Supporting information

Naphthalimide Based Reversible Colorimetric and Luminescent Sensor for Detecting Trace water in Organic Solvent

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Material Methods:

All reagents were purchased from commercial sources and used as received without further purification.^{1}H NMR spectra were recorded on Bruker DPX-300 MHz and 400 MHz spectrometers, and chemical shifts were calibrated against TMS. UV–Vis spectra were recorded using a HITACHI UH4150 spectrophotometer. Mass spectra were obtained on a Q-TOF Micro YA263 mass spectrometer. SEM images were collected using a JEOL JSM-6700F scanning electron microscope in tapping mode.
Fluorescence spectra were recorded on a HORIBA Scientific Fluoromax-4 spectrofluorometer. RGB values were calculated using the online tool ImageColorPicker.

UV-visible spectroscopic studies:

Stock solutions of NMI-S2 (1.0 mM) were prepared in THF. An aliquot (100 µL) was transferred to a vial, and the solvent was evaporated in a water bath. The residue was then redissolved in an appropriate amount of THF or DMSO to achieve the desired solvent composition, giving a final concentration of 0.1 mM. The solutions were equilibrated at room temperature for 1 h before spectral measurements.

To prepare the 1:1 complex (NMIS2·1F), 0.1 µL of a 1.0 M TBAF solution was added to 1 mL of 0.1 mM NMI-S2 solution in THF, giving final concentrations of 0.1 mM for both NMI and TBAF. Similarly, for higher fluoride equivalents (1:5, 1:10, 1:25, and 1:50), the concentration of TBAF was adjusted accordingly while maintaining NMI S2 concentration at 0.1 mM.

For water titration studies, 50 equivalents of TBAF were added to a 0.1 mM solution of NMI-2 in THF or DMSO and equilibrated for 1 h at room temperature. Spectra were then recorded after the gradual addition of water to the NMI·50F solution.

The same procedure was followed for the BF_3 titration experiments.

Fluorescence Spectroscopic Studies:

Photoluminescence spectra were recorded using the same sample preparation and titration protocol as described for absorption measurements.

FT-IR Characterization:

At first the sample was mixed with KBr to make a pellet, then it was placed in the chamber inside the instrument and spectrum was recorded at room temperature.

Scanning Electronic Microscopy (SEM):

For SEM analysis, 20 μL of a 0.1 mM solution of NMI-S2 adducts, prepared with varying ratios of NMI and F^- (0.1 mM) and different water contents, was dropped onto a microscopic cover glass. The samples were dried in a vacuum desiccator for 48 hours before the images were taken.

Method for Calculating the Detection Limit (LOD):

The limit of detection (LOD) was determined from the linear plots—change in absorbance/emission intensity and G/R values vs wt% water—using the equation:

$$\text{LOD} = \frac{3\sigma}{m_s}$$

where **σ** is the standard deviation of the blank and $\mathbf{m_s}$ is the slope of the calibration curve. The calculated values are summarized below.

LOD Calculation Details-

Method	**THF**	**DMSO**
UV-Vis Titration	Slope= 3.09E+01, S.D=0.160309 LOD=0.015(%v/v)	slope=27.47368, S.D =0.090165 LOD= 0.0098 (%v/v)
Emission Titration	Slope=1.48E+07, S.D=57159.31 LOD=0.011(%v/v)	slope=1.57E+07, S.D=63523.49 LOD=0.012 (%v/v)
G/R Ratio Analysis	Slope=15.28032, S,D=0.051464 LOD= 0.0101(%v/v)	Slope=2.11905, S.D=0.011189 LOD= 0.0158(%v/v)

Moisture (%) Determination Using Color Palette and G/R Calibration Curve:

To prepare a 0.1 mM solution, 0.0744 mg of the compound (M.W. = 744.03 g/mol) was taken in each vial (using the dilution method and solvent evaporation) and dissolved in 1 mL of the required solvent (e.g., DMSO-d_6 or others). Subsequently, 50 equivalents of F^- were added to each solution. After addition of F^-, each solution showed a distinct color change. Photos of the solutions were taken, and color pellets and their R, G, B values were obtained using ImageColorPicker.com.

These color pellets were compared with the previously prepared reference color palette to estimate the water content. The G/R ratios were also calculated and matched with the G/R calibration curve, giving accurate water percentages. Both methods gave closely matching results, enabling detection of very small amounts of water in deuterated and other DMSO solvents.

Calculation of Water Content in Solid Samples (w/w%):

For solid samples, 150 mg of sugar or salt was weighed, and 1 mL of dry DMSO was added. The mixture was then combined with 0.0744 mg of the NMI compound to prepare a 0.1 mM solution. The water percentage (v/v) was determined using the previously described color-based method. This value was used to calculate the total water volume, which was converted to weight and divided by the weight of the solid sample to obtain the w/w% water content.

Determination of Moisture Content in Other Organic Solvents and Oils

In this experiment, 900 µL of anhydrous DMSO containing the (NMI-S2 + 50F) sensor was mixed with 100 µL of the test organic solvent or oil. The mixture was allowed to equilibrate, and the resulting color change was recorded. The water content in the total 1 mL solution was determined using the previously established calibration method. Based on this measured value, the actual percentage of water present in the 100 µL of the respective solvent or oil was calculated.

For example, after mixing 100 µL acetone with 900 µL dry DMSO, the measured water content in the total solution was 0.126% (v/v). Since the DMSO was anhydrous, all the detected water originated from the acetone sample. Therefore, the actual water content in acetone was calculated using the following relation:

Water content in acetone = (0.126 × 1000) / 100 = 1.26% (v/v)

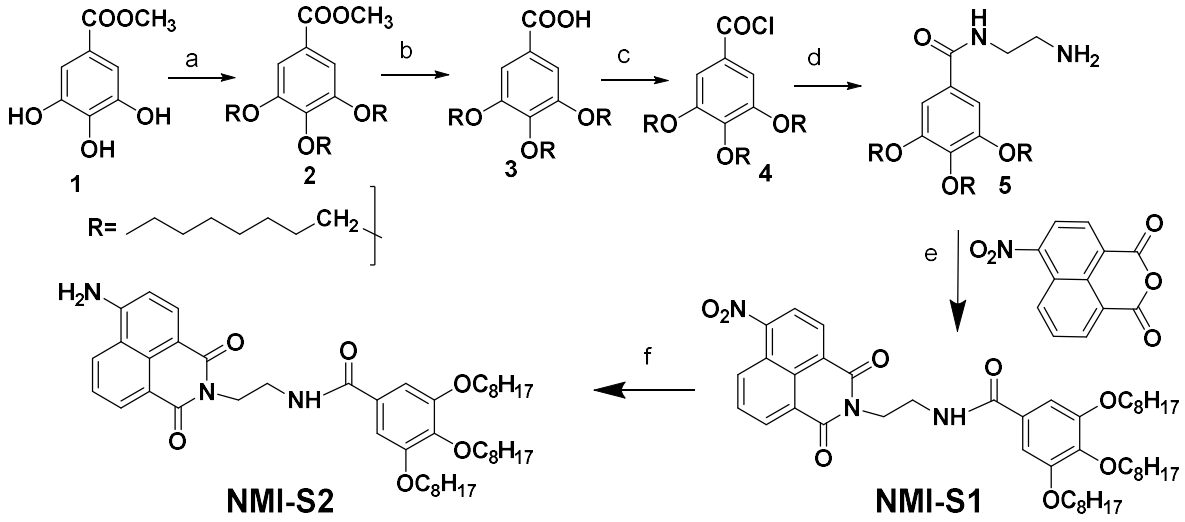
This result confirms that the measured water content in the final diluted solution corresponds to 1.26% (v/v) water in the original acetone sample. Similarly, the moisture content in other organic solvents and oil samples was calculated using the same method (see tableS2).

Karl-Fischer Titration for Detection of H_2O(%) in TBAF:

Prior to analysis, TBAF was treated with activated 4 Å molecular sieves under the same conditions as used in all sensing experiments. The treated TBAF sample was then subjected to Karl Fischer (KF) titration to determine the water content (% w/w). Based on the obtained values, the corresponding water content (% v/v) was calculated.All measurements were performed using an 870 KF Titrino Plus instrument (Metrohm) with Karl Fischer reagent purchased from Merck. The resulting data are provided in the Supporting Information (SI).(see tableS4)

Synthesis scheme and procedure: The synthetic scheme & procedure of NMI-S2 is outlined below:

Scheme:



Reagents and conditions: a) n-octyl bromide, K_2CO_3, 80^0C b) KOH, Ethanol/H_2O c) $SOCl_2$, DCM,0^0C d) Ethylene diamine, DCM, 0^0C-RT, e) DCM, Et_3N, 0^0C-RT. a) Toluene, 100^0C, 24h , b) Ethyl acetate, H_2 , Pd/C, rt, 24h,

Scheme 1: Schematic representation of the synthesis of **NMI-S2**

3,4,5-Tris(octyloxy)methyl benzoate (2): Compound 1 (2.0 g, 10.8 mmol), anhydrous K_2CO_3 (10.44 g, 75.6 mmol), and *n*-octyl bromide (6.27 g, 32.5 mmol) were dissolved in DMF (50 mL) in a round-bottom flask and stirred at 80 °C for 48 h under an inert atmosphere. After completion, the reaction mixture was cooled to room temperature and poured into ice-cold water (250 mL) then extracted with diethyl ether (3 × 50 mL), and the combined organic layers were washed with brine (100 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to afford the crude product as a light brown oil. The residue was purified by column chromatography on silica gel using hexane as the eluent to give the desired product as a colorless oil (78% yield).

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) = 7.27 (s, 2H), 4.02-4.12 (m, 6H), 3.90 (s, 3H), 1.71-1.87 (m, 6H), 1.49-1.30 (m, 6H), 1.30-1.18 (m, 24H), 0.90-0.78 (m, 9H).

3,4,5-Tris (octyloxy) methyl benzoic acid (3). A solution of compound 2 (3.03 g, 5.83 mmol) in ethanol (15 mL) was treated with an aqueous solution of KOH (1.96 g, 34.9 mmol in 15 mL) and the mixture was stirred at 100 °C for 5 h. After completion, the reaction mixture was cooled to room temperature and slowly poured into a solution of concentrated HCl (5 mL) in ice-cold

water (125 mL). The resulting white precipitate was collected by filtration, washed with distilled water, and dried under vacuum to afford the crude product as a white powder (75% yield), which was used in the next step without further purification.

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) = 7.31 (s, 2H), 4.06-4.00 (m, 6H), 1.84-1.70 (m, 6H), 1.50- 1.43 (m, 6H), 1.31-1.25 (m, 24H), 0.92-0.86 (m, 9H).

3,4,5-tris(octyloxy)benzoyl chloride (4): Compound 3 (0.40 g, 0.79 mmol) was dissolved in dry dichloromethane (10 mL), and freshly distilled thionyl chloride (3 mL) was added dropwise to the solution. The reaction mixture was stirred at room temperature for 12 h. After completion, the excess thionyl chloride was removed by distillation, and the residue was dried under vacuum to achieve the crude product as a light-yellow waxy material in quantitative yield. The product was neither characterized nor purified and was used directly in the subsequent step.

N-(2-aminoethyl)-3,4,5-tris(octyloxy) benzamide (5): A solution of compound 4 (0.79 mmol) in dry dichloromethane (10 mL) was added dropwise to an ice-cooled flask containing ethylenediamine (10 mL). The reaction mixture was then stirred at room temperature for 15 h.

Then it was diluted with dichloromethane (20 mL), and washed successively with water (3 × 30 mL), saturated $NaHCO_3$ solution (30 mL), and brine (30 mL). The organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure to afford the crude product. The residue was dissolved in ethanol (15 mL) and kept in a refrigerator for 2 h, during which a white precipitate formed. The solid was collected by filtration, and the solvent from the filtrate was removed under reduced pressure to afford the product as a light yellow, waxy solid. The product was used directly in the subsequent step without further purification.[1]

^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ (ppm) = 7.91 (br s, 1H), 5.02 (br s, 2H), 7.00 (s, 2H), 3.95 (m, 6H), 3.61 (t, 2H), 3.07 (t, 2H), 1.74 (m, 6H), 1.44 (m, 6H), 1.28 (m, 24H), 0.89 (m, 9H).

ESI-MS: m/z calculated for [$C_{33}H_{60}O_4N_2$] (M)= 548.46 (exact mass), found 549.46(M+1).

Compound NMI-S1: Compound 5 (0.632 g, 1.15 mmol) and 4-nitro-1,8-naphthalic anhydride (0.270 g, 1.09 mmol) were dissolved in dry toluene (45 mL) in a round-bottom flask, and the reaction mixture was stirred at 100 °C for 24 h under an argon atmosphere. After completion, the mixture was cooled to room temperature, and then the solution was evaporated to get the

crude product. Purification by column chromatography on silica gel using 20% ethyl acetate in hexane as the eluent furnished NMI-C1 as a light yellow solid in 60% yield.

^{1}H-NMR (400 MHz, $CDCl_3$, TMS): δ (ppm) = 8.90 (d, 1H), 8.72 (d, 1H), 8.70 (d, 1H),8.40 (d, 1H), 7.98 (t, 1H), 6.90 (s, 2H), 3.5 (t, 4H), 3.95 (t, 6H), 1.74 (m, 6H), 1.34 (m,6H), 1.30 (m, 24H), 0.90 (t, 9H).

^{13}C NMR (CDCl3, TMS): δ (ppm) = 167.94, 165.21, 164.36, 153.44, 150.62, 140.89, 132.46, 129.93, 129.14, 126.60, 124.02, 122.69, 105.38, 73.29, 69.14, 39.91, 36.60, 31.84, 30.92, 29.12, 26.12, 22.12, 22.67, 14.00.

ESI-MS: m/z calculated for $[C_{45}H_{63}N_3O_8Na]$ $(M+Na)^+$ =796.4615, Found-796.4511.

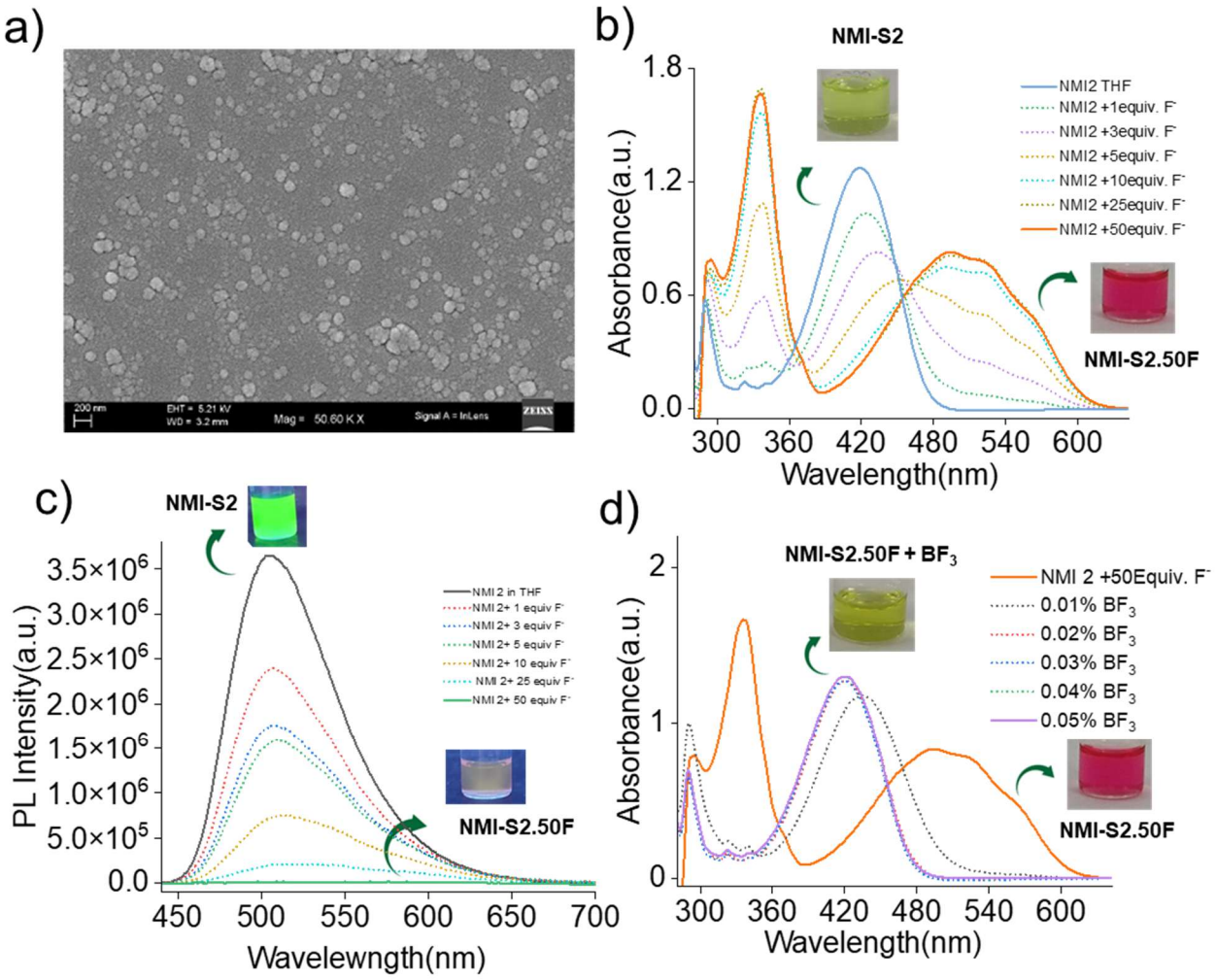
Compound NMI-S2: At first, NMI-S1(0.20 g,0.575 mmol) was dissolved in degassed ethyl acetate, and Pd/C was added carefully. The reaction mixture was stirred under a hydrogen atmosphere at room temperature for 24 h. The catalyst was removed by filtration through Celite 545 filtering agent, and the solvent was evaporated under reduced pressure to afford the crude brown product. The residue was washed with hexane to yield the pure product as a yellow solid in 93% yield.

^{1}H-NMR (300MHz, $CDCl_3$ TMS):δ (ppm) = 8.56 (d, 1H), 8.40 (d, 1H), 8.20 (d, 1H),7.50 (t, 1H), 7.05 (t, 2H), 6.8 (d, 1H), 4.00 (t, 6H), 3.5 (t, 4H), 1.74 (m, 6H), 1.34 (m ,6H), 1.30 (m, 24H), 0.90 (m, 9H).

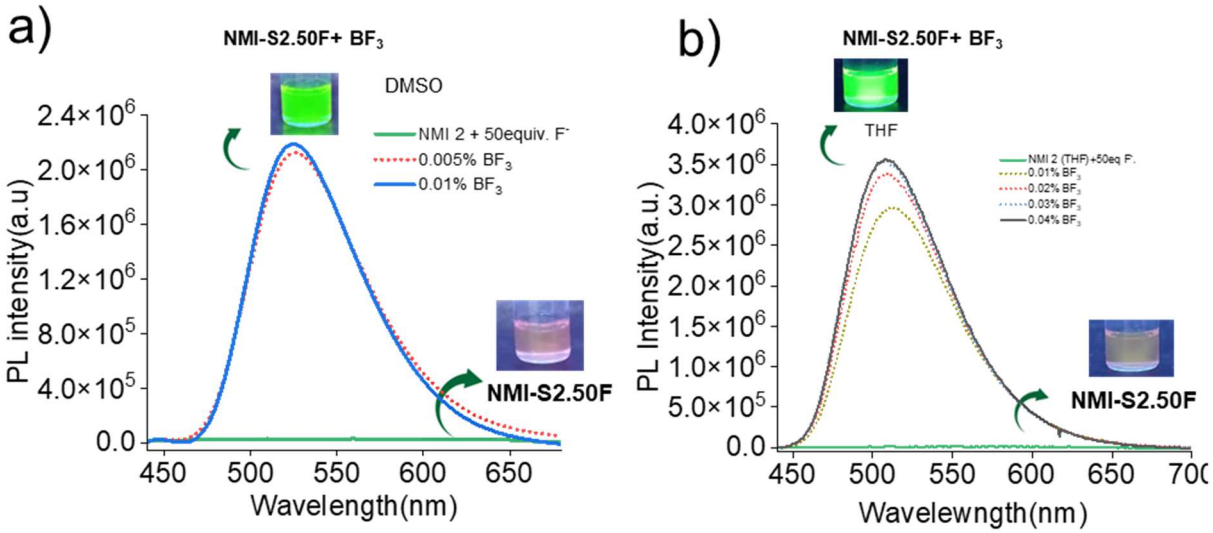
^{1}13C-NMR (CDCl3, TMS): δ (ppm) =167.5, 165.4, 157.5, 152.9, 144.9, 140.6, 139.1, 138.9, 135.7, 131.8, 129.2, 127.2, 124.6, 122.8, 119.7, 116.9, 112.2, 105.2, 69.0, 42.9, 39.2, 31.8, 29.4, 25.9, 22.7, 14.1

ESI-MS: m/z calculated for $C_{45}H_{65}N_3O_6Na$ M+Na)+ = 766.4873, Found-766.5182

Additional Figures:



FigureS1. a) SEM image of nanostructure formed in THF; b) UV/Vis absorption spectra of NMI-S2 (C = 0.1 mM) with variable F^- concentration and formation of magenta colour solution of anionic NMI-S2 in THF; e) Fluorescence spectral change and associated colour change after addition of F- anion in THF; f) Regeneration of neutral NMI-S2 as probed by UV/Vis spectral change in presence of F^- scavenger BF_3 in THF.



FigureS2. Regeneration of neutral NMI-S2 as monitored by PL spectral changes and associated colour change upon addition of the fluoride scavenger BF_3 in (a) DMSO and (b) THF

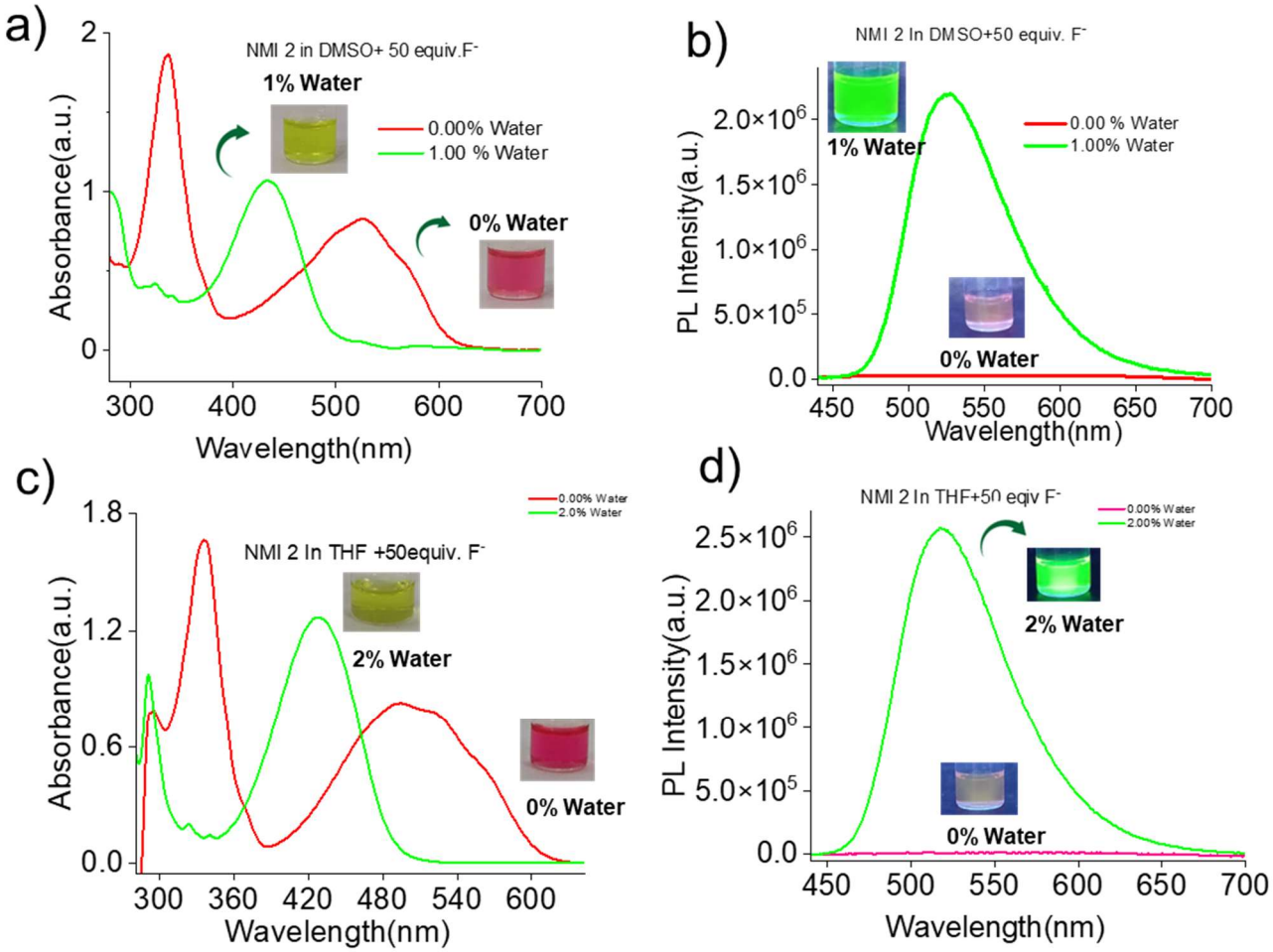


Figure S3. UV–Vis and PL responses of NMI-S2.50F upon water addition: UV–Vis in DMSO (a) and THF (c); PL in DMSO (b) and THF (d), with corresponding solution photographs included.

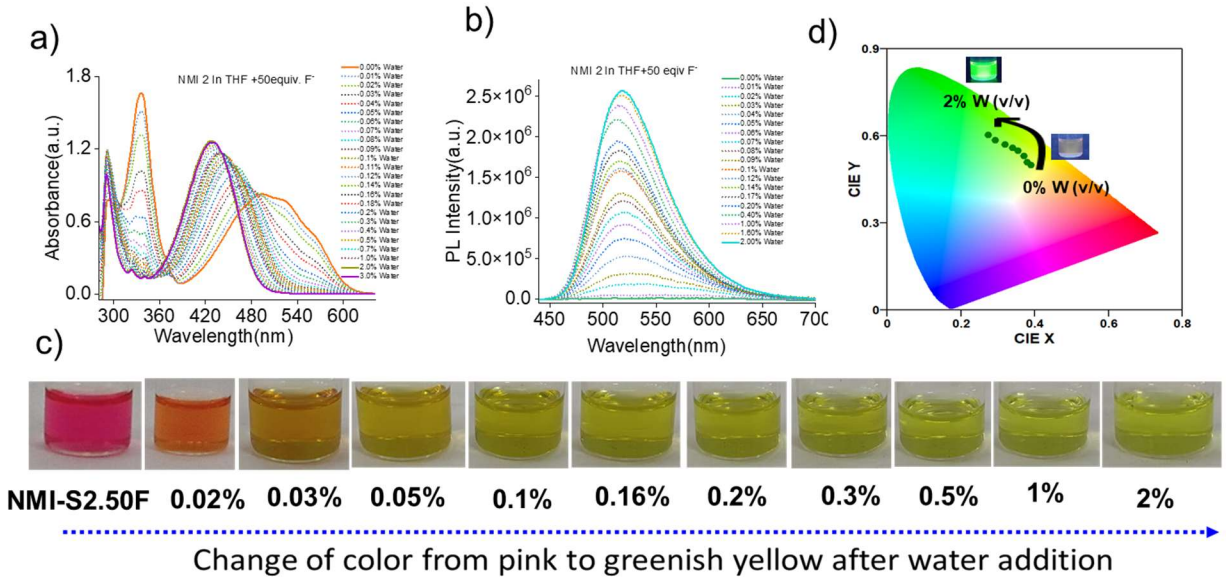


Figure S4. a) UV/Vis and b) Fluorescence titration of NMI-S2.50F with 0-3 and 0-2 % (v/v) of water content; c) Visual colour change from magenta to greenish yellow upon systematic addition of water; d) CIE 1931 diagram displaying the (x, y) colour coordinates of NMI-S2.50F with different water content. Solvent = THF, Temperature = 25°C. conc=0.1mM

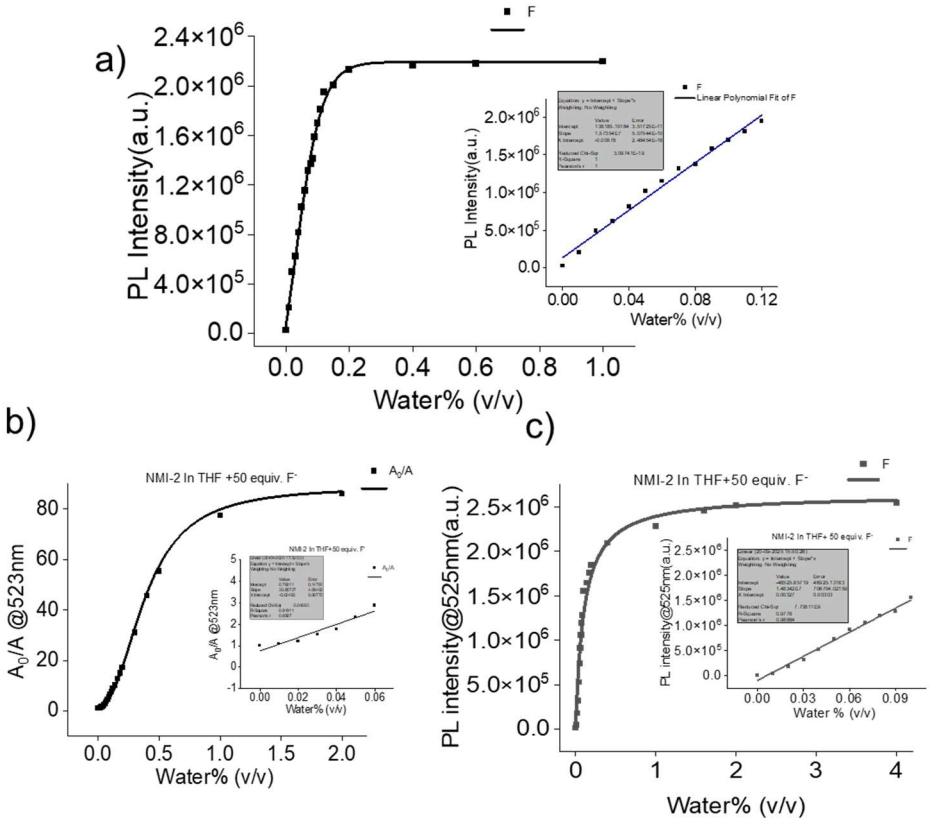


Figure S5.(a) PL intensity vs % water (v/v) in DMSO; (b) A_0/A vs % water (v/v) in THF; (c) PL intensity vs % water (v/v) in THF for NMI-S2.50F (c = 0.1 mM, T = 25 °C). Inset: Linear relationship of PL intensity and A_0/A with water content at very low percentages in each case.

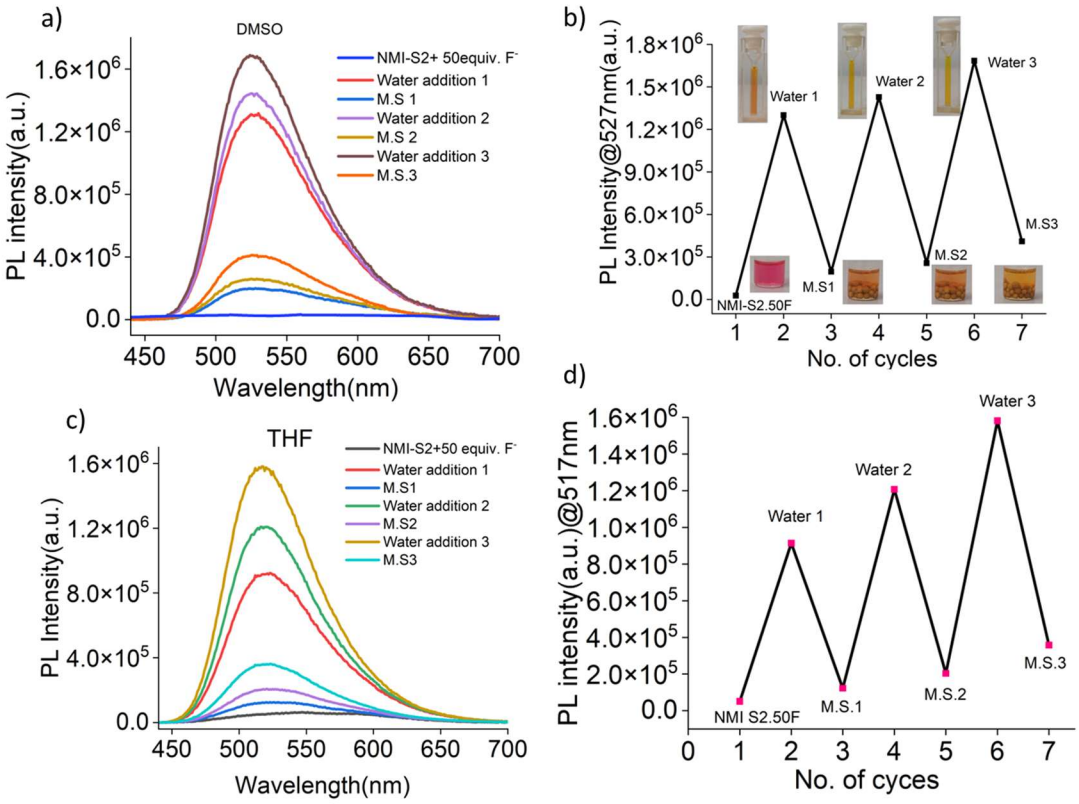


Figure S6. PL spectra showing reversible sensing using molecular sieves.(a, c) PL spectra of NMI-S2.50F in DMSO and THF.(b, d) Fluorescence changes after adding water and molecular sieves alternately at room temperature.

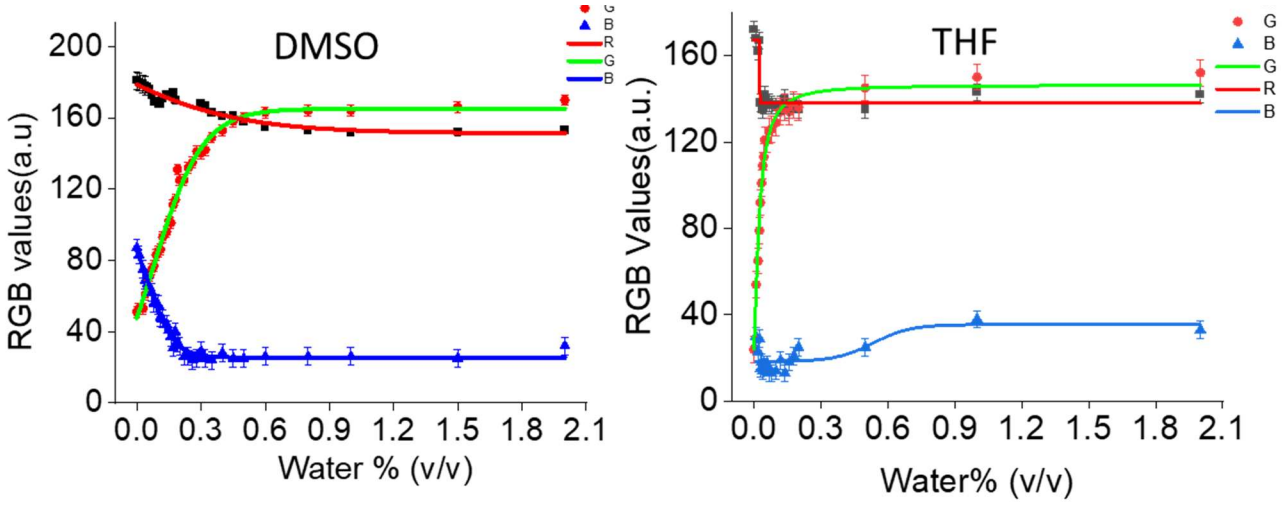


Figure S7. RGB analysis of NMI-S2.50F solutions with varying % water (v/v) using the Image Color Picker web tool, showing variations in R, G, and B values in (a) DMSO and (b) THF.

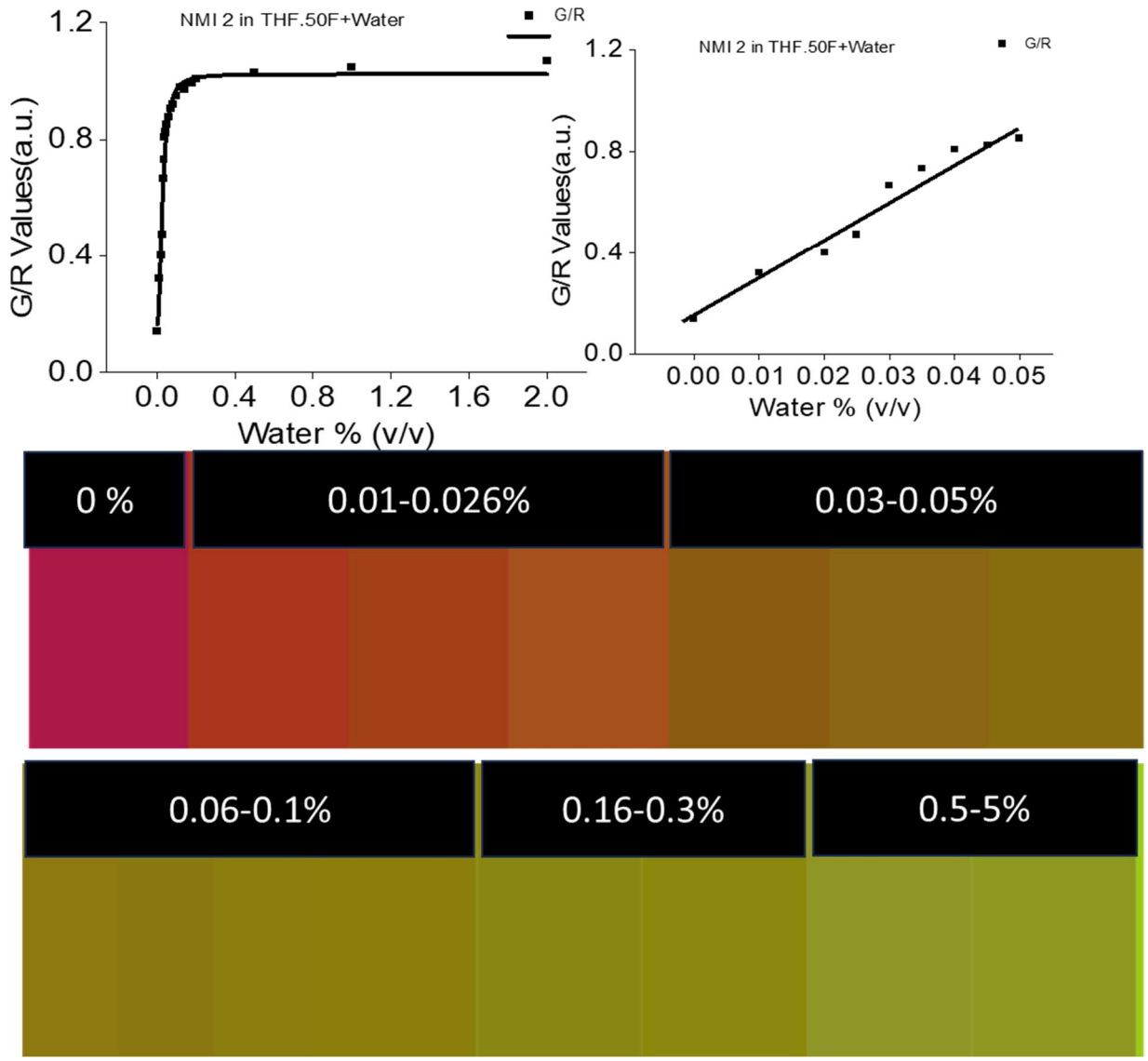


Figure S8. (a) Determination of the RGB components of THF solutions of NMI-S2.50F containing various percentages of water using a smartphone-based colour-picker, and corresponding G/R vs water content plot. Inset: Linear relationship between G/R and water content at very low percentages. (b) Colour palette generated from images of NMI-S2.50F solutions with varying water content using the colour-picker software. Solvent: THF; concentration: 0.1 mM.

Sample Name	TBAF ml	Water%(v/v)	Total water in 5 µL TBAF (µL)	Water (%) in the total 1 mL probe solution	Average Water (%)
TBAF 1 after treatment with (molecular sieves)	0.041079295	**0.02724**	0.001362	**0.0001362**	(0.0001362+0.00034958+0.00005902)/3= **0.000182**
TBAF 2 after treatment with (molecular sieves)	0.041299559	**0.069916**	0.0034958	**0.00034958**	
TBAF 3 after treatment with (molecular sieves)	0.050770925	**0.011804**	0.0005902	**0.00005902**	

Table S1 Calculation of residual water content (v/v %) in molecular sieves treated TBAF solution by Karl Fischer titration. TBAF sample was measured three times and the average amount of water introduced in 1 ml probe solution by 5 µl TBAF (50 equivalent with respect to NMI) is 0.00182 µl. Hence, % of background water is 0.000182 (v/v%), which can be considered as negligible level of background water.

Sample name	Sample solution image	Color palette	G/R ratio	% water from calibration curve (v/v)	% water from color chart (v/v)	Total water contains(µL)	Water%(w/w)
Salt+1ml Solution			G/R = 0.38±0.01	0.05±0.01%	0.04-0.07%	0.5±0.1	0.33
Salt+2 ml Solution			G/R = 0.324±0.01	0.024±0.01%	0-0.03%	0.48±0.2	0.32
Salt+3 ml Solution			G/R = 0.305±0.01	0.015±0.01%	0-0.03%	0.45±0.3	0.3

Table S2 Water Content (%) of Salt Sample after Extraction with Different Volumes of DMSO (1, 2, and 3 mL). The extracted water volumes are 50, 48 and 45 µl for 1, 2 and 3 ml of DMSO respectively. The obtained values are very precisely matched and slight difference is within the experimental error. Hence, 1 ml of DMSO is sufficient for efficient and reliable moisture extraction under the present experimental conditions.

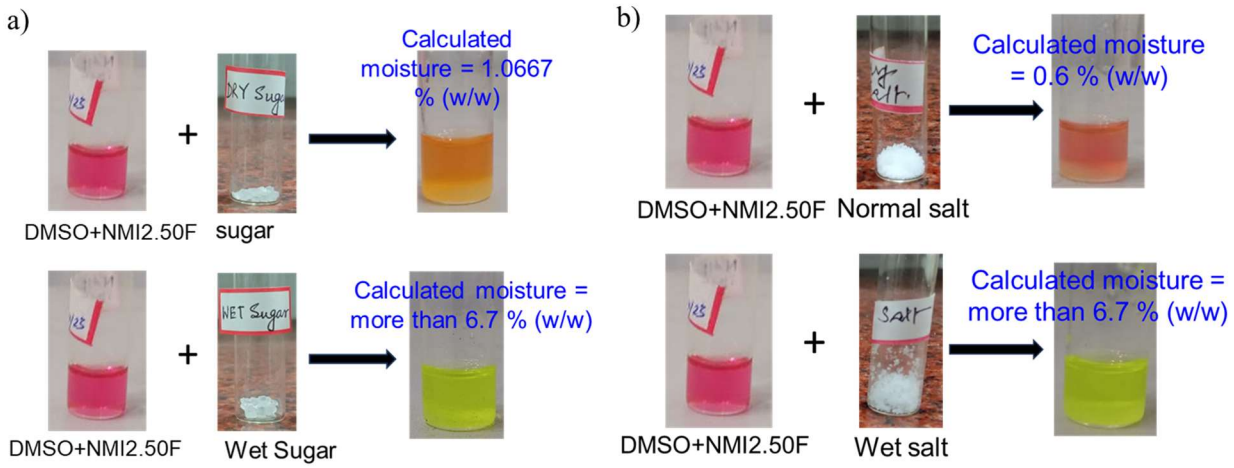


Figure S9. Visual colour changes of the NMI-S2 sensor in the presence of a) Salt, b) Sugar with variable moisture content, and determination of the weight % of moisture. Solvent: DMSO

Sample name	Sample solution image	Color palette	G/R ratio	% of water from calibration curve (v/v)	% of water from color chart (v/v)	% of water in solid sample (w/w(%))
Normal sugar			G/R = 0.591	0.153%	0.14-0.16%	1.0667%
Wet sugar			G/R = 1.12	>1%	>1%	>6.7%
Normal salt Brand-1			G/R = 0.46	0.09%	0.07-0.01%,	0.6%
Normal salt Brand-2			G/R = 0.548	0.132%	0.12-0.14%	0.86%
Wet salt Brand-1			G/R = 1.124	>1%	>1%	>6.7%

Table S3. Determination of moisture content in solid samples.

For normal salt brand-1, after the extraction, the residual water calculated by KF method is 0.013% (w/w). Hence, total water % = Extracted water% +residual water% = 0.6 +0.013 =0.613% (w/w). So, % recovery = (0.6/0.613) *100 = 98%.

Sample name	Sample solution image	Color palette	G/R ratio	% Water from calibration curve (v/v)	% Water from color chart (v/v)	Water presence in Solvent/oil
Acetonitrile S1(dry)			0.280±0.01	0.004≈ 0%	0-0.02%	0-0.04%
Acetonitrile S2			0.558± 0.01	0.136%	0.11-0.14%	≈1.36%
Acetone S1(dry)			0.278±0.01	0.002≈ 0%	0-0.02%	0-0.02%
Acetone S2			0.536±0.01	0.126%	0.11-0.14%	≈1.26%
DCM S1(dry)			0.287±0.01	0.007%	0-0.03%	≈0.07%
DCM S2			0.577 ± 0.01	0.145%	0.11-0.14%	≈1.45%
Petrol			0.657 ± 0.01	0.183%	0.2%	≈1.83%
Diesel			0.777 ±0.01	0.256%	0.21-0.3%	≈2.56%
Refined vegetable oil			0.275 ±0.01	0.001%≈ 0%	0%	0-0.01%

Table S4. Determination of moisture content in organic solvents and oil.

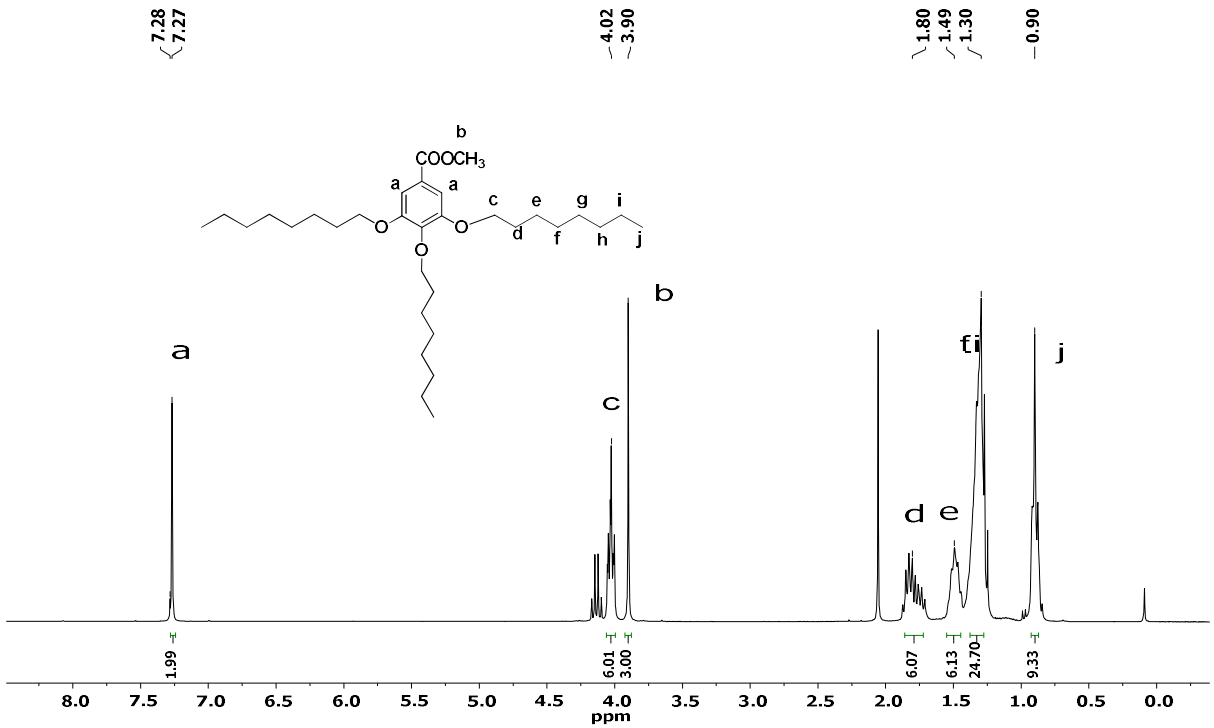


Figure S10: ^{1}H- NMR spectrum of **3,4,5-Tris(octyloxy)methyl benzoate (2):** Solvent-$CDCl_3$

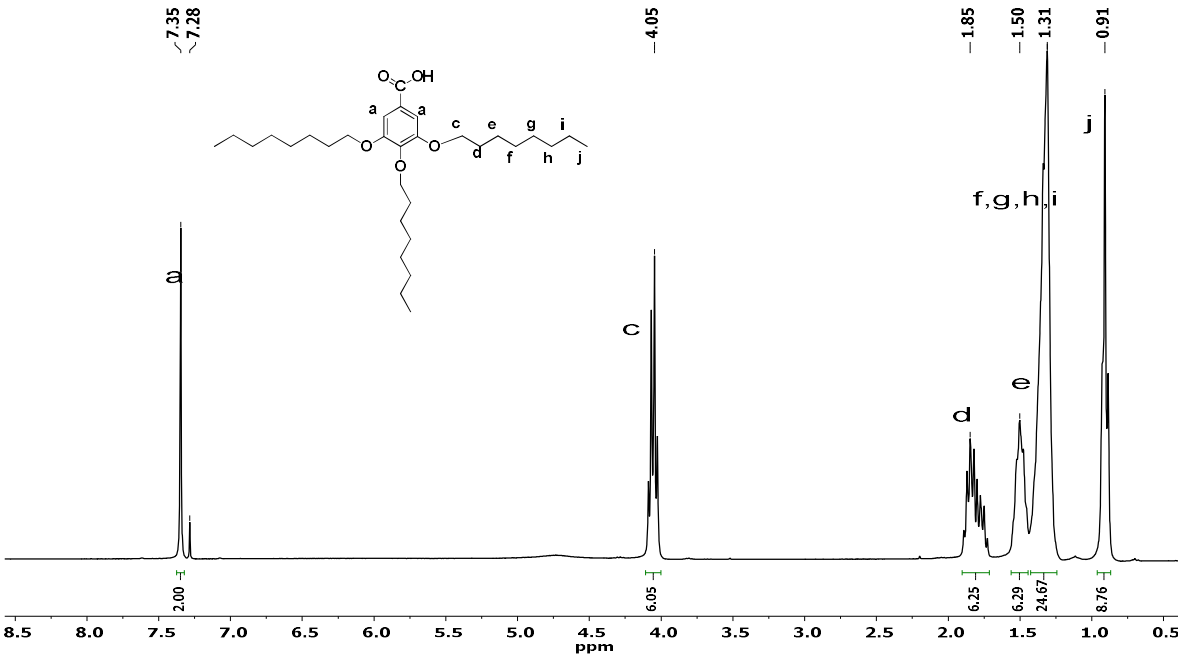


Figure S11: ^{1}H- NMR spectrum of **3,4,5-Tris (octyloxy) methyl benzoic acid (3).** Solvent-$CDCl_3$

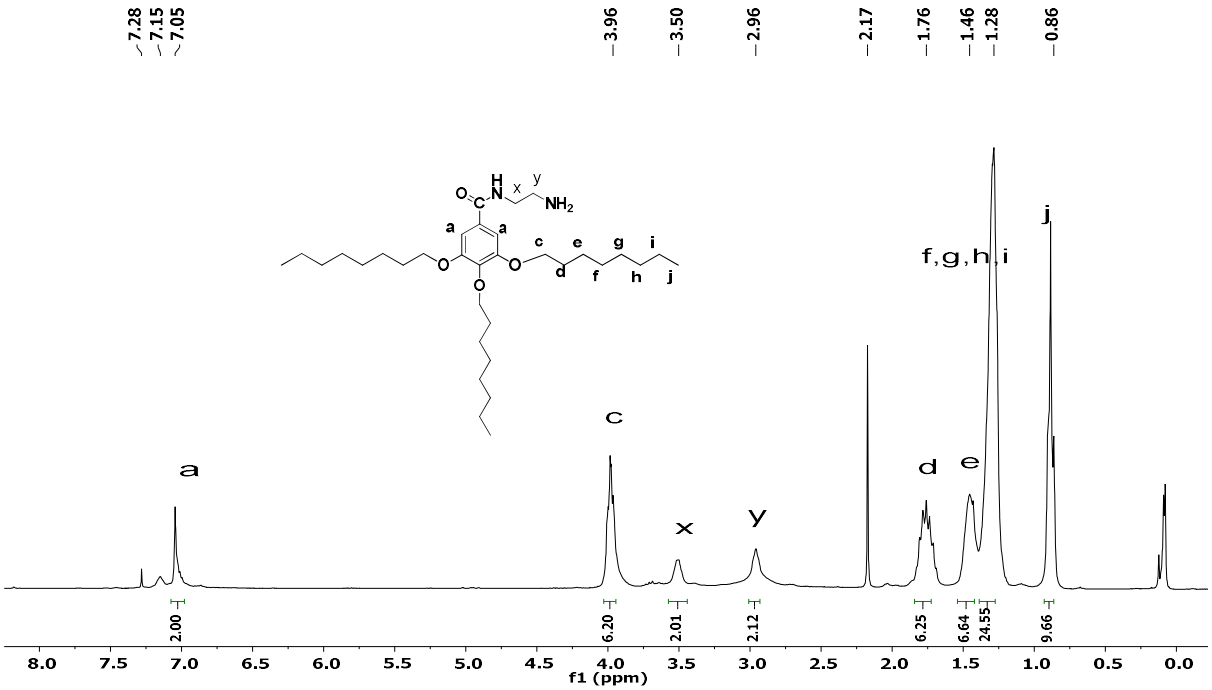


Figure S12: ^{1}H- NMR spectrum of **N-(2-aminoethyl)-3,4,5-tris(octyloxy) benzamide (5):** Solvent-$CDCl_3$

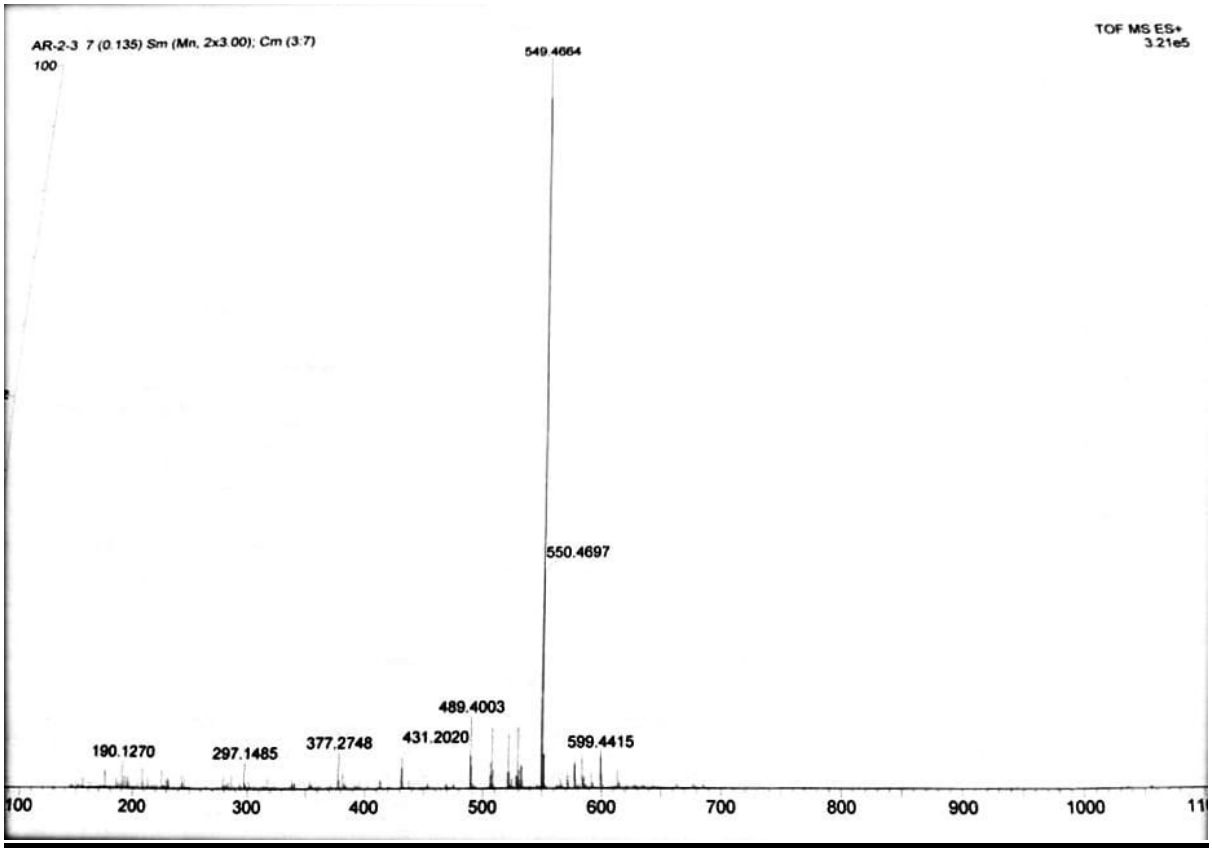


Figure S13: ESI-MS spectrum of **N-(2-aminoethyl)-3,4,5-tris(octyloxy) benzamide (5).**

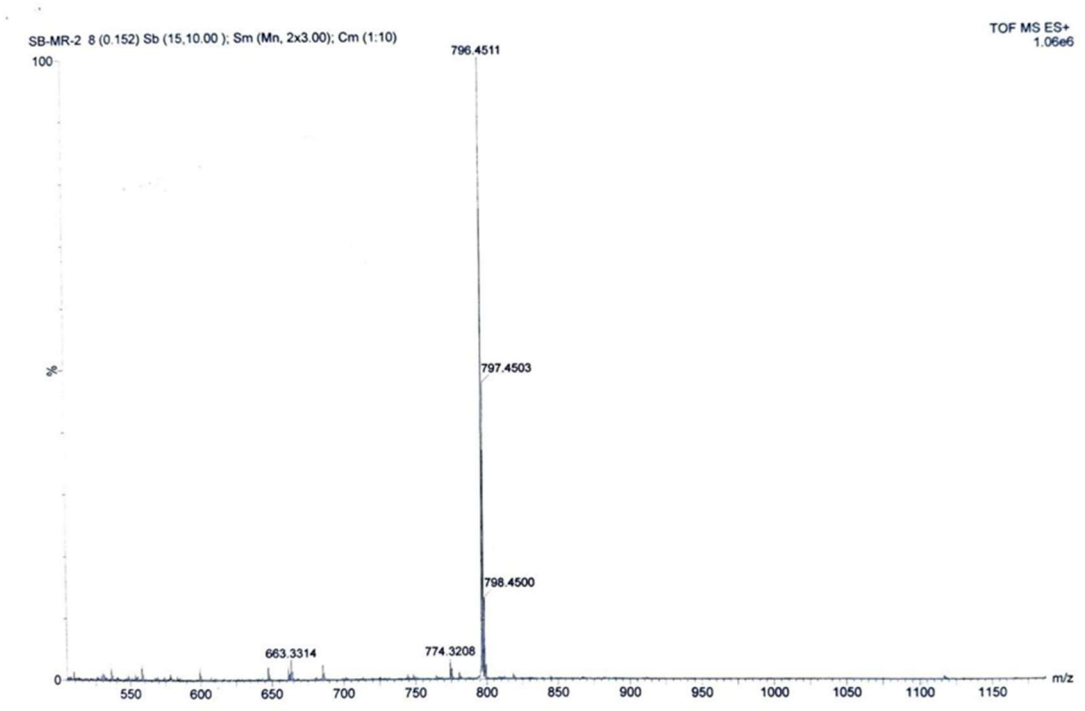


Figure S14: ESI-MS spectrum of N-(2-(6-nitro-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)ethyl)-3,4,5-tris(octyloxy)benzamide(**NMI-S1).**

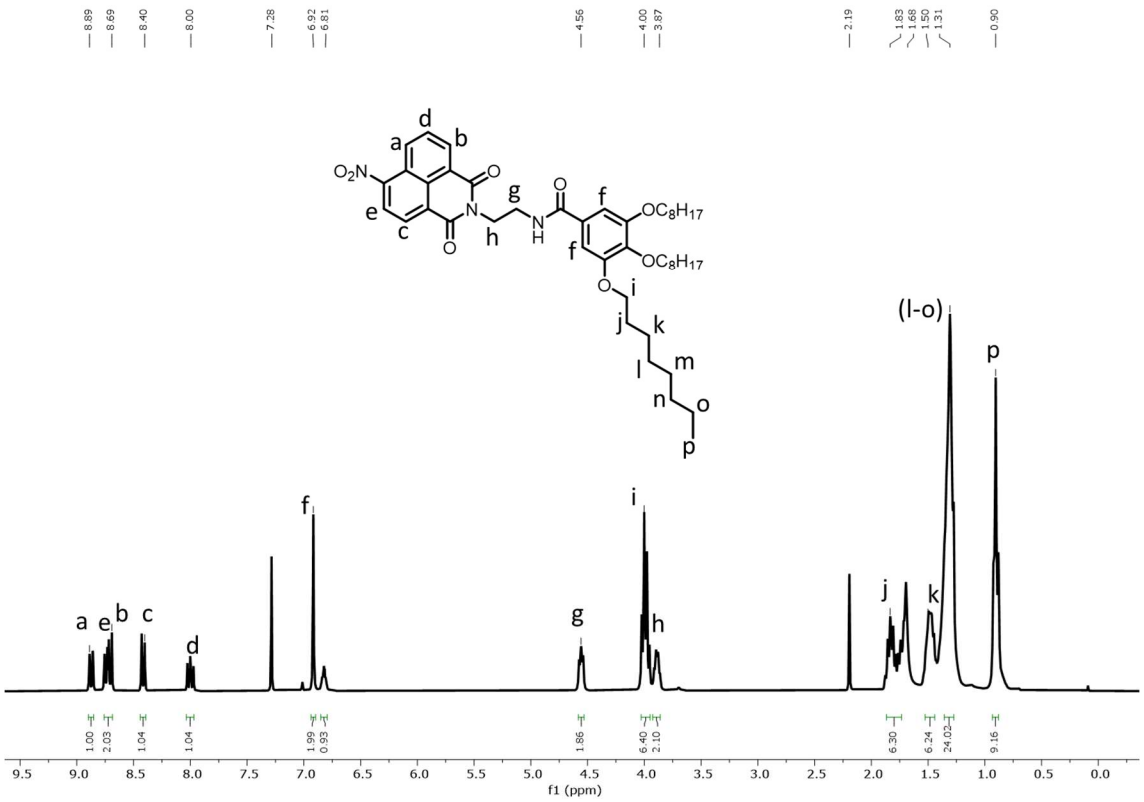


Figure S15: ^{1}H- NMR spectrum of N-(2-(6-nitro-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)ethyl)-3,4,5-tris(octyloxy)benzamide(**NMI-S1).** Solvent-$CDCl_3$

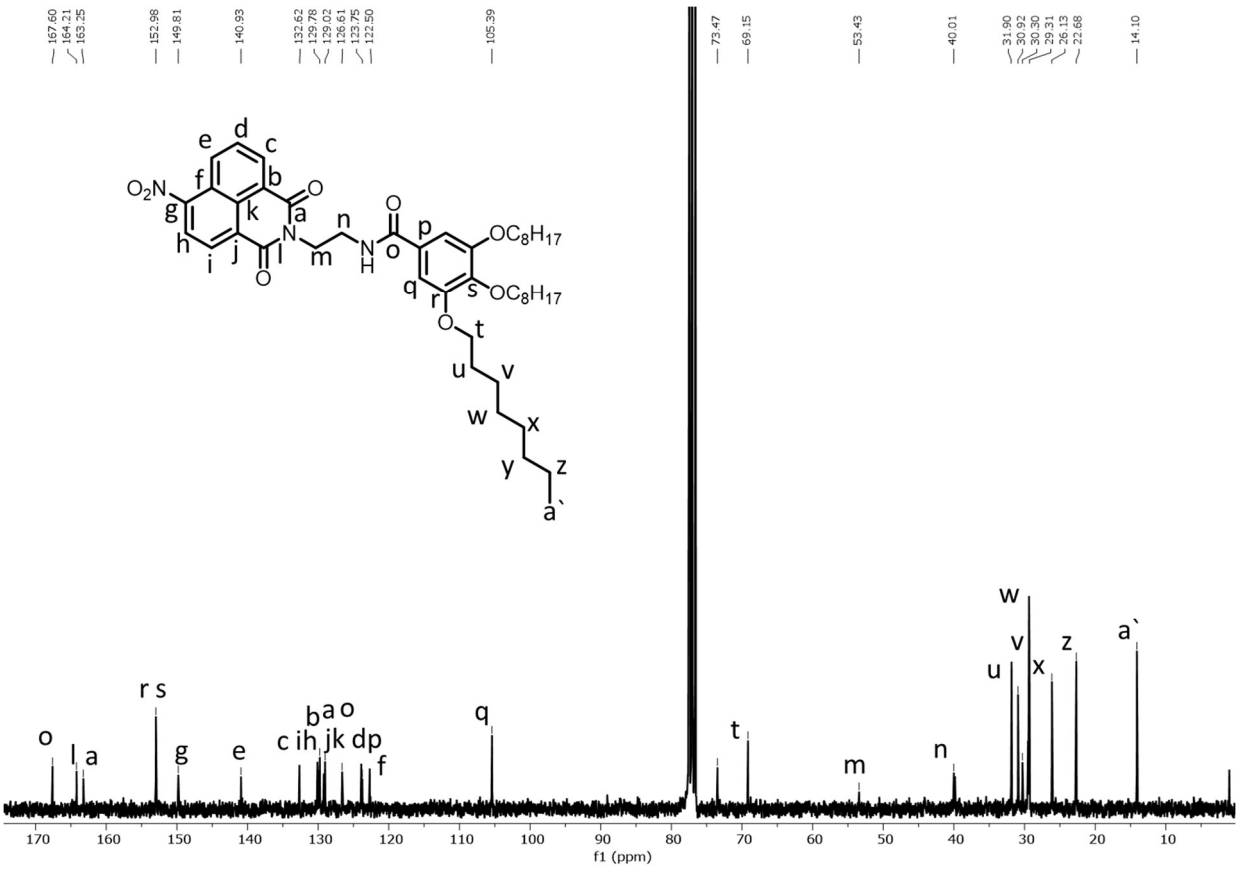


Figure S16: ^{13}C- NMR spectrum of N-(2-(6-nitro-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)ethyl)-3,4,5-tris(octyloxy)benzamide(**NMI-S1).** Solvent-$CDCl_3$

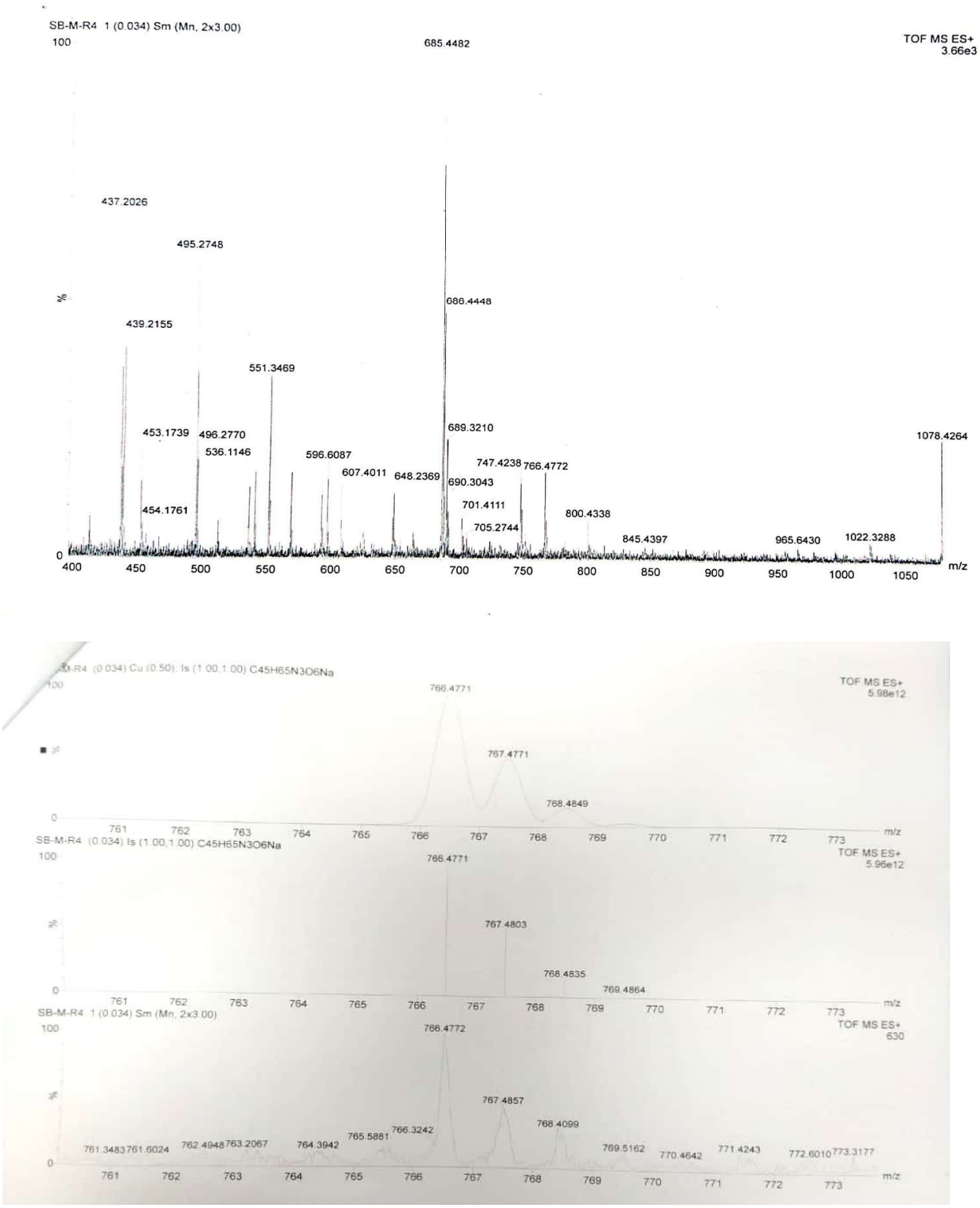


Figure S17: ESI-MS spectrum of Compound N-(2-(6-amino-1,3-dioxo-1H-benzo[de]isoquinolin-2(3H)-yl)ethyl)-3,4,5-tris(octyloxy)benzamide(**NMI-S2)**.

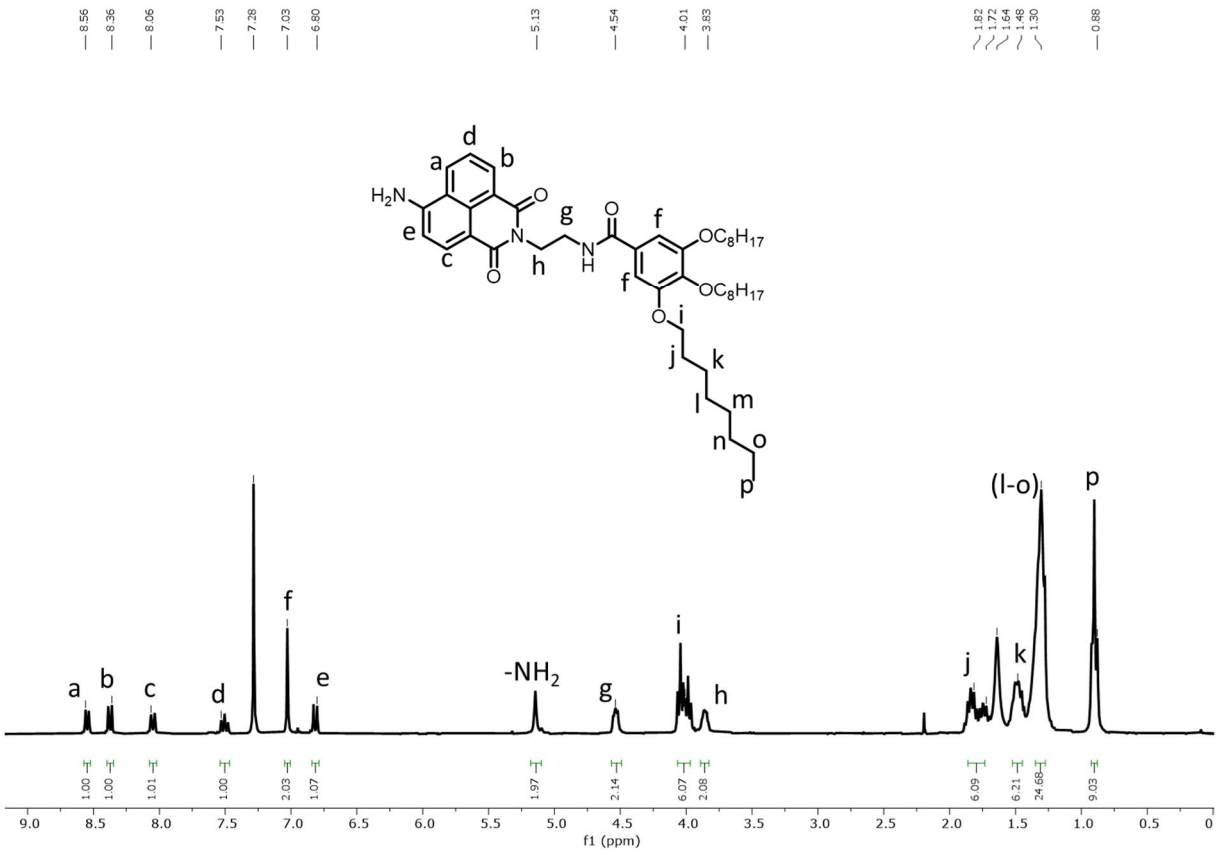


Figure S18: ^{1}H- NMR spectrum of Compound **NMI-S2**. Solvent-$CDCl_3$.

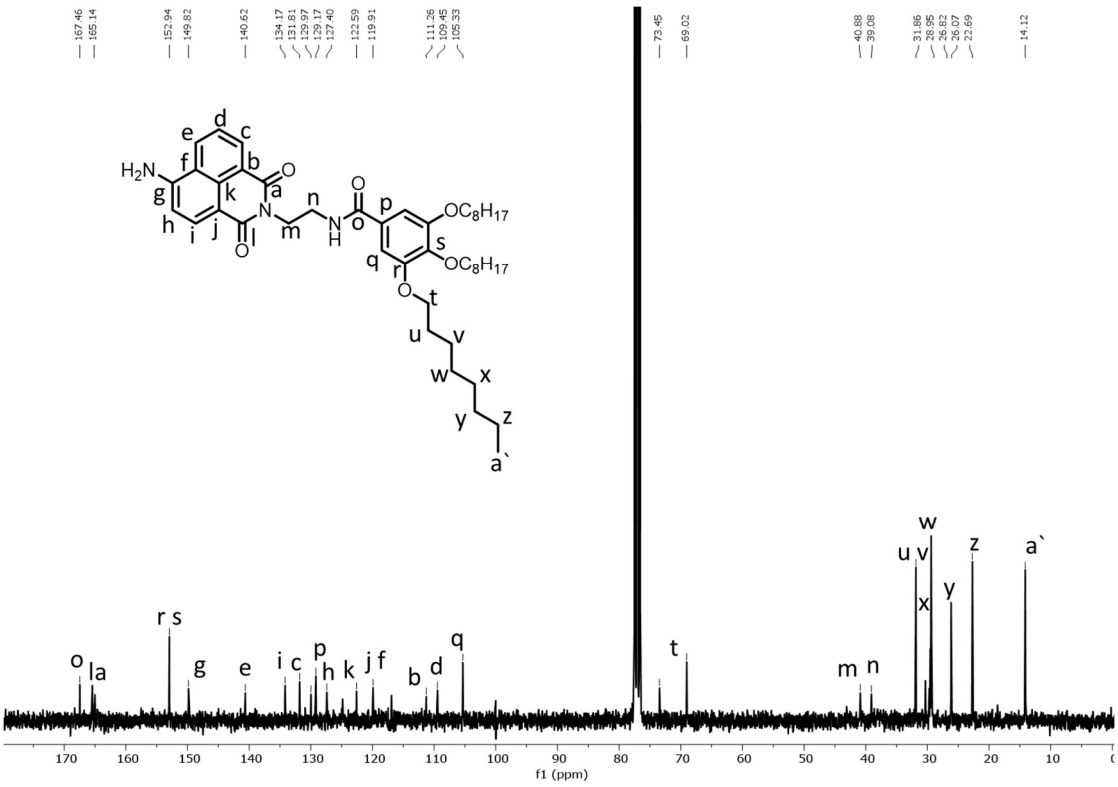


Figure S19: ^{13}C- NMR spectrum of Compound **NMI-S2**. Solvent-$CDCl_3$.