

Supporting Information

Aggregation induced generation of circularly polarized luminescence in naphthaleneimide-based nanostructures with high dissymmetry factor

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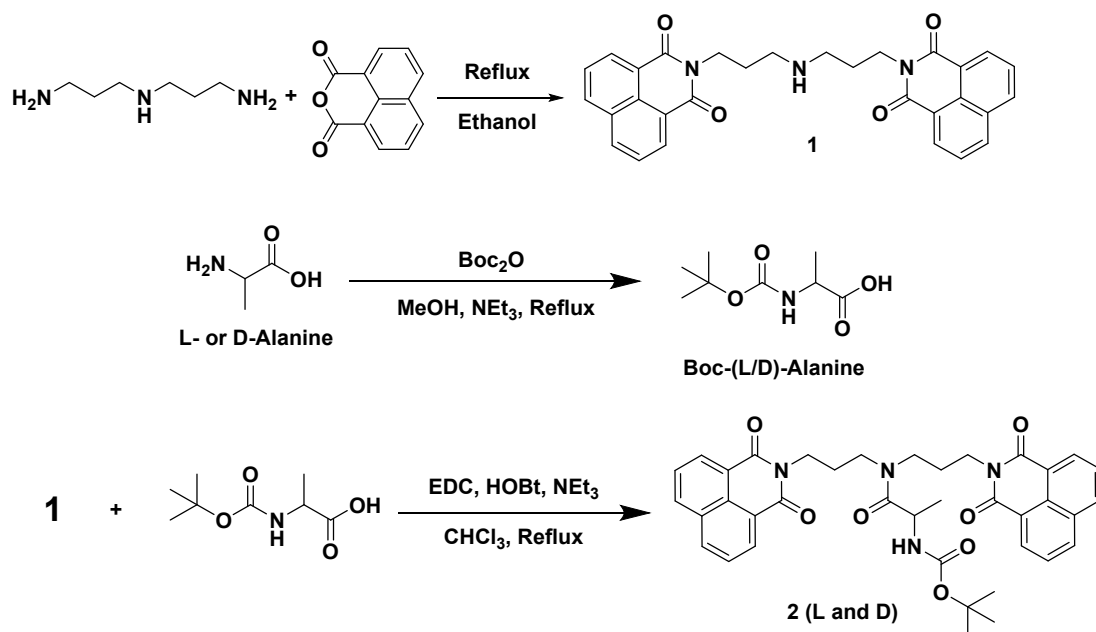
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1. General Information

All reagents from commercial sources were used without further purification unless otherwise stated. Thin layer chromatography (TLC) was carried out on aluminium plates coated with silica gel mixed with fluorescent indicator having particle size of 25 μm and was sourced from Merck India. Starting materials, L and D-Alanine, Di-tert-butyl dicarbonate, 1,8- Naphthalic anhydride, bis(3-aminopropyl)amine, 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide (EDC) and 1-hydroxybenzotriazole (HOBt) were purchased from TCI India. NMR spectra were recorded at room temperature conditions using a 400 MHz Bruker spectrometer. Mass spectrometry was performed on UHD Accurate-Mass Q-TOF LC/MS Maker-Agilent Technologies. UV-Vis. Absorption spectra were recorded using an Agilent Cary-60 Spectrophotometer. Fluorescence spectra were obtained using Cary Eclipse Fluorescence Spectrophotometer. Solid State Fluorescence spectra were recorded using HORIBA CANADA QM-8450-22-C. The CPL measurements were done using JASCO CPL-300 CPL spectrometer. Time-resolved studies were performed in a HORIBA DeltaFlex Time-Correlated Single Photon Counting system using 320 nm Delta-diode as the excitation. SEM imaging was performed using a ZEISS EVO18-SEM with an accelerating voltage of 10 kV.

2. Synthetic procedure for compounds 2(L) and 2(D)



Synthetic Procedure: Compound **1** was synthesized following standard procedure reported elsewhere.¹ $R_f = 0.32$ (9:1 $\text{CHCl}_3/\text{MeOH}$), **MP:** 120 $^\circ\text{C}$. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): δ 1.93 (q, 4H), 2.71 (t, 4H), 4.26 (t, 4H), 7.76 (t, 4H), 8.2 (d, 4H), 8.6 ppm (d, 4H). **HRMS (m/z):** calculated for $\text{C}_{30}\text{H}_{26}\text{N}_3\text{O}_4$ (H^+), 492.1923; found, 492.1929.

For the synthesis of compound **2** (L and D) following procedure was followed: Boc-protected alanine² (L or D), was taken in a 250 ml two necked round bottomed flask and anhydrous CHCl₃ was added under nitrogen atmosphere. The stirred solution was cooled over an ice bath. To this solution, 1-Hydroxybenzotriazole (HOBt) and 1-(3-Dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride (EDC·HCl) were added, followed by the addition of triethyl amine. The reaction mixture was then allowed to warm to the room temperature under constant stirring. After 30 minutes, compound **1** was added and mixture was stirred at room temperature for 6 h. Reaction progress was monitored by TLC. To reach the reaction completion, mixture was further refluxed for 12 h. The cooled reaction was then washed with brine and organic layer was dried over Na₂SO₄. Solvent was removed on rotary evaporator under reduced pressure to obtain the crude product which was further purified by column chromatography (silica, 60-120 mesh), using CHCl₃/MeOH as the eluent. **Yield:** 80 %. **R_f** = 0.80 (9:1 CHCl₃/MeOH). **MP:** 180 °C. **¹H NMR** (CDCl₃, 400 MHz): δ 1.32-1.44 (m, 12H), 1.95-2.20 (m, 4H), 3.32-3.79 (m, 4H), 4.12-4.32 (m, 4H), 4.6 (m, 1H), 5.39-5.49 (d, 1H), 7.70-7.80 (m, 4H), 8.17-8.25 (m, 4H), 8.50-8.60 (m, 4H). **¹³C NMR** (CDCl₃, 100 MHz): δ = 19.63, 26.25, 27.81, 28.32, 37.87, 38.02, 43.58, 45.37, 46.33, 76.83, 77.67, 79.30, 122.37, 127.95, 131.11, 131.44, 133.91, 155.03, 163.95, 172.99, 173.10. **HRMS (m/z):** calculated for C₃₈H₃₈N₄O₇ (H⁺), 662.74; found, 663.82.

3. Emission and Solid-state Photoluminescence spectra

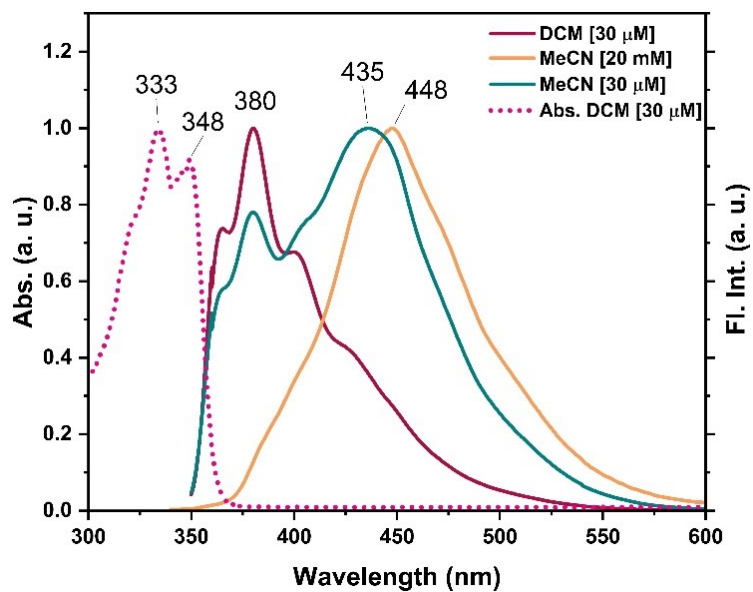


Fig. S1: Normalised absorption in DCM and fluorescence spectra of **2(D)** in various DCM, MeCN dilute and MeCN concentrated solutions ($\lambda_{\text{ex}} = 340$ nm).

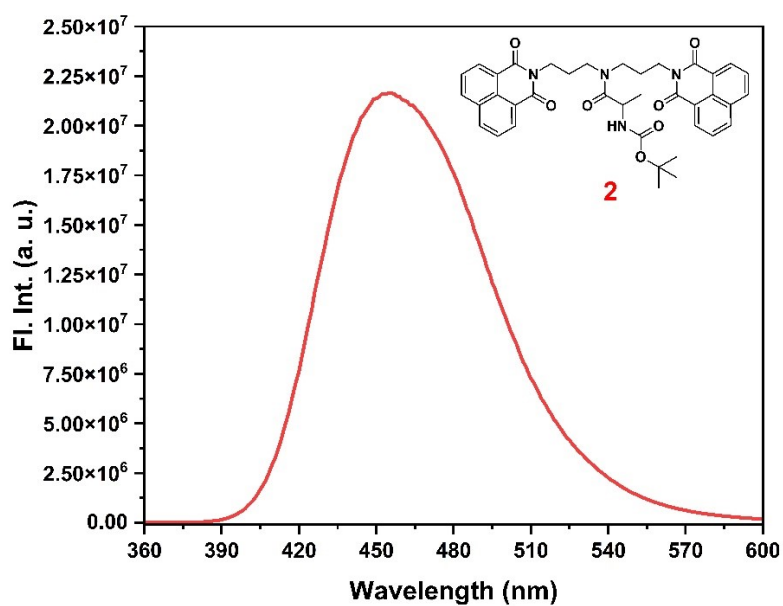


Fig. S2: Solid state photoluminescence spectrum of **2(D)** ($\lambda_{\text{ex}} = 340$ nm).

4. Fluorescence and CPL spectra in aggregated and solid state

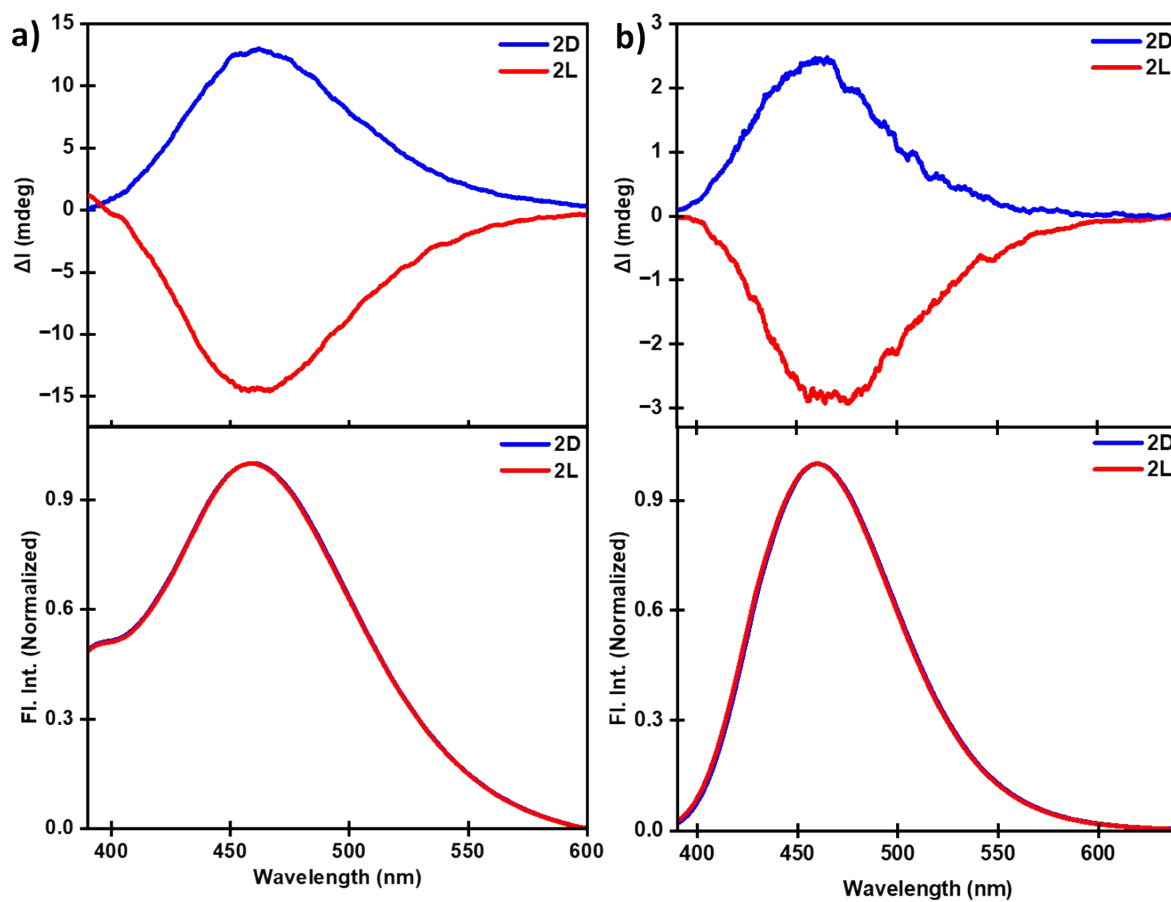


Fig. S3: CPL and the corresponding normalized fluorescence spectra of 2 in (a) MeCN:H₂O (1:1), and (b) KBr pellet.

5. Fluorescence Lifetime Measurement

Fluorescence lifetime measurements were performed using a HORIBA DeltaFlex Time-Correlated Single Photon Counting (TCSPC) system equipped with a 320 nm Delta-diode as the excitation source. Samples were prepared from a 30 μM solution of **2(D)** in DCM, MeCN and MeCN/H₂O (1:1) mixture. For solid state measurement the thin film sample was prepared by drop casting saturated DCM solution on to a glass film and allowed to dry at room temperature.

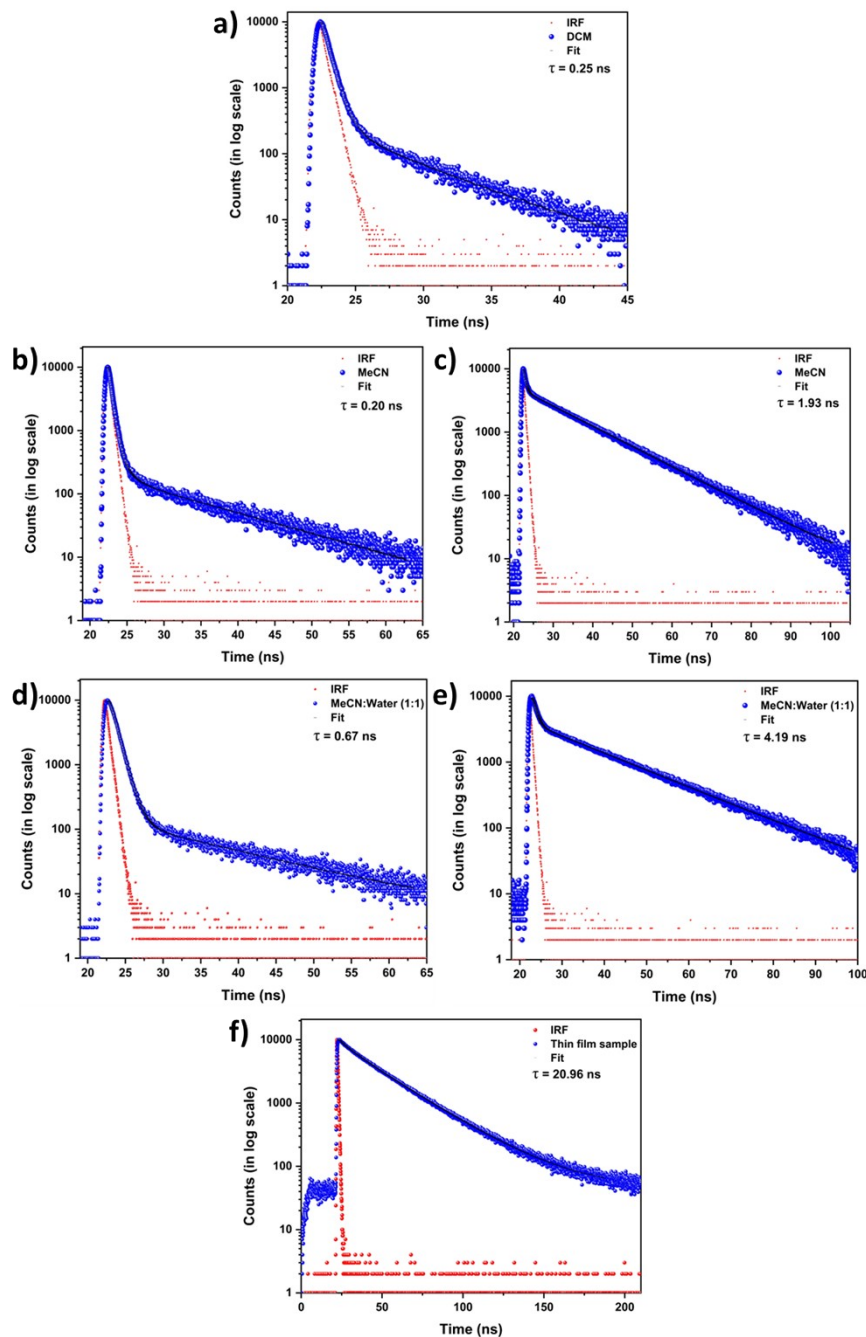


Fig. S4: Plots showing fluorescence lifetime decay curves (blue dots), corresponding fit (solid black line) and instrument response function (IRF, dotted red line) upon exciting the samples with (λ_{ex}) 320 nm light: (a) DCM ($\lambda_{\text{em}}=380$ nm); (b) MeCN ($\lambda_{\text{em}}=380$ nm); (c) MeCN ($\lambda_{\text{em}}=430$ nm); (d) MeCN:Water ($\lambda_{\text{em}}=390$ nm); (e) MeCN:Water ($\lambda_{\text{em}}=440$ nm); and (f) thin film ($\lambda_{\text{em}}=450$ nm).

Table T1. Summary of time resolved fluorescence lifetime measurement ($\lambda_{\text{ex}} = 320 \text{ nm}$).

a) DCM				
Monitor Wavelength $\lambda_{\text{em}} = 380 \text{ nm}$				
fitted decay times (Γ^i)	pre-exponential coefficients (α^i)	Relative Amplitude/%	Average Lifetime	χ^2
$\Gamma^1 = 0.840643 \text{ ns}$	$\alpha^1 = 0.026863$	8.96	0.252095 ns	1.009038
$\Gamma^2 = 5.39929 \text{ ns}$	$\alpha^2 = 0.005735$	12.28		
$\Gamma^3 = 0.205237 \text{ ns}$	$\alpha^3 = 0.967402$	78.76		

b) MeCN				
Monitor Wavelength $\lambda_{\text{em}} = 380 \text{ nm}$				
fitted decay times (Γ^i)	pre-exponential coefficients (α^i)	Relative Amplitude/%	Average Lifetime	χ^2
$\Gamma^1 = 1.24376 \text{ ns}$	$\alpha^1 = 0.009809$	5.87	0.207969 ns	1.093423
$\Gamma^2 = 13.1978 \text{ ns}$	$\alpha^2 = 0.003121$	19.81		
$\Gamma^3 = 0.156605 \text{ ns}$	$\alpha^3 = 0.98707$	74.33		

c) MeCN				
Monitor Wavelength $\lambda_{\text{em}} = 430 \text{ nm}$				
fitted decay times (Γ^i)	pre-exponential coefficients (α^i)	Relative Amplitude/%	Average Lifetime	χ^2
$\Gamma^1 = 0.229507 \text{ ns}$	$\alpha^1 = 0.871939$	10.35	1.933612 ns	1.140578
$\Gamma^2 = 13.5364 \text{ ns}$	$\alpha^2 = 0.8061$	89.65		

d) MeCN:Water				
Monitor Wavelength $\lambda_{\text{em}} = 390 \text{ nm}$				
fitted decay times (Γ^i)	pre-exponential coefficients (α^i)	Relative Amplitude/%	Average Lifetime	χ^2
$\Gamma^1 = 0.901429 \text{ ns}$	$\alpha^1 = 0.521978$	69.83	0.673805 ns	1.047293
$\Gamma^2 = 14.5988 \text{ ns}$	$\alpha^2 = 0.005177$	11.22		
$\Gamma^3 = 0.270062 \text{ ns}$	$\alpha^3 = 0.472845$	18.95		

e) MeCN:Water				
Monitor Wavelength $\lambda_{\text{em}} = 440 \text{ nm}$				
fitted decay times (Γ^i)	pre-exponential coefficients (α^i)	Relative Amplitude/%	Average Lifetime	χ^2
$\Gamma^1 = 0.778027 \text{ ns}$	$\alpha^1 = 0.786174$	14.59	4.191145 ns	1.126154
$\Gamma^2 = 16.7401 \text{ ns}$	$\alpha^2 = 0.213826$	85.41		

f) Thin film sample				
Monitor Wavelength $\lambda_{\text{em}} = 450 \text{ nm}$				
fitted decay times (Γ^i)	pre-exponential coefficients (α^i)	Relative Amplitude/%	Average Lifetime	χ^2
$\Gamma^1 = 10.5665 \text{ ns}$	$\alpha^1 = 0.166954$	8.41	20.96923 ns	0.980378
$\Gamma^2 = 27.2977 \text{ ns}$	$\alpha^2 = 0.696629$	90.69		
$\Gamma^3 = 1.38357 \text{ ns}$	$\alpha^3 = 0.136417$	0.90		

6. SEM images of **2(D)**

SEM images were acquired using the ZEISS EVO 18-SEM field emission scanning electron microscope, employing a 10 kV accelerating voltage. SEM sample was prepared by dissolving 2.8 mg of **2(D)** in 3.0 ml of MeCN/H₂O mixture (1:1). Sample was transferred on to a glass film and allowed to dry at room temperature. Gold sputtered sample was used for viewing.

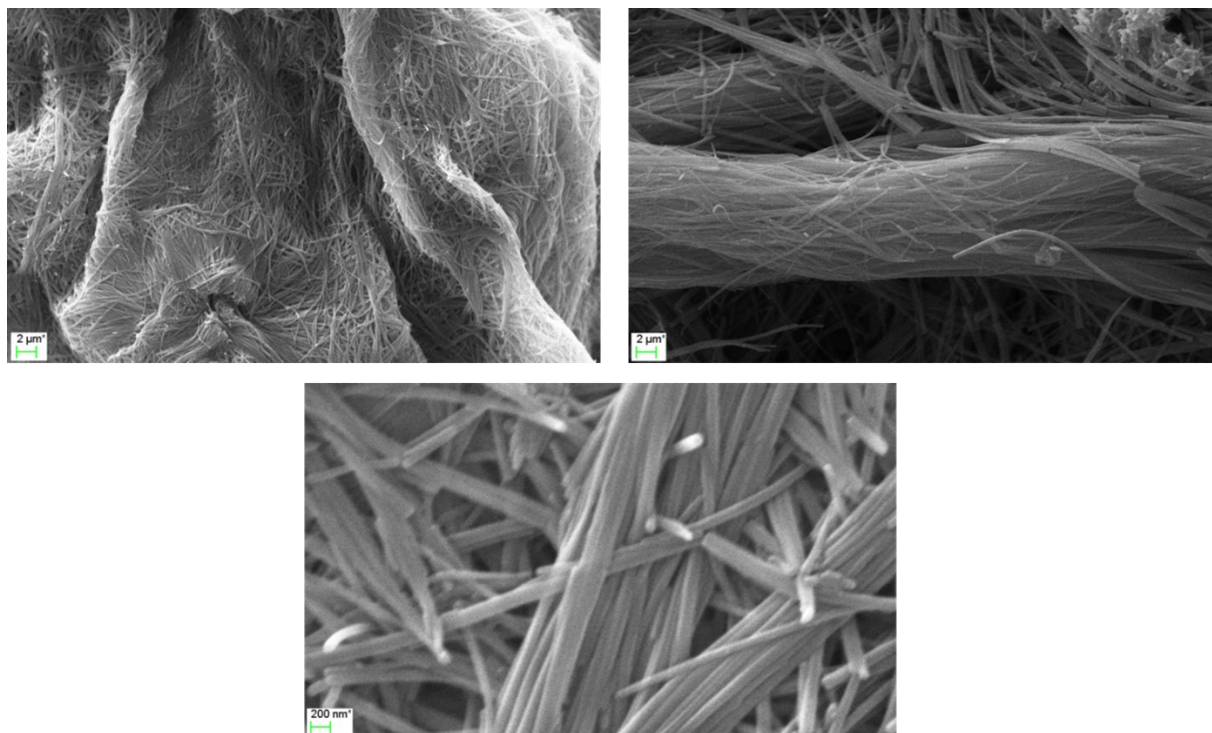


Fig. S5: SEM images of **2(D)** (1.44 mM) obtained from a MeCN:H₂O (1:1) mixture.

7. TD-DFT study and simulated CD spectrum

The optimized structure of the molecule was obtained using the Gaussian 09 software package.³ The most stable configuration was achieved with the def2svp basis set and pbepbe functional in dichloromethane (DCM) environment. Time dependent density functional theory (TD-DFT) calculations showed that the simulated absorption and CD spectra matches well with the experimental data. Additionally, natural bonding orbital (NBO) calculations were performed to visualize the orbitals and the transitions corresponding to the absorption maxima.

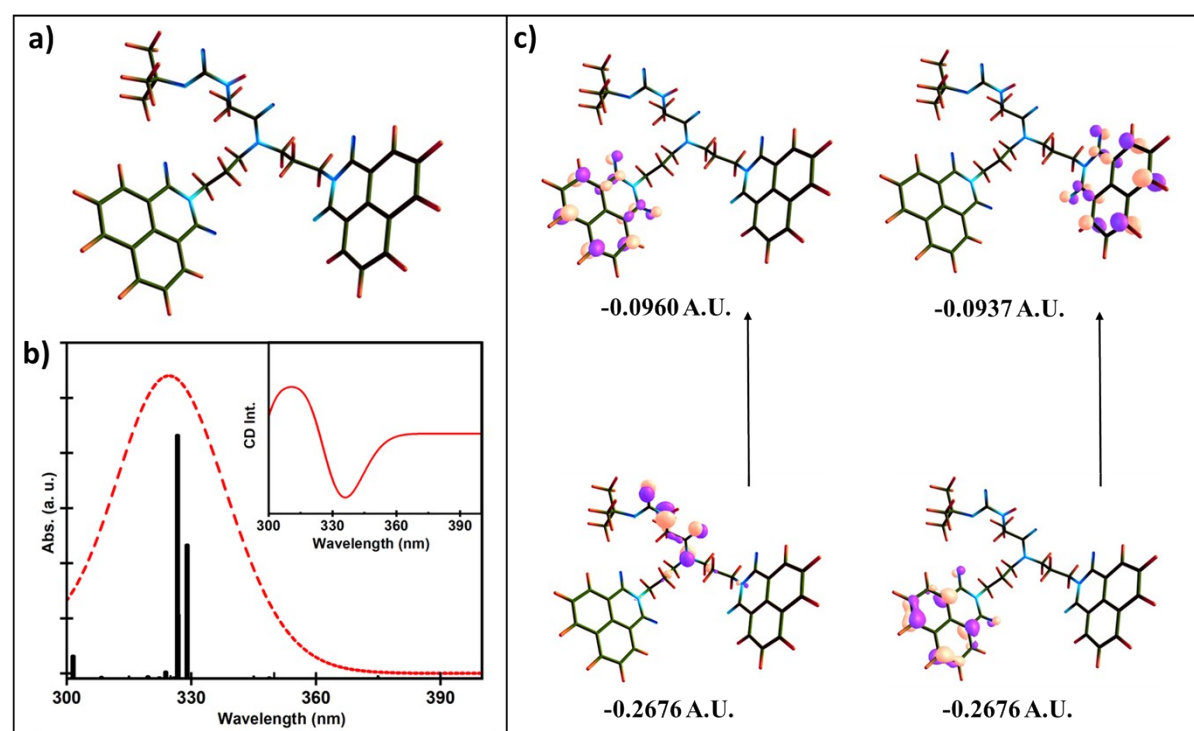


Fig. S6: (a) The geometry optimized structure of the molecule (**2**). (b) Theoretically simulated absorption spectra and simulated CD spectra (inset) obtained from TD-DFT calculation. (c) NBO diagram of the electronic transitions corresponding to the major two absorptions.

8. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$

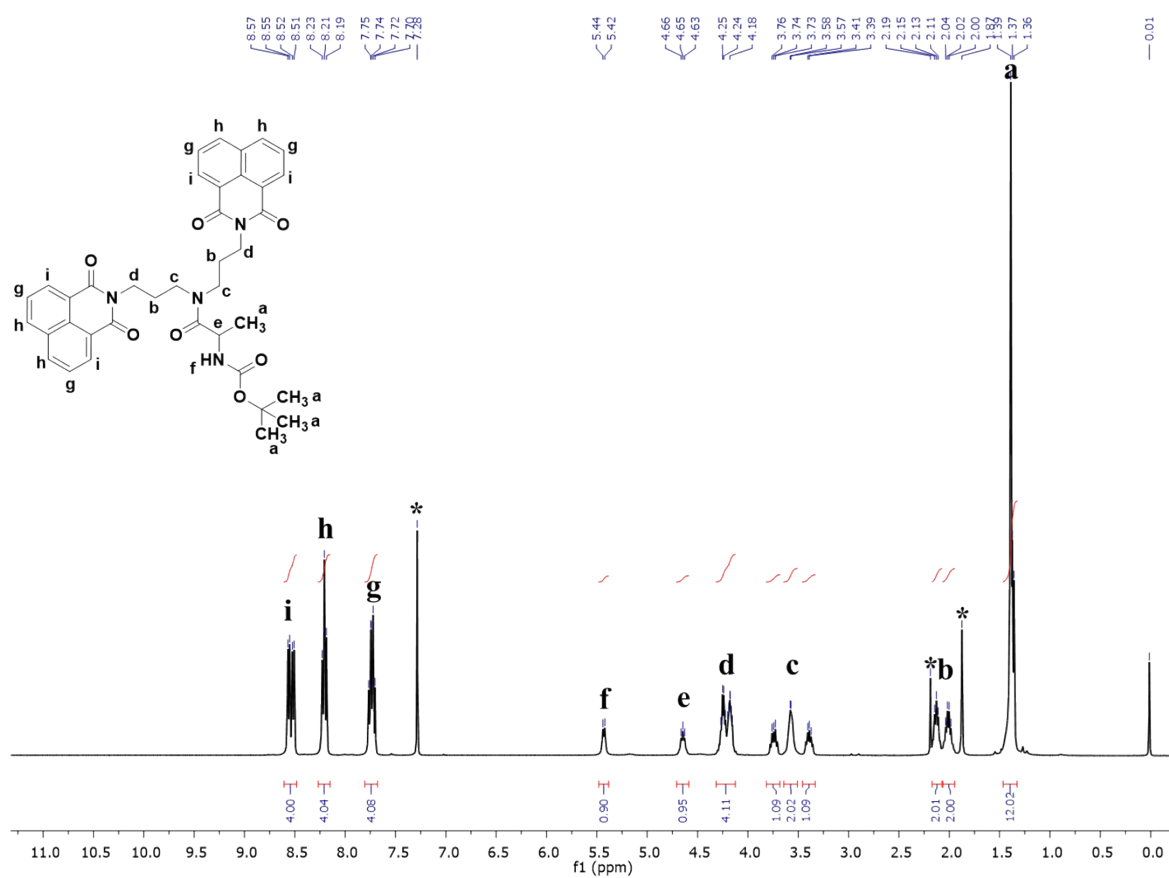


Fig. S7: $^1\text{H-NMR}$ spectrum of 2 in CDCl_3 . (* indicates peaks from residual solvent)

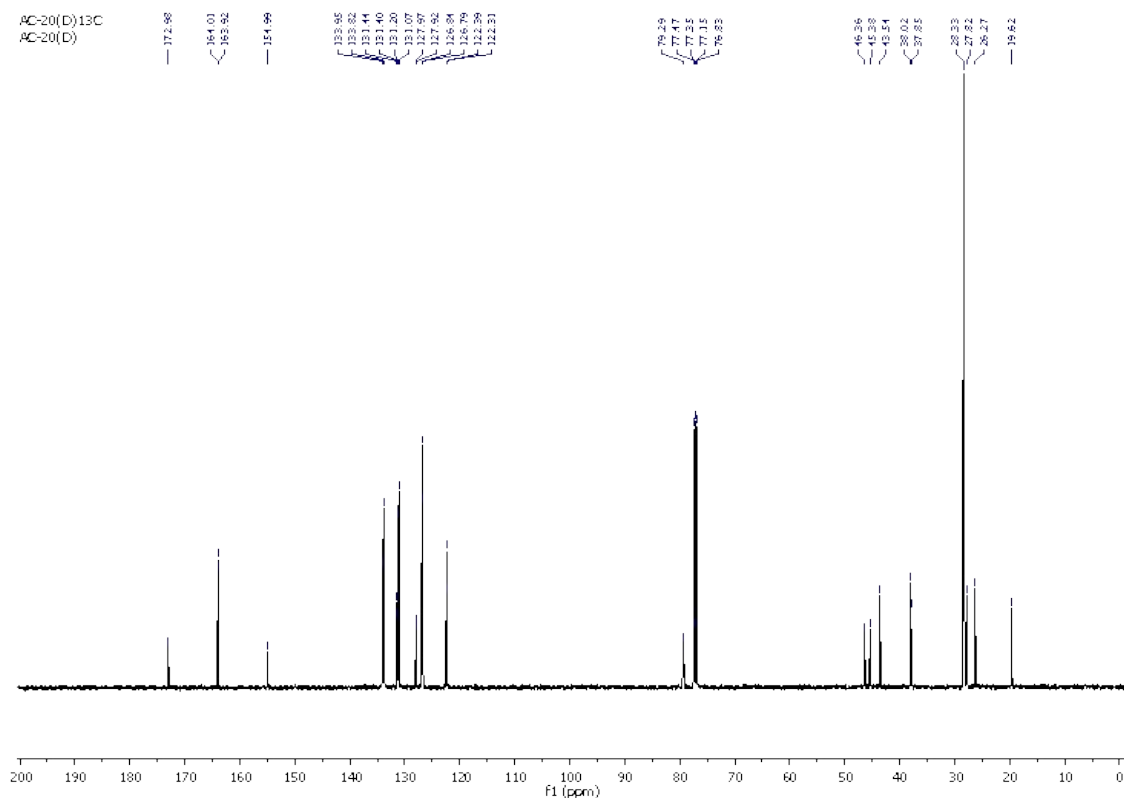


Fig. S8: ^{13}C NMR (CDCl_3 , 100 MHz) spectrum of **2**.

9. ESI-Mass Spectrum

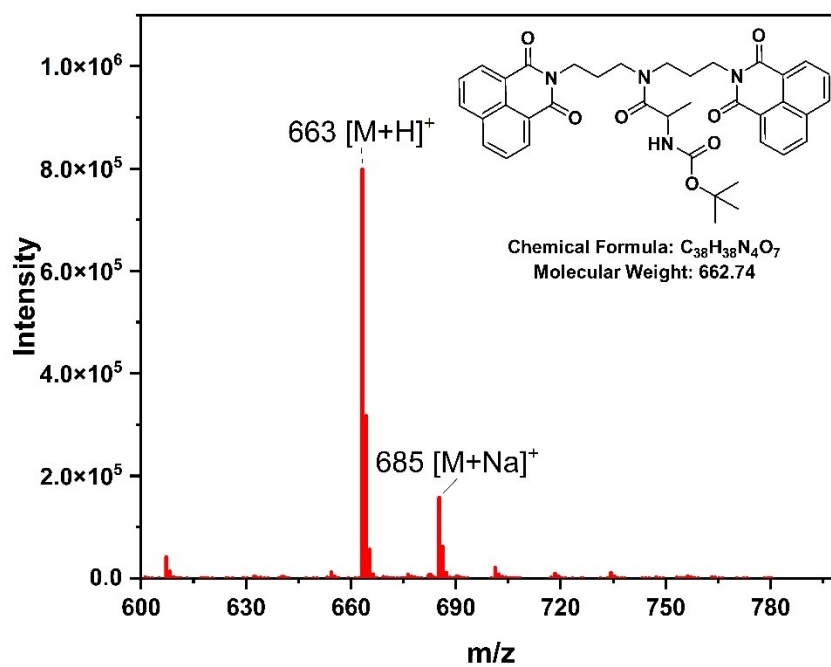


Fig. S9: Mass Spectrum of **2**.

10. References:

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