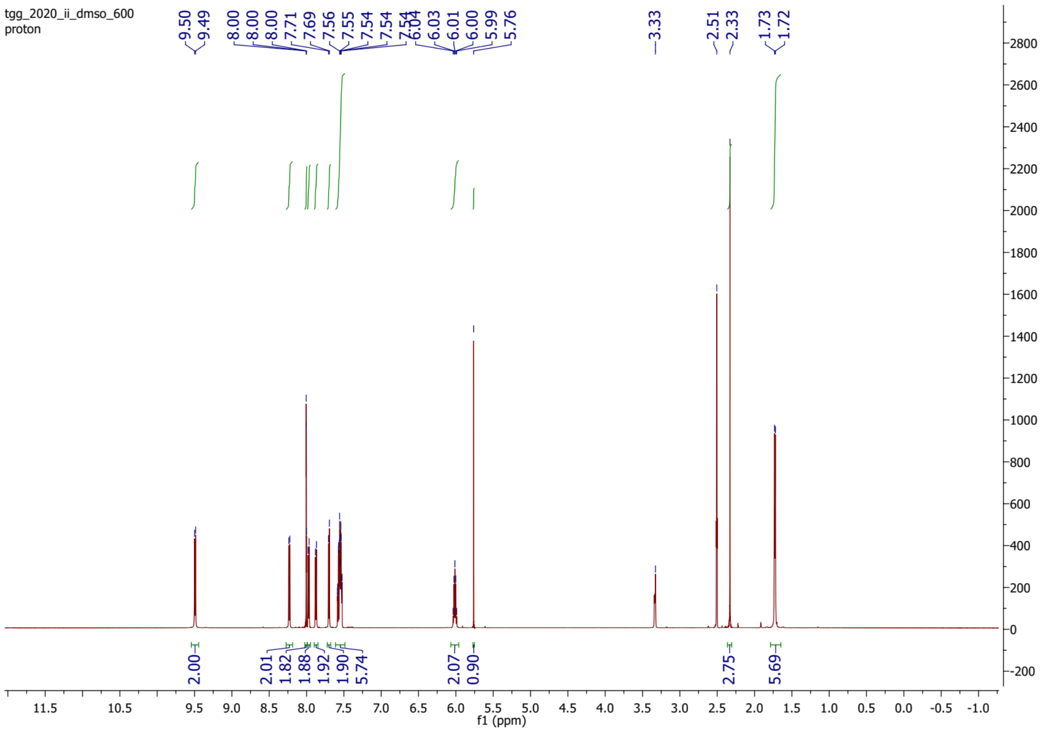


Figure S 4: ^{1}H NMR spectra of 1-DPA-acetate in DMSO-D$_6$ (600 MHz)

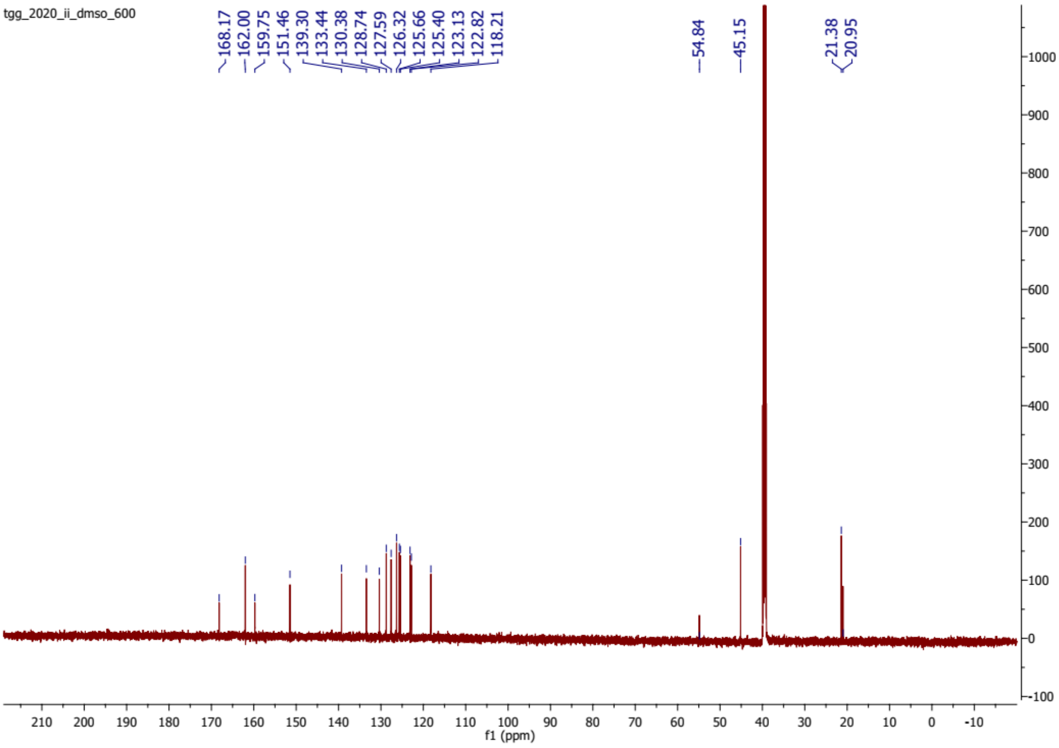
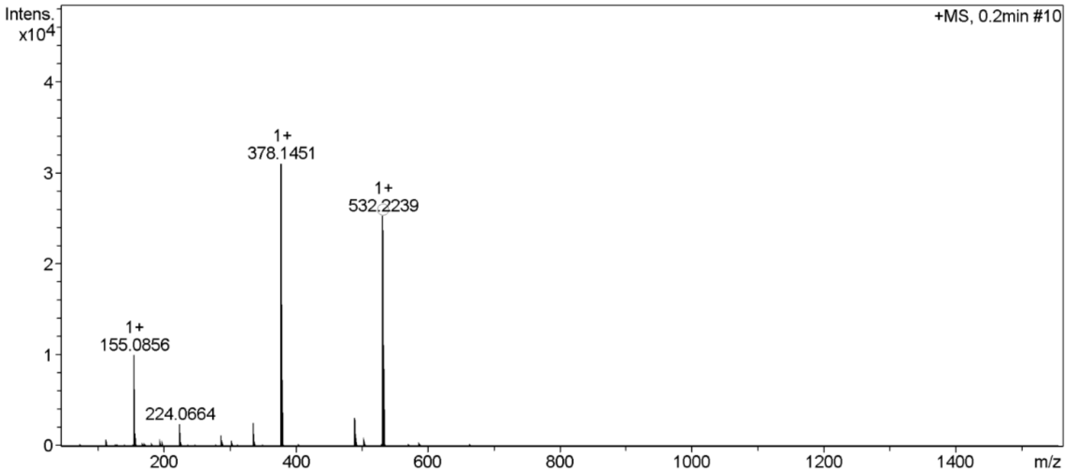


Figure S 5: ^{13}C NMR spectra of 1-DPA-acetate in DMSO-D$_6$ (600 MHz)



Meas. m/z	#	Ion Formula	m/z	err [mDa]	err [ppm]	rdb	N-Rule	e⁻ Conf	mSigma
532.223901	1	$C_{33}H_{30}N_3O_4$	532.223083	-0.8	-1.5	20.5	ok	even	8.0

Figure S 6: HRMS spectrum of 1-DPA-acetate

4 X-ray crystallography (CSD numbers 2427466-2427468)

4.1 Experimental and crystal structure of 1-DPA

The colourless crystal of $C_{66}H_{69}N_6O_8S_2$ (1-DPA) with approximate dimensions of 0.13 × 0.06 × 0.05 was grown from a 50% dimethyl sulfoxide (DMSO)-water solution. The data was solved and refined in the $P2_12_12_1$ space group with 2 distinct molecules within the asymmetric unit as well as two fully occupied DMSO molecules as illustrated in Figure S7.

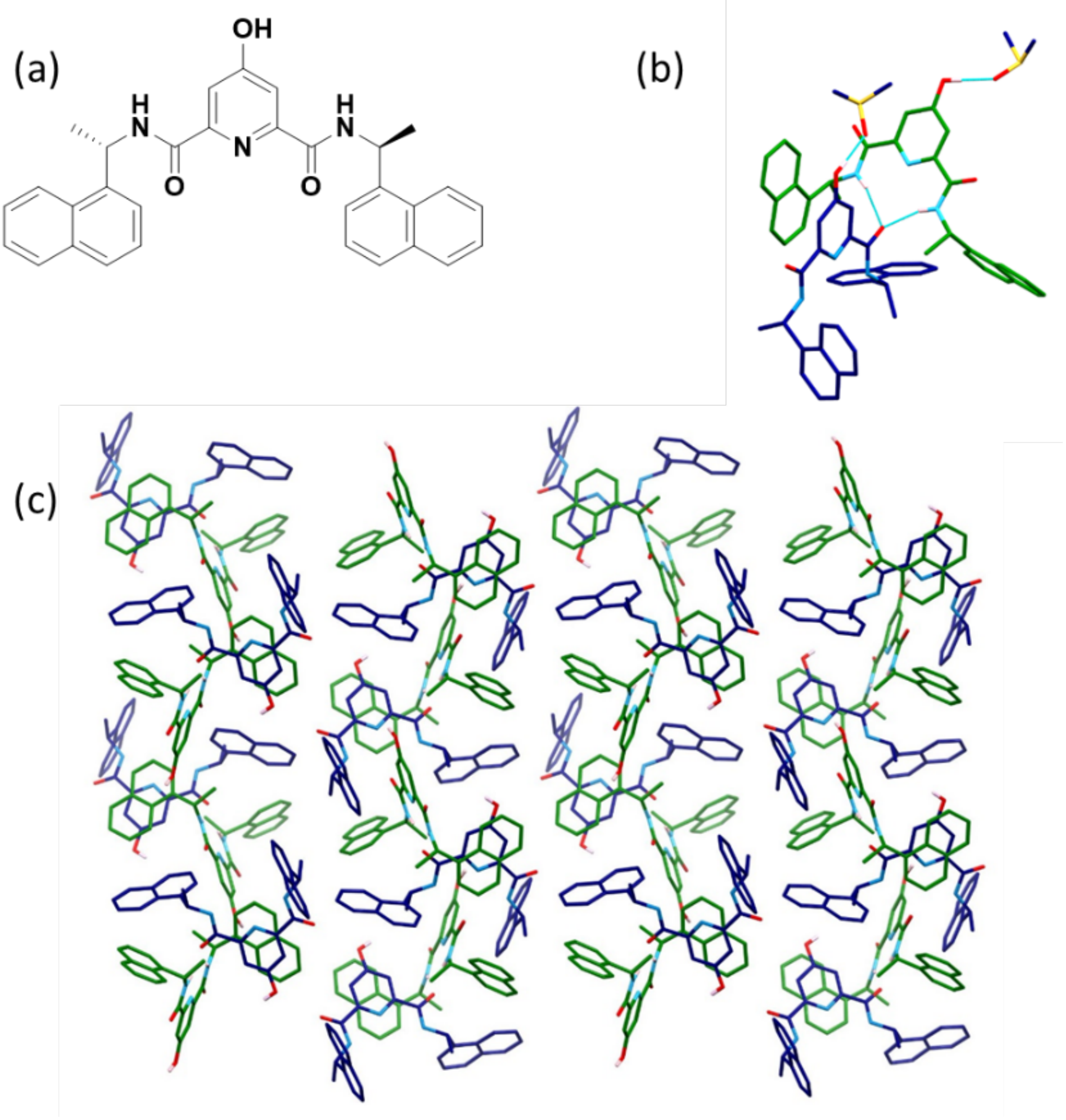


Figure S 7: (a) 1-DPA ligand, (b) unit cell structure, (c) extended structure of 1-DPA ligand, 1-DPA ligand in each asymmetric unit are colored green and blue for clarity.

4.2 Experimental and crystal structure of 1-DPA-acetate

Colourless plates of $[2(C_{33}H_{29}N_3O_4)\cdot 0.7(CH_2Cl_2)]$ were grown by slow evaporation of a solution of the ligand in dichloromethane. The crystal with dimensions of 0.326 × 0.086 × 0.028 mm was coated in NVH immersion oil, mounted on a MicroMount (MiTeGen, USA) and maintained at a constant temperature of 100 K using a Cobra cryostream. The asymmetric unit contains two independent ligand molecules and disordered solvent, modelled as a dichloromethane molecule at 0.7 occupancy and an acetonitrile molecule at 0.3 occupancy as illustrated in Figure S8.

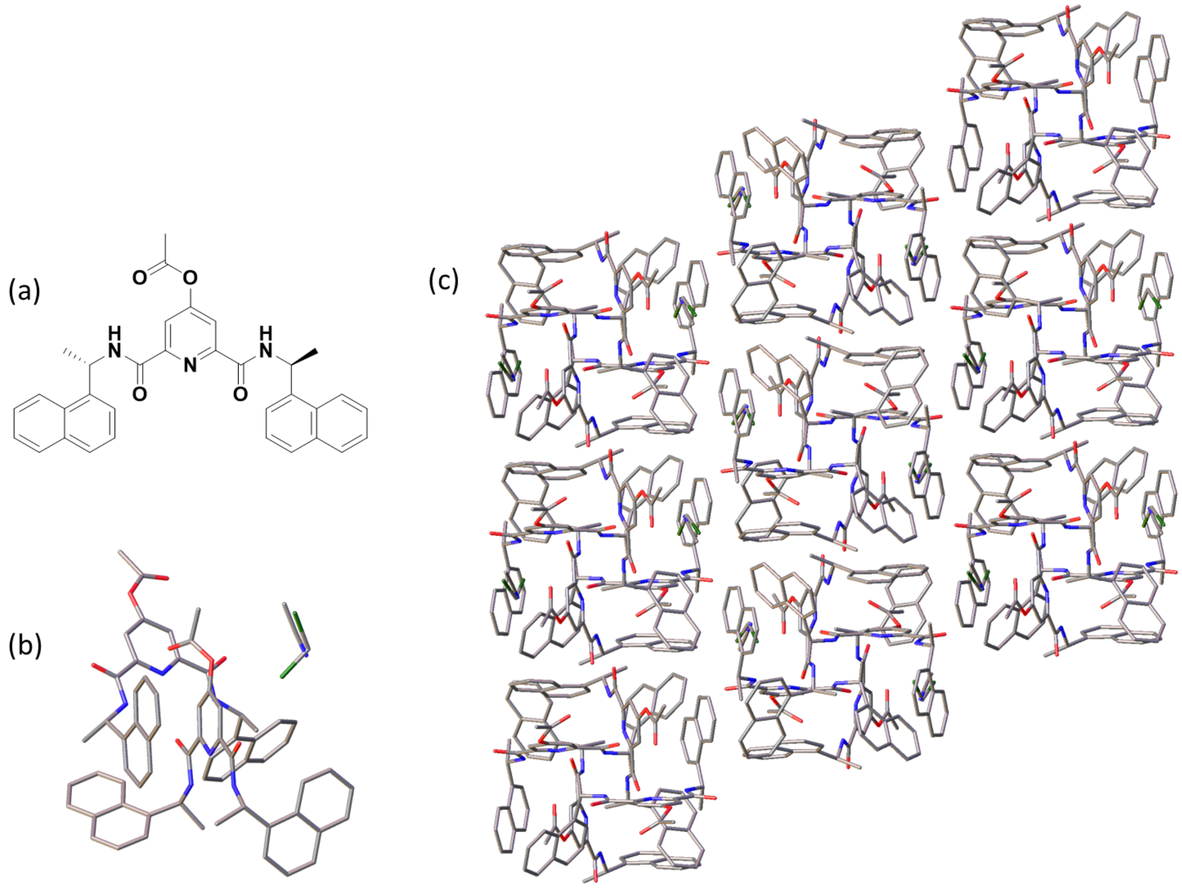


Figure S 8: (a) 1-DPA-acetate ligand, (b) unit cell structure, (c) extended structure of 1-DPA acetate ligand.

4.3 Experimental and crystal structure of Eu^{3+}-1-DPA complex

Eu(1-DPA)$_3$(ClO$_4$)$_3$ complex was synthesized by microwave reaction of 1-DPA ligand with Eu(ClO$_4$)$_3$ in methanol at 70 °C for 10 minutes following earlier reports.[1b, 1d] The crystals ($C_{94}H_{85}Cl_3EuN_9O_{22}$) were grown by slow diffusion of diethyl ether into a saturated methanol solution of Eu(1-DPA)$_3$(ClO$_4$)$_3$ complex. A specimen of $C_{94}H_{85}Cl_3EuN_9O_{22}$, approximate dimensions 0.072 mm x 0.133 mm x 0.207 mm, was used for the X-ray crystallographic analysis. A colourless, block-shaped crystal was mounted on a MiTeGen micromount with NVH immersion oil. Data for tcd1909c2 were collected from a shock-cooled single crystal at 100(2) K on an APEX2 Duo (Bruker AXS, Karlsruhe, Germany) Kappa diffractometer with a microfocus sealed X-ray tube using a mirror optics as monochromator and an APEX2 detector. The diffractometer was equipped with a Cobra (Oxford Cryosystems Ltd, Oxford, UK) low temperature device and used Cu Kα radiation (λ = 1.54178 Å). All data were integrated with SAINT v8.38B and a multi-scan absorption correction using SADABS 2016/2 was applied.[2h,2i] The structure was solved by dual methods with SHELXT v2018/2 and refined by full-matrix least-squares methods against F^2 using SHELXL v2019/3.[2d,2e] All non-hydrogen atoms were refined with anisotropic displacement parameters. All C-bound hydrogen atoms were refined isotropic on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and displacement parameter restraints. Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre.[2j] CCDC 2427467 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/structures. This report was generated using FinalCif.[2k]

Refinement details for tcd1909c2

Metrically orthorhombic but solved and refined as a pseudo-merohedral twin in the monolinic S.G. C2 with a refined twin ratio of 0.492(7). One naphthalene/methyl naphthalene moiety per half complex was disordered and modelled over two locations using a rigid model with geometric (DFIX, SADI, DANG, RIGU) and displacement (SIMU) restraints and constraints (EADP). Eu1 complex, C26-C37, 36:64% and Eu2 complex, C85-C94, 69:31% occupied. Donor hydrogens were not located but added geometrically and refined using a riding model.

Anions - there is a total of 4 unique perchlorate sites in the asymmetric unit. Two perchlorates (Cl1, Cl4) are half occupied and modelled with rigid groups. The other two sites are fully occupied and disordered over two locations with occupancies Cl2, 50:50% and Cl3 75:25% occupied and modelled as rigid groups with restraints (RIGU, SIMU, ISOR) and constraints (EADP).

The Olex2 mask routine was used to remove the diffraction component of the disordered MeOH solvent, a solvent mask was calculated and 692 electrons were found in a volume of 2390Å^3 in 1 void per unit cell. This is consistent with the presence of 10 [CH4O] per Asymmetric Unit which accounts for 720 electrons per unit cell. The chirality of the enantiopure complexes was confirmed as by the Flack parameter 0.004(7). The model has chirality at C11:S, C26B:S, C46:S, C68:S, C83:S, C103:S.

The unit cell determination gives two unique cells, a small cell, of 13.18, 22.29, 19.22 Angstroms, beta = 110.03 degrees, and a larger cell 13.17, 36.09, 22.27, with beta approx. 90 degrees. Using the smaller cell, a solution/refinement can be found in P2(1), using a solvent mask, with R1 = 9.39% and refined as an inversion twin to determine the Flack parameter (0.056(7)). The larger cell can be either Orthorhombic C or lower symmetry Monoclinic C. Solution and refinement in either of these yields a structure in C222(1), R1 = 9.04%, a very unusual space group, and C2, R1 = 7.42%, (as a pseudomerohedral twin) respectively, both using a solvent mask. The latter structure is presented here as the optimal solution/refinement. See Figure 1 in main manuscript and below where the space filling is also shown Figure S9.

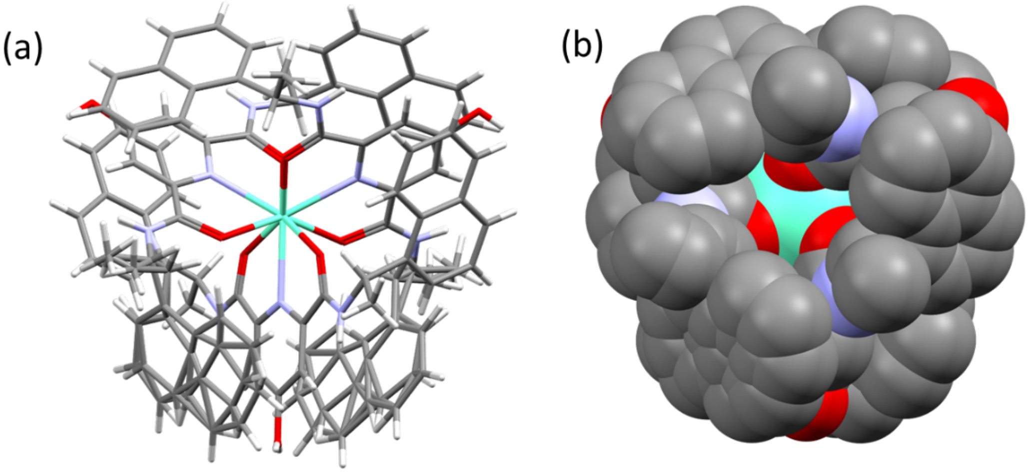


Figure S 9: (a) Eu^{3+}-1-DPA complex, (b) and the space filled model showing the Eu(III) ion fully engulfed by the three ligands. Viewed down the crystallographic b axe.

4.4 Table S 1: Crystal data and structure refinement for 1-DPA (JIL117).

Identification code	JIL117
Empirical formula	$C_{66}H_{69}N_6O_8S_2$
Formula weight	1138.39
Temperature/K	100.0
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	13.2792(4)
b/Å	16.8732(6)
c/Å	26.4228(8)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5920.4(3)
Z	4
ρ_{calc}g/cm^3	1.277
μ/mm^{-1}	1.310
F(000)	2412.0
Crystal size/mm^3	0.13 × 0.06 × 0.05
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.214 to 125.472
Index ranges	$-15 \le h \le 15$, $-19 \le k \le 18$, $-30 \le l \le 30$
Reflections collected	106332
Independent reflections	9355 [R_{int} = 0.1631, R_{sigma} = 0.0695]
Completeness to theta = 67.679°	98.41%
Absorption correction	Multi-scan
Max. and min. transmission	0.7522 and 0.6174
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9355/2/752
Goodness-of-fit on F^2	1.034
Final R indexes [I>=2σ (I)]	R_1 = 0.0582, wR_2 = 0.1432
Final R indexes [all data]	R_1 = 0.0819, wR_2 = 0.1566
Largest diff. peak/hole / e Å^{-3}	0.28/-0.25
Flack parameter	0.017(16)

4.5 Table S 2: Crystal data and structure refinement for 1-DPA acetate (etl146).

Identification code	etl146
Empirical formula	$C_{33.65}H_{30.15}Cl_{0.7}N_{3.15}O_4$
Formula weight	567.47
Temperature / K	100.01
Wavelength / Å	1.54178
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Unit cell dimensions / Å	a = 12.173(2)
	b = 17.814(3)
	c = 25.973(5)
α / °	90
β / °	90
γ / °	90
Volume / Å^3	5632.3(18)
Z	8
Density (calculated) / g/cm^3	1.338
Absorption coefficient / mm^{-1}	1.303
F(000)	2384.0
Crystal size / mm^3	0.326 × 0.086 × 0.028
Theta range for data collection / °	3.008 to 70.065
Index ranges	$-14 \le h \le 14$, $-21 \le k \le 21$, $-31 \le l \le 31$
Reflections collected	139091
Independent reflections	10631 [R_{int} = 0.0647, R_{sigma} = 0.0264]
Completeness to theta = 67.679°	99.9%
Absorption correction	Multi-scan
Max. and min. transmission	0.7533 and 0.6397
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	10631/38/798
Goodness-of-fit on F^2	1.048
Final R indices [$I>2\sigma(I)$]	R_1 = 0.0341, wR_2 = 0.0864
R indices (all data)	R_1 = 0.0369, wR_2 = 0.0882
Absolute structure parameter	0.014(5)
Largest diff. peak and hole / e.Å^{-3}	0.14 and -0.29

4.6 Table S 3. Crystal data and structure refinement for Eu^{3+}-1-DPA complex (tcd1909c2).

Identification code	tcd1909c2
Empirical formula	$C_{103}H_{121}Cl_3EuN_9O_{31}$
Formula weight	2239.39
Temperature	100(2) K
Wavelength	1.54178 Å
Crystal system	monoclinic
Space group	C2 (5)
Unit cell dimensions	a = 13.1792(5) Å
	b = 36.1412(14) Å
	c = 22.3025(8) Å
α	90 °
β	89.9907(19) °
γ	90 °
Volume	10623.0(7) Å^3
Z	4
Density (calculated)	1.400 Mg/m^3
Absorption coefficient	5.612 mm^{-1}
F(000)	4656
Crystal size	0.207 x 0.133 x 0.072 mm^3
Theta range for data collection	3.96 to 137.16 (0.83 Å)
Index ranges	$-15 \le h \le 15$, $-43 \le k \le 43$, $-26 \le l \le 26$
Reflections collected	77019
Independent reflections	19420, R_{int} = 0.0730, R_{sigma} = 0.0629
Completeness to theta = 67.679°	100.0 %
Absorption correction	multi-scan
Max. and min. transmission	0.7531 and 0.5482
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	19420 / 2842 / 1168
Goodness-of-fit on F^2	1.045
Final R indices [$I \geq 2\sigma(I)$]	R1 = 0.0742, wR2 = 0.1976
R indices (all data)	R1 = 0.1116, wR2 = 0.2313
Absolute structure parameter	0.004(7)
Largest diff. peak and hole	0.38 and −0.63 e.Å^{-3}

5 Serial dilution experiment for 1-DPA ligand in 50% H_2O/EtOH

To understand the self-assembly property of **1-DPA** in solution a serial dilution experiment was carried out. With increasing concentration, the absorption increases at 280 nm and 320 nm, respectively (Figure S10).

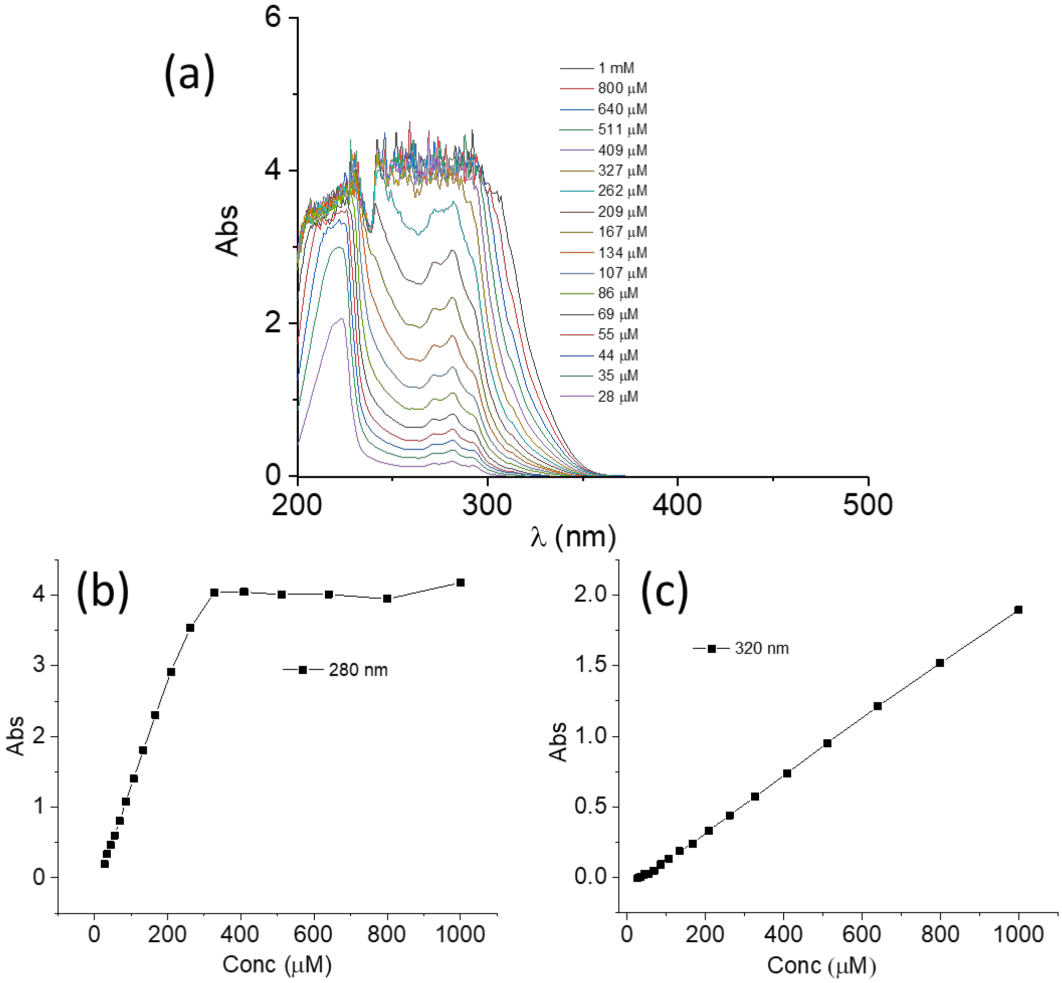


Figure S 10:(a) UV-Vis absorption spectra recorded for 1-DPA (1 mM) solution on serial dilution in 50% H_2O/EtOH, (b) absorption at 280 nm and (c) absorption at 320 nm plotted with increasing concentration (28-1000 μM).

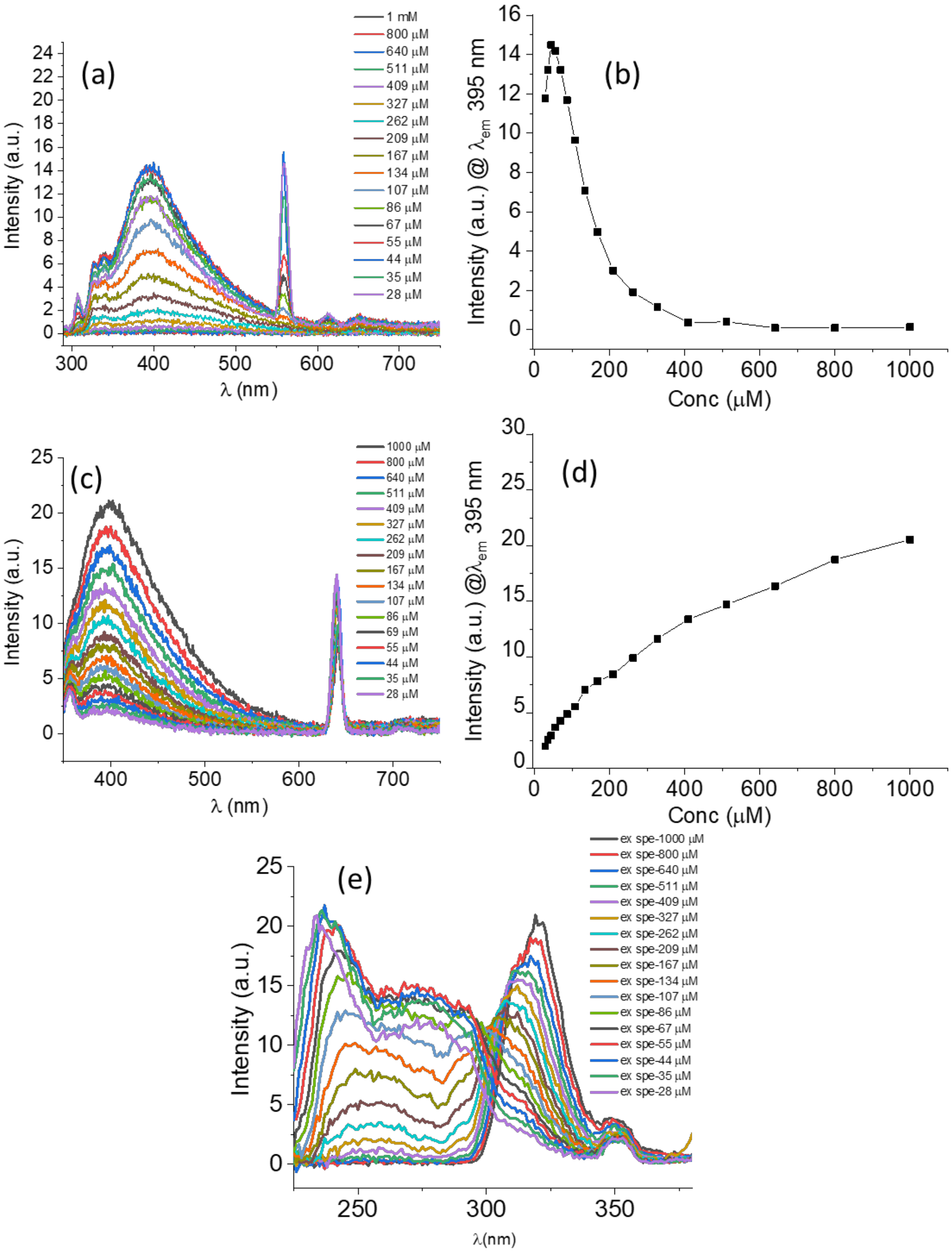


Figure S 11: (a) The emission spectra of 1-DPA in 50% H_2O*/EtOH on* λ_{ex} *280 nm and (b) Emission at 395 nm on* λ_{ex} *280 nm plotted with increasing concentration and (c) The emission spectra of 1-DPA on* λ_{ex} *320 nm and (b) Emission at 395 nm on* λ_{ex} *320nm, and (e) excitation spectra for emission at* λ_{em} *395 nm with varying concentration.*

6 SEM images of 1-DPA in 50% H_2O/EtOH

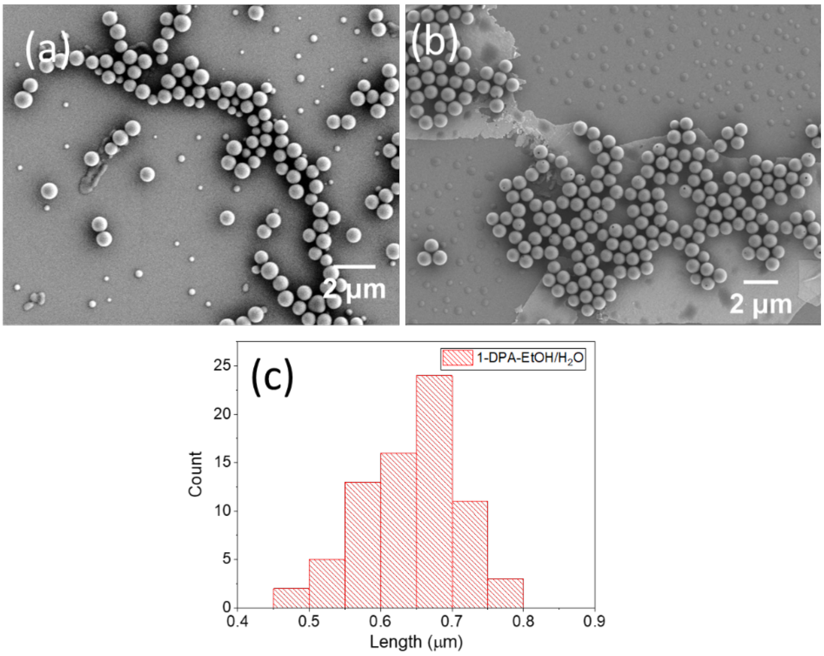


Figure S 12: (a, b) SEM images dropcasted and dried 1-DPA (1 mM) solution in 50% H_2O/EtOH, (c) histogram plot for particle size distribution of 1-DPA solution in 50% H_2O/EtOH.

7 SEM images of 1-DPA in 60% H_2O/THF

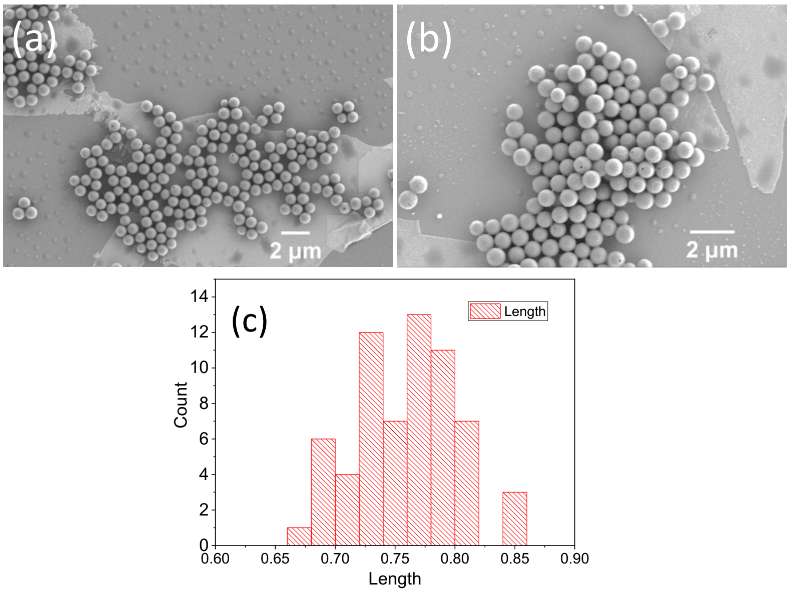


Figure S 13: (a, b) SEM images dropcasted and dried 1-DPA (1 mM) solution in 60% H_2O/THF, (c) histogram plot for particle size distribution.

8 SEM images of Eu^{3+}-1-DPA complex with increasing EuAc concentration in 50% EtOH/H_2O

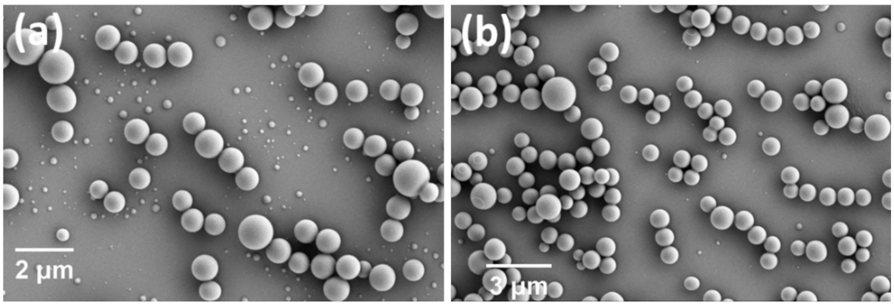


Figure S 14: SEM images of dropcasted and dried 1-DPA (1 mM)-EuAc (0.1 eq) in 50% H_2O*/EtOH*

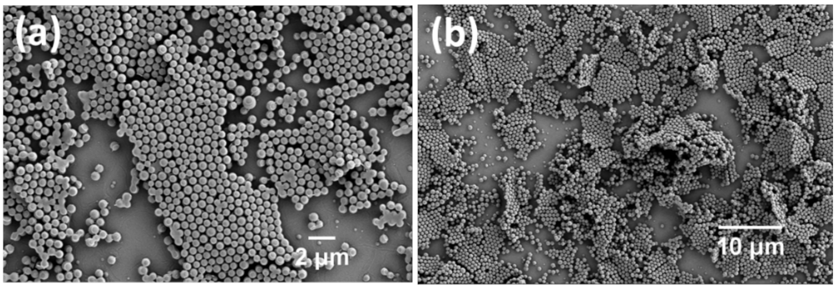


Figure S 15: SEM images of dropcasted and dried 1-DPA (1 mM)-EuAc (0.2 eq) in 50% H_2O*/EtOH*

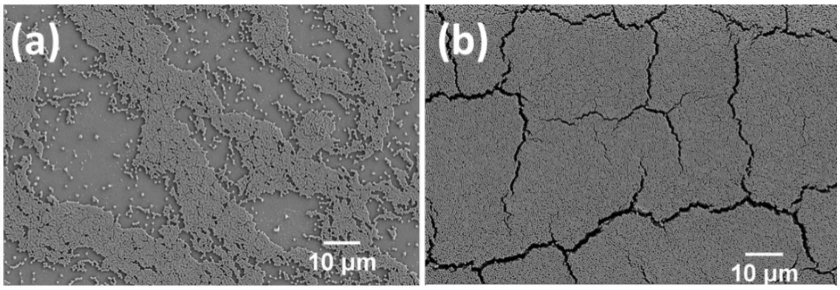


Figure S 16: SEM images of dropcasted and dried 1-DPA (1 mM)-EuAc (0.3 eq) in 50% H_2O*/EtOH*

9 UV-Vis spectra of Eu^{3+}-1-DPA complex on addition of increasing percentage of water

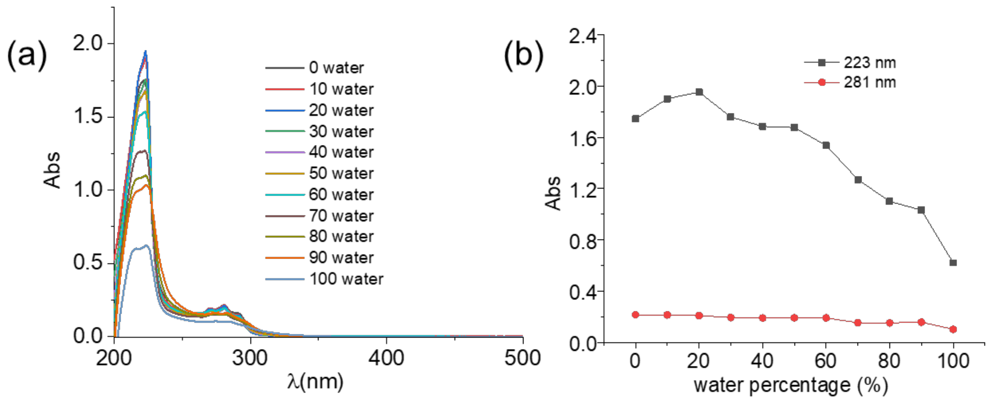


Figure S 17: (a) Absorption spectra of Eu^{3+}-DPA complex (10 µM/0.33 µM) with an increase in water percentage in H_2O/EtOH mixture, (b) Absorption at λ_{max} 223 nm, 281 nm with increasing water percentage.

10 Temperature dependent measurement for Eu^{3+}-1-DPA complex in 50% H_2O/EtOH

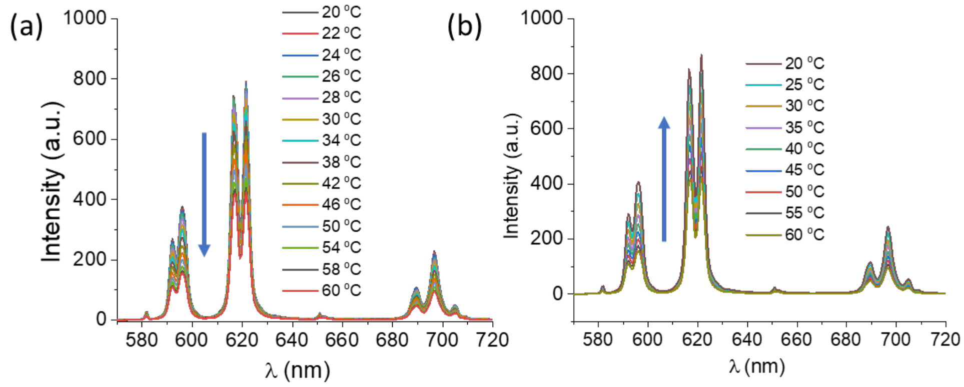


Figure S 18: Evolution of emission spectra of Eu^{3+}-1-DPA complex (1 mM/0.33 mM) for λ_{ex} 324 nm with (a) increasing temperature, and (b) with decreasing temperature.

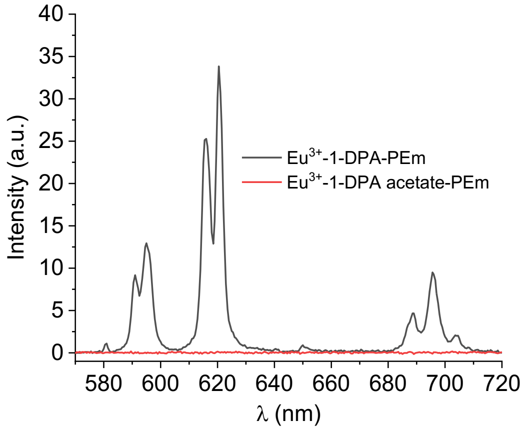


Figure S 19: Phosphorescence spectra of Eu^{3+}-1-DPA (33.3 µM /100 µM) complex and Eu^{3+}-DPA-acetate (33.3 µM /100 µM) complex in 60% H_2O/THF.

11 SEM images of Eu^{3+}-1-DPA-acetate complex in 50% H_2O/EtOH with time

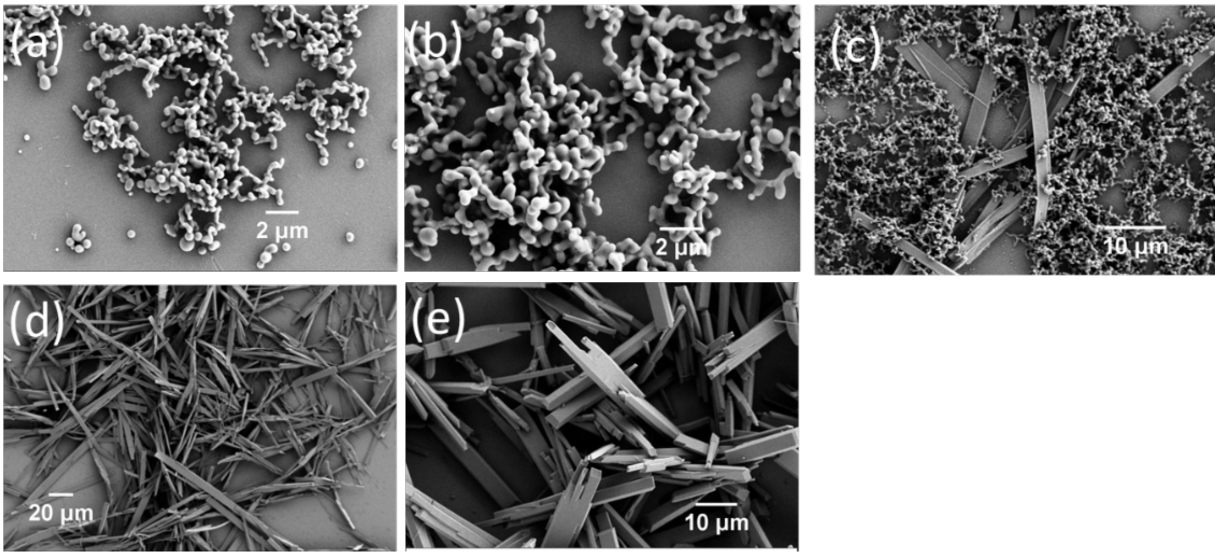


Figure S 20: SEM images of dropcasted and dried Eu^{3+}-1-DPA-acetate complex (1 mM/0.33 mM) in 50% H_2O/EtOH (a) 5 min, (b) 15 min, (c) 30 min, (d) 50 min, (e) 16h after preparation.

12 Fluorescence spectra for Eu^{3+}-1-DPA acetate complex hydrolysis reaction in 50% H_2O/EtOH

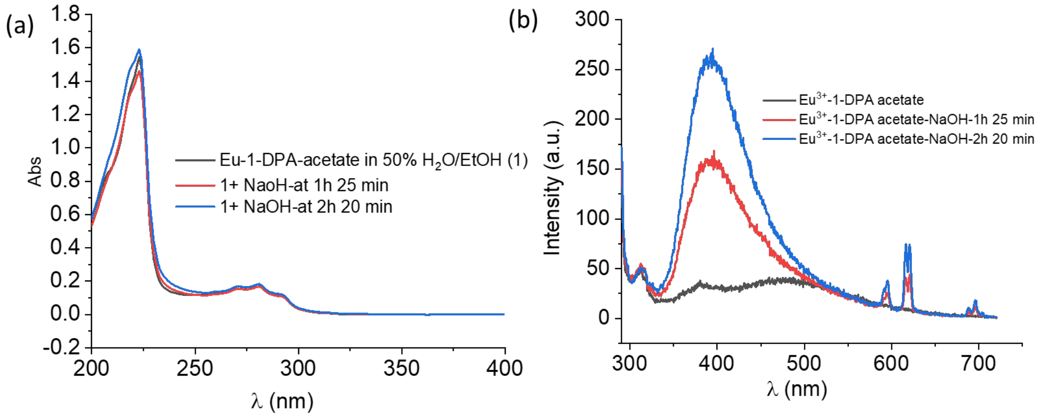


Figure S 21: (a) Change in absorption spectra of Eu^{3+}-DPA acetate (3.3 µM/10 µM) complex solution in 50% H_2O/EtOH with time after addition of NaOH. (b) Increase in (total) fluorescence emission of Eu^{3+}-DPA acetate (3.3 µM/10 µM) complex solution in 50% H_2O/EtOH with time for λ_{ex} 281 nm after addition of NaOH.

13 SEM images of Eu^{3+}-1-DPA acetate complex hydrolysis reaction product in 50% H_2O/EtOH

1-DPA acetate solution (2 mM) was prepared in ethanol, 1-DPA acetate (2.64 mL, 2 mM) was mixed with Eu acetate solution (172.6 µL, 10.09 mM) and water (2.468 mL) was added to prepare DPA-acetate (1 mM)-Eu (0.33 mM) complex suspension in 50% H_2O/EtOH. NaOH (2.56 µL, 3N) was added to the suspension and kept stirring at 50 °C for 80 min. The emission spectra were recorded with time and the sample was drop-casted for recording SEM.

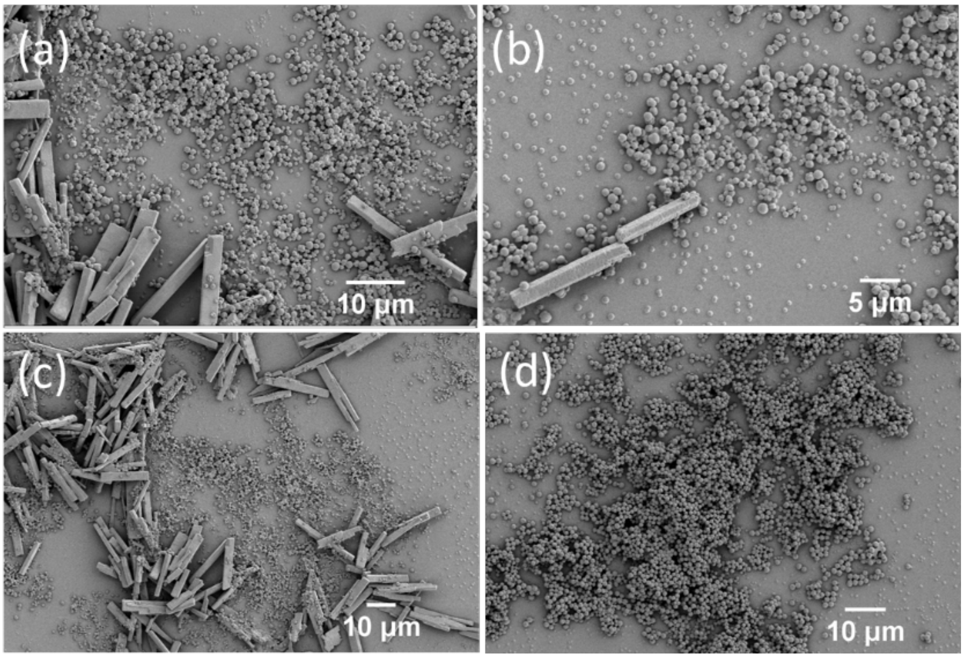


Figure S 22: SEM images of dropcasted and dried Eu^{3+}-1-DPA-acetate complex hydrolysis reaction product 80 min after the reaction.

14 Emission spectra after in situ acetylation reaction of Eu^{3+}-1-DPA complex in 50% H_2O/THF

1-DPA solution (5 mM) was prepared in THF, EuAc solution (10 mM) solution was prepared in H_2O. From stock solutions, DPA (1 mM)-Eu (0.33 mM) complex (5 mL) solution was prepared in 50% H_2O/THF. Acetic anhydride (1 µL, 2.1 eq) and pyridine (1 µL, 2.5 eq) were added and stirred at room temperature for 1h and emission spectra were recorded.

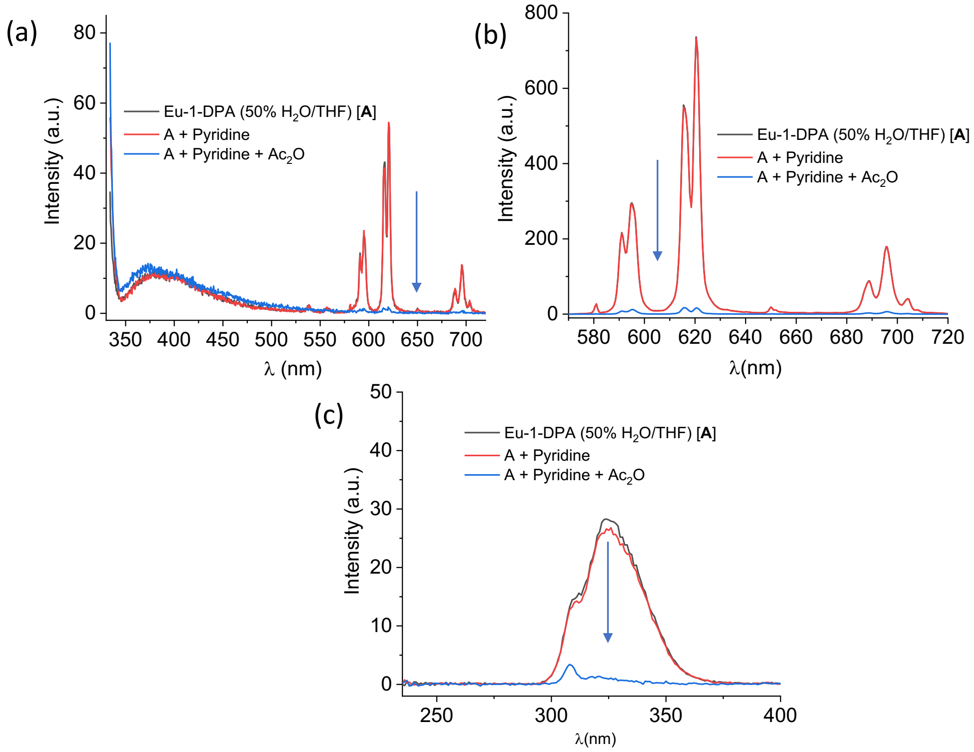


Figure S 23: (a) (Total) fluorescence emission spectra of Eu^{3+}-DPA complex (black line), after addition of pyridine (red line). and after addition of pyridine+ acetic anhydride (blue line), (b) Phosphorescence emission spectra of DPA-Eu complex (black line), after addition of pyridine (blue line), and after addition of pyridine+ acetic anhydride (red line), (c) Excitation spectra of Eu^{3+}-DPA complex (black line), after addition of pyridine (blue line), and after addition of pyridine with acetic anhydride (red line).

15 Absorption spectra after insitu acetylation reaction of Eu^{3+}-1-DPA

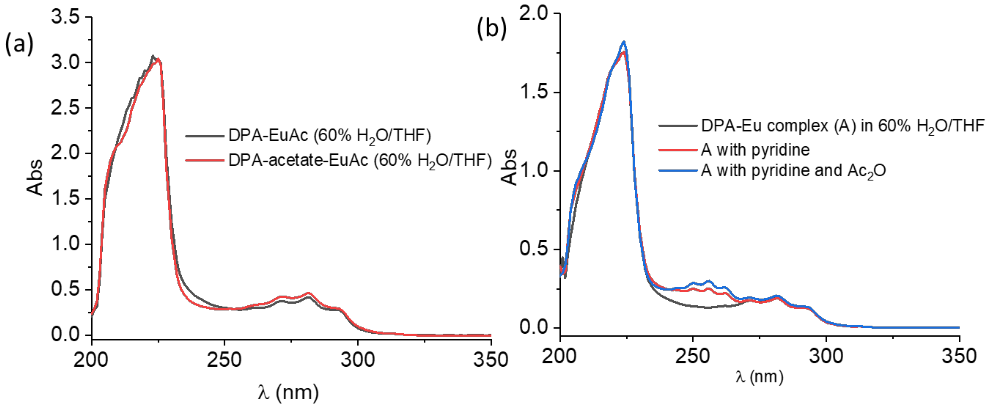


Figure S 24: (a) absorption spectra of Eu^{3+}-1-DPA (10/30 µM) complex and Eu^{3+}-1-DPA-acetate complex (10/30 µM), (b) Absorption spectra of Eu^{3+}-1-DPA (3.3 /10 µM) complex alone (black line) and with the addition of pyridine (red line), and with pyridine and acetic anhydride (blue line).

16 NMR spectra after in situ acetylation reaction of Eu^{3+}-1-DPA complex

Following the in situ acetylation reaction in 50% H_2O/THF as described in section 14, THF was removed and the reaction mixture was extracted with ethyl acetate. Following that the compound was dried and NMR and mass analysis were performed.

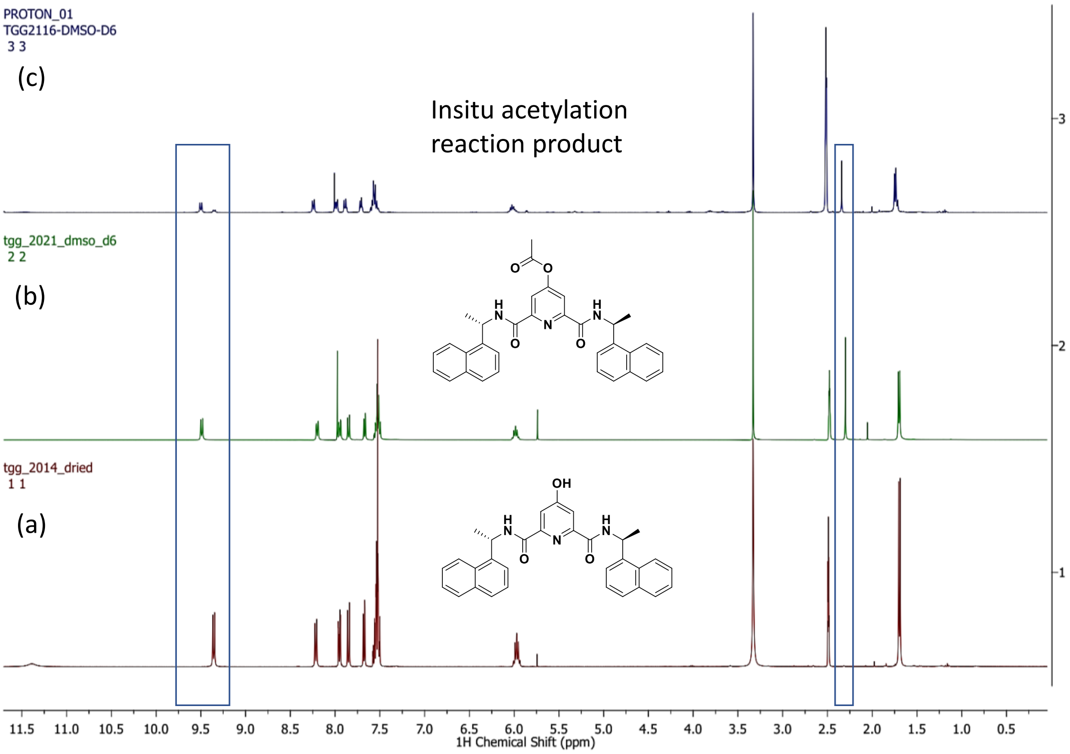


Figure S 25: NMr spectra recorded in DMSO-D$_6$ for (a) insitu acetylated product of Eu^{3+}-1-DPA complex in 50% H_2O/THF, (b) 1-DPA-acetate, (c) 1-DPA

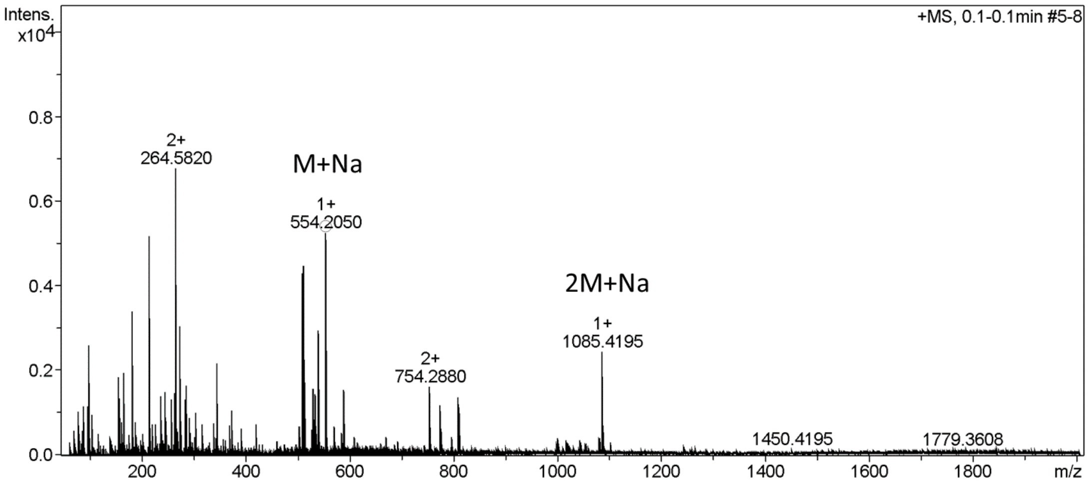


Figure S 26: HRMS of the reaction product of insitu acetylation reaction of Eu^{3+}-1-DPA complex in 50% H_2O/THF

17 Esterification and de-esterification cycle for of Eu^{3+}-1-DPA complex in 60% H_2O/THF

To Eu^{3+}-1-DPA complex solution in 60% H_2O/THF, was added pyridine (1 µL) and acetic anhydride (1 µL) under stirring condition. After 1h of the reaction, the emission spectra and lifetime were recorded. NaOH (3N, 7 uL, 4.2 eq) was added and kept stirring at room temperature for 48h, before recording emission spectra.

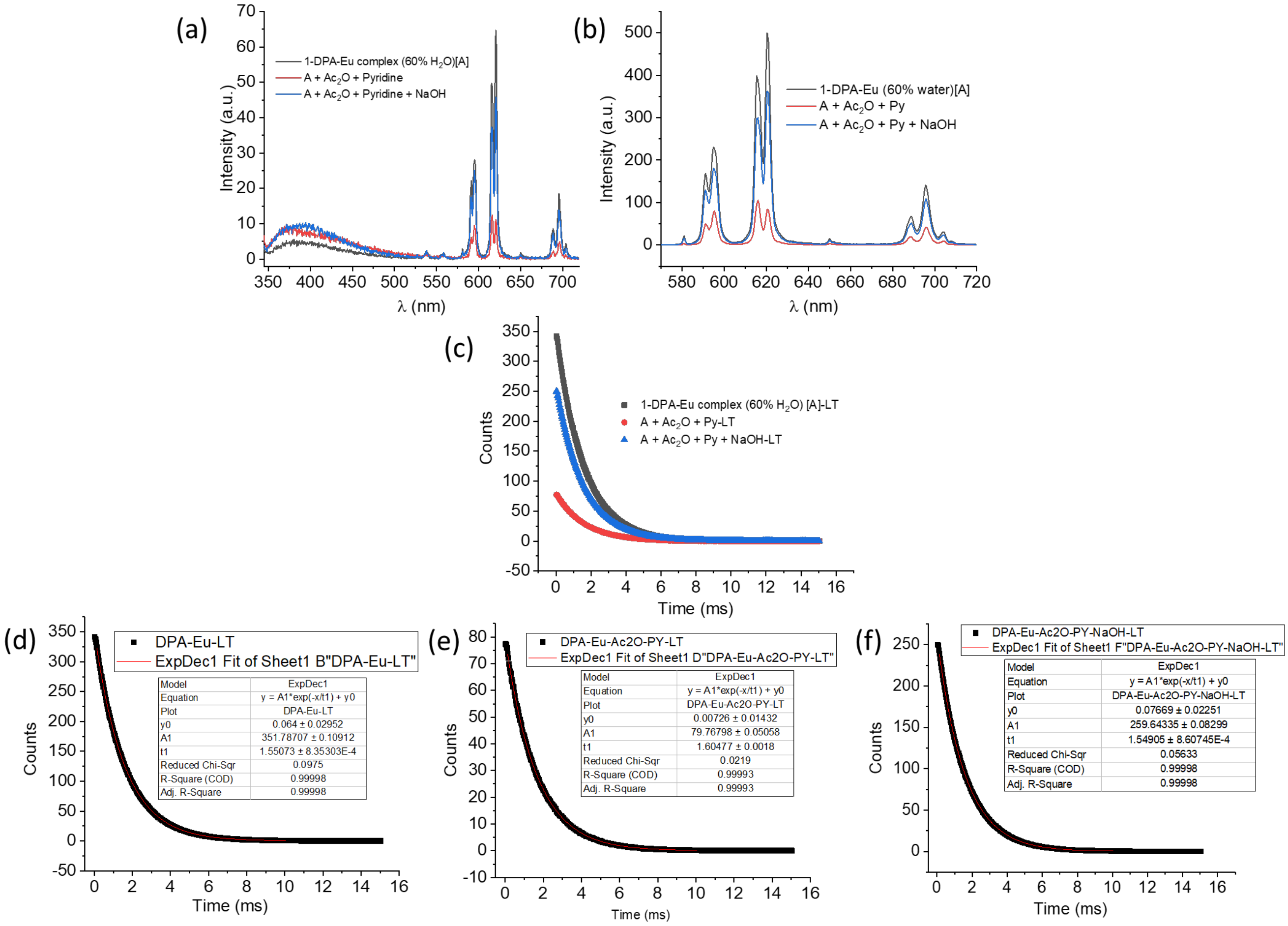


Figure S 27: (a) (Total) fluorescence emission spectra, (b) Phosphorescence emission spectra, (c) lifetime data for esterification and de-esterification cycle in 60% H_2O/THF. Fitted decay profile for (d) Eu-1-DPA complex in 60% H_2O/THF, (e) Eu-1-DPA complex on in situ esterification by Ac_2O and pyridine in 60% H_2O/THF, (f) de-esterification by NaOH in 60% H_2O/THF.

Table S 4: Luminescence lifetime for Eu-1-DPA complex at λ_{em} 616 nm (λ_{ex} 328 nm) on in situ esterification/de-esterification

Samples	τ (ms)
Eu-1-DPA complex	1.550 ± 0.0083
Eu-1-DPA + Ac_2O+Pyridine	1.6 ± 0.0018
Eu-1-DPA + Ac_2O+Pyridine+NaOH	1.549 ± 0.0086

References:

1. a) J. P. Leonard, P. Jensen, T. McCabe, J. E. O’Brien, R. D. Peacock, P. E. Kruger and T. Gunnlaugsson, *J. Am. Chem. Soc*., 2007, **129**, 10986–10987. b) O. Kotova, J. A. Kitchen, C. Lincheneau, R. D. Peacock and T. Gunnlaugsson, *Chem. - A Eur. J*., 2013, **19**, 16181–16186. C) S. J. Bradberry, A. J. Savyasachi, R. D. Peacock and T. Gunnlaugsson, *Faraday Discuss*., 2015, **185**, 413–431. d) D. F. Caffrey, T. Gorai, B. Rawson, M. Martínez-Calvo, J. A. Kitchen, N. S. Murray, O. Kotova, S. Comby, R. D. Peacock, P. Stachelek, R. Pal and T. Gunnlaugsson, *Adv. Sci.*, 2024, **11**, 2307448.
2. a) Bruker APEX-3, Bruker-AXS Inc., Madison, WI, 2016. b) SADABS, Bruker-AXS Inc., Madison, WI, 2016. c) Sheldrick, G. M. SADABS. University of Göttingen, Germany 1996, d) G. M. Sheldrick, *Acta Crystallogr. Sect. A.* 2015, **71**, 3-8. e) G. M. Sheldrick, *Acta Crystallogr. Sect. C.* 2015, **71**, 3-8. f) A. L. Spek, *Acta Crystallogr. Sect. C.*, 2015, **71**, 9-18. g) Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42* (2), 339–341. h) Bruker, SAINT, v8.38B, Bruker AXS Inc., Madison, Wisconsin, USA. i) L. Krause, R. Herbst-Irmer, G. M. Sheldrick, D. Stalke, J. Appl. Cryst. **2015**, *48*, 3–10, doi:10.1107/S1600576714022985. j) C. R. Groom, I. J. Bruno, M. P. Lightfoot, S. C. Ward, Acta Cryst. **2016**, *B72*, 171–179, doi:10.1107/S2052520616003954. k) D. Kratzert, FinalCif, V151, https://dkratzert.de/finalcif.html.