

Supplementary Information

A naphthalene-phenanthro[9,10-d]imidazole-based π -conjugated molecule with self-assembly-induced tuneable multiple fluorescence output exhibits artificial light-harvesting properties

Priya Rana ^{a, #}, Mallayasamy Siva ^{a, #}, Rabindranath Lo ^{b, *}, and Priyadip Das ^{a, *}

^aDepartment of Chemistry, SRM Institute of Science and Technology, SRM Nagar, Potheri, Kattankulathur, Tamil Nadu-603203, India

^bInstitute of Organic Chemistry and Biochemistry, Czech Academy of Sciences Flemingovo náměstí 542/2, Prague 160 00, Czechia

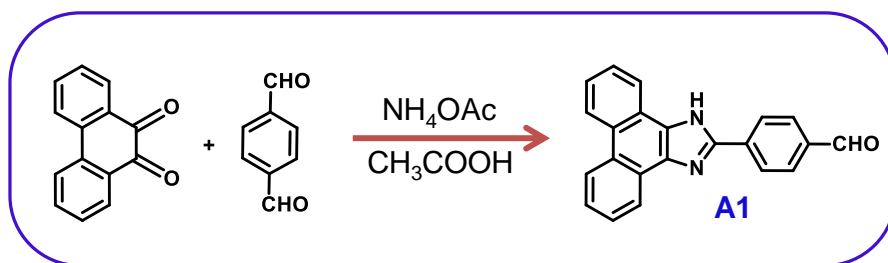
[#]Equal contribution

^{*}Corresponding author

^{*}Email: priyadipscmcri@gmail.com, priyadip@srmist.edu.in, and rabindranath.lo@uochb.cas.cz

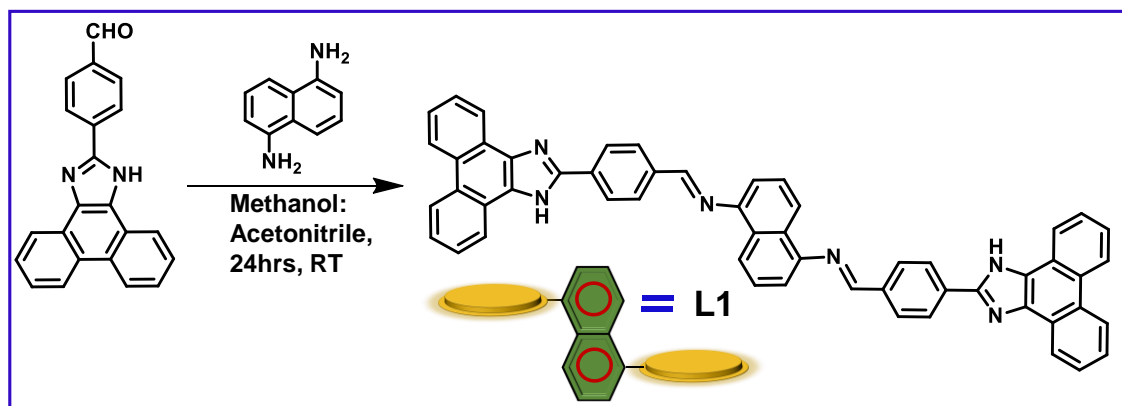
Experimental section

Synthesis of A1: A mixture of terephthalaldehyde (786.6 mg, 5.7 mmol), 9,10-phenanthrenequinone (400 mg, 1.90 mmol), and ammonium acetate (2.929 g, 38 mmol) in glacial acetic acid (15 mL) was heated at 100°C for 30 min with stirring. The hot reaction mixture was cooled to room temperature, whereupon a yellow solid separated. The yellow solid was collected by filtration and washed with dilute aqueous NaHCO₃ solution, and finally with water. This yellow residue was dried and purified by column chromatography on silica gel eluting with CH₃OH/CHCl₃ (5:95, v/v). Yield = 345.6 mg, (1.02 mmol, 54.07%) (Scheme S1). (¹H NMR, DMSO-*d*₆, 500 MHz, δ ppm): 10.02 (s, 1H), 8.81 (d, *J* = 6.5 Hz, 2H), 8.60 (d, *J* = 7.8 Hz, 2H), 8.51 (d, *J* = 8.2 Hz, 2H), 8.06 (d, *J* = 8.2 Hz, 2H), 7.72 (t, *J* = 7.4 Hz, 2H), 7.64 (t, *J* = 7.1 Hz, 2H).



Scheme S1: Synthetic methodologies adopted for the synthesis of **A1**

Synthesis of L1: **L1** was prepared by condensation of **A1** (200mg, 0.62 mmol) in acetonitrile with Naphthalene 1,5-diamine (49.00mg, 0.31 mmol) in dry methanol (30 mL) and the mixture was stirred at room temperature for 24 hours. The progress of the reaction was monitored by TLC. On completion of the reaction, the precipitate was separated as a yellow-colored product which was filtered, dried, and recrystallized from cold methanol. Yield: 210.58 mg (0.27 mmol, 88.65%) (Scheme S2). (^1H NMR, $\text{DMSO-}d_6$, 500 MHz, δ ppm): 13.64 (s, 2H, 2CH=N,), 10.02 (s, 2H, 2NH,), 8.87-8.86(m,4H), 8.54-8.49 (m,4H), 8.46-8.44 (m, 4H), 8.05 (d, $J = 8.0$ Hz, 4H), 7.69 (t, $J = 8.0$ Hz, 4H), 7.60 (s, 4H). ^{13}C NMR (125 MHz, $\text{DMSO-}d_6$, δ ppm):197.83, 197.55, 189.48, 157.02, 151.89, 142.08, 139.76, 135.35, 133.41, 132.79, 132.45, 131.73, 129.36, 128.07, 127.42, 127.24, 119.95, 117.07. ESI-MS (m/z): $[\text{M}]^+ = 766.28$ (calculated); 767.45 (observed) (Scheme S2).



Scheme S2: Synthetic methodologies adopted for the synthesis of **L1**.

Spectroscopic characterization:

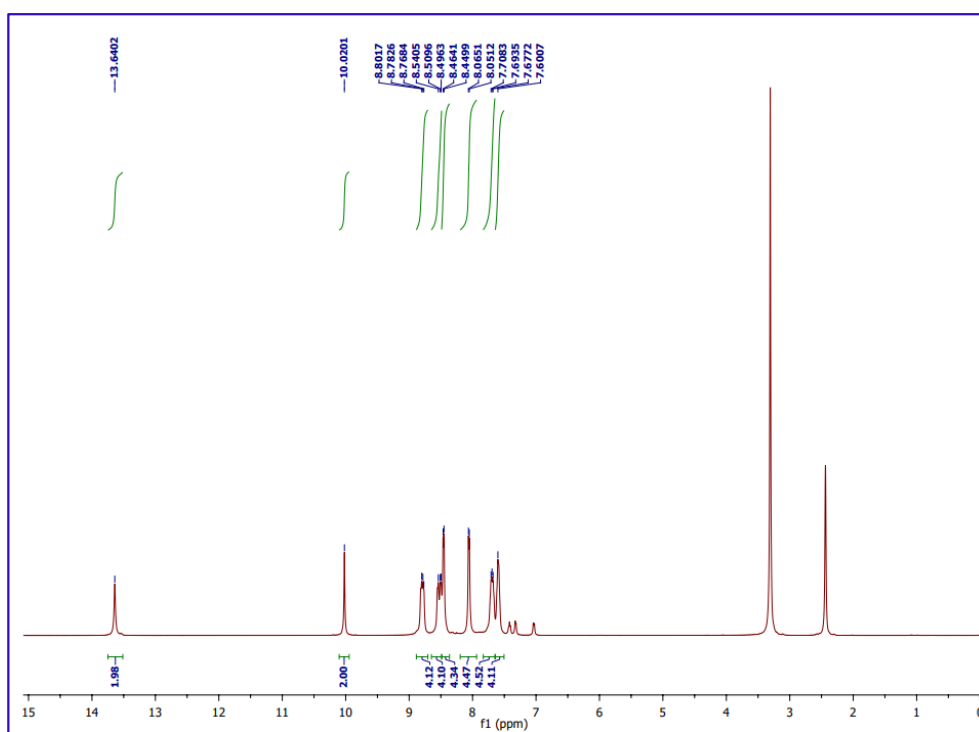


Figure S1: ^1H NMR ($\text{DMSO-}d_6$, 500 MHz, δ ppm) of L1.

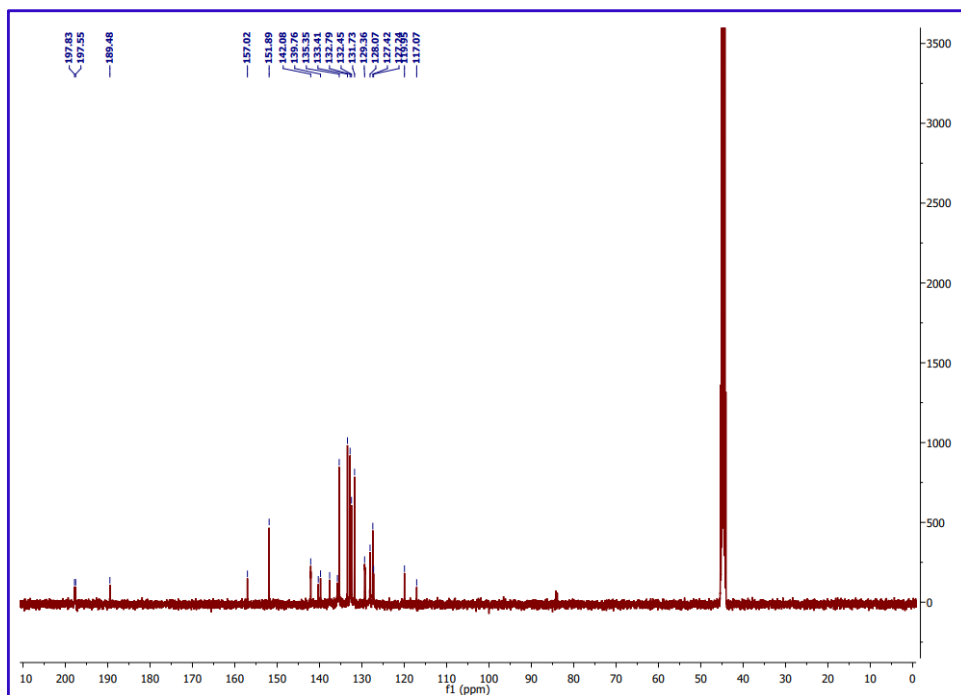


Figure S2: ^{13}C NMR (DMSO- d_6 , 126 MHz, δ ppm) of L1.

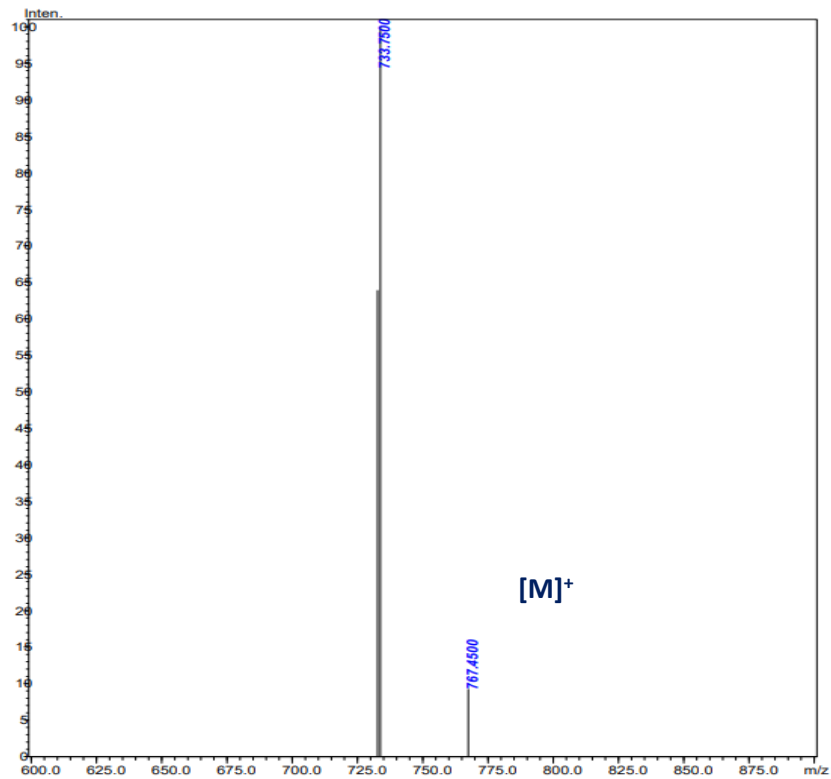


Figure S3: ESI Mass spectra of L1.

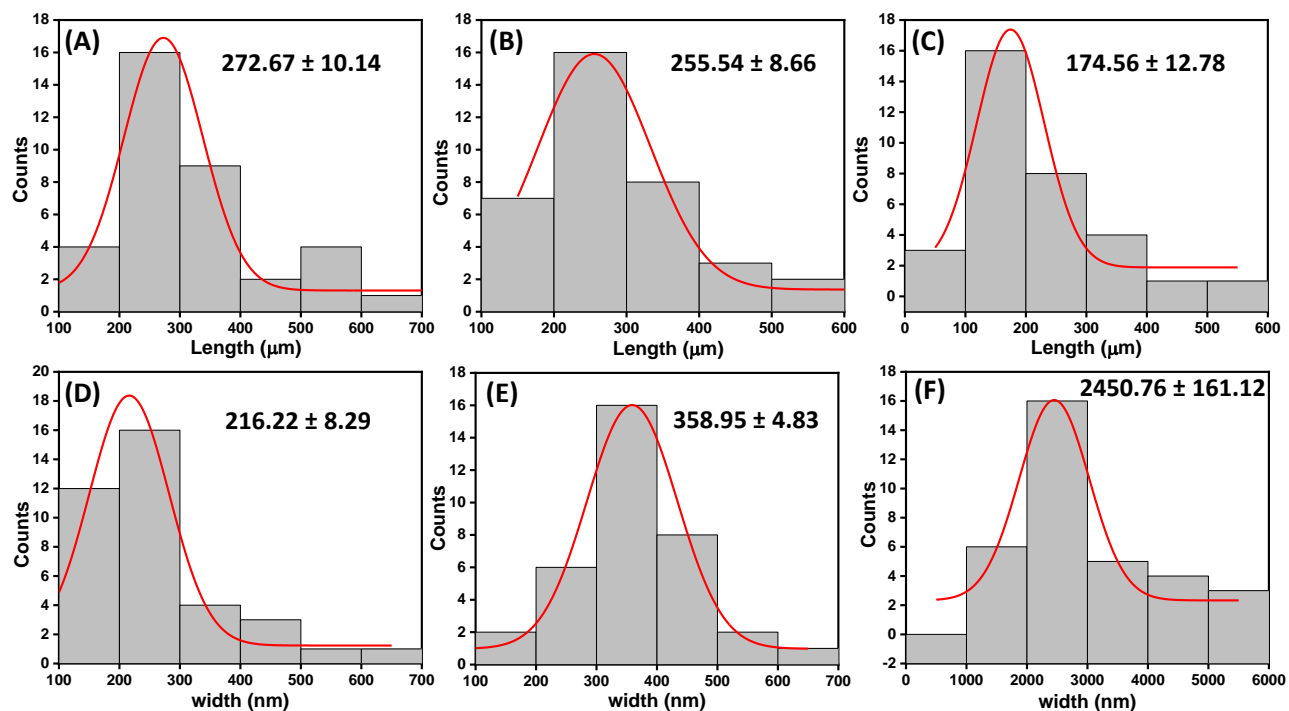


Figure S4. Length distribution of the self-assembled structures formed by **L1** in THF : water = 7 : 3 mixture (A), THF : water = 4 : 6 mixture (B), and THF : water = 1 : 9 mixture (C) obtained from HR-SEM images. Width distribution of the self-assembled structures formed by **L1** in THF : water = 7 : 3 mixture (D), THF : water = 4 : 6 mixture (E), and THF : water = 1 : 9 mixture (F) obtained from HR-SEM images.

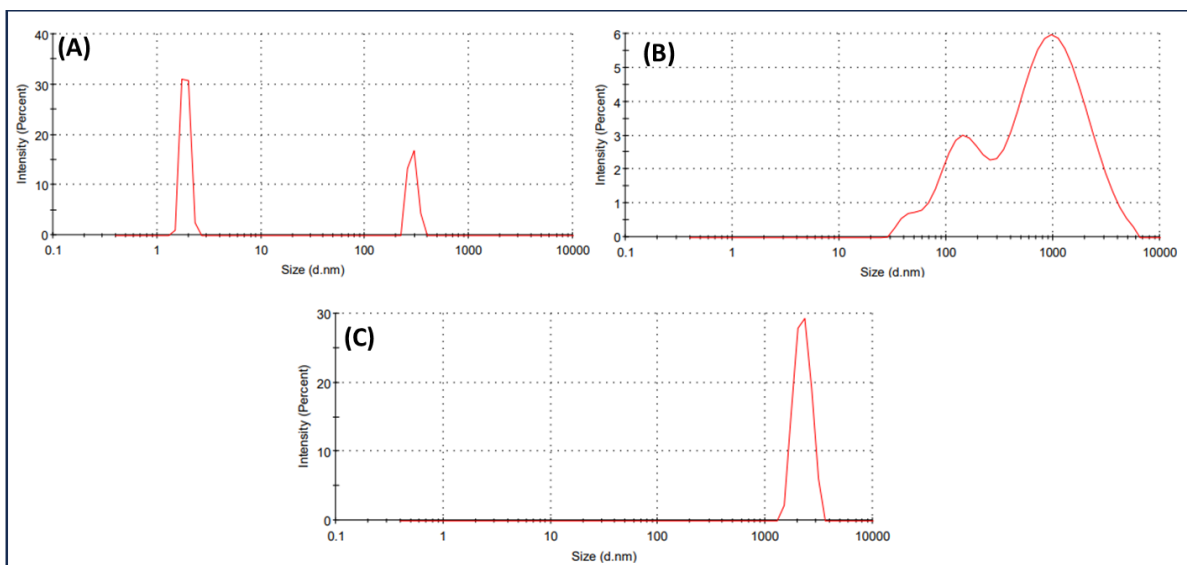


Figure S5: Size distribution obtained from DLS measurements for **L1** in (A) THF : water = 7 : 3 mixture, (B) THF : water = 4 : 6 mixture, and (C) THF : water = 1 : 9 mixture is 224 nm, 374 nm, and 2155nm respectively.

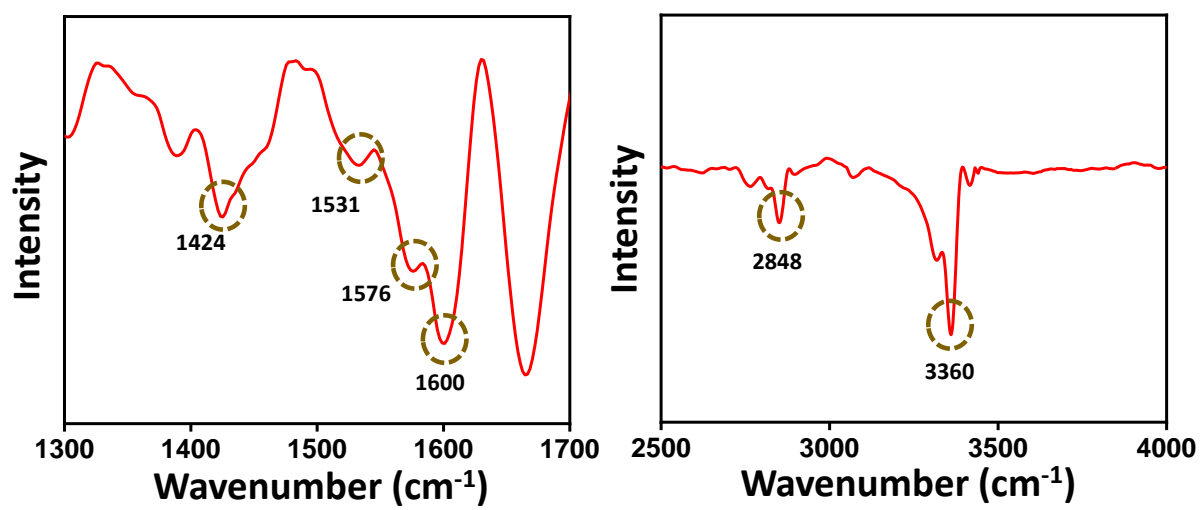


Figure S6: The FT-IR spectra of the dried mass of **L1** obtained in its unassembled or monomeric form.

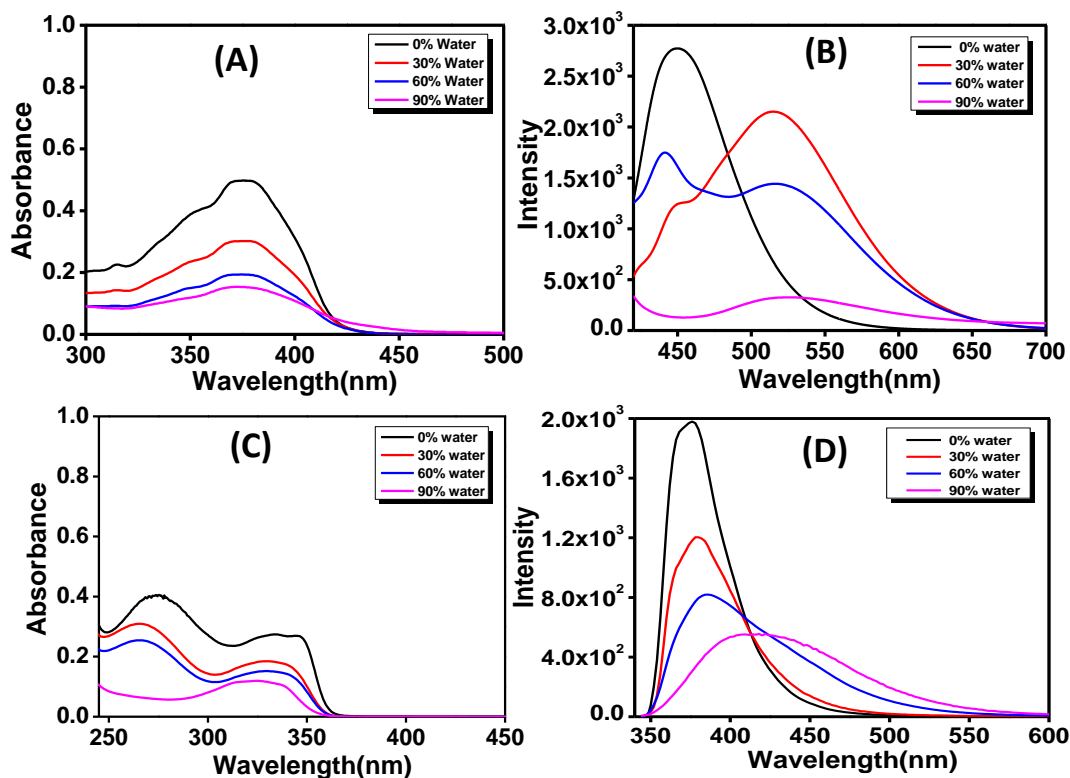


Figure S7: (A, B) UV-Vis absorbance and emission spectra of A1 (Aldehyde) and (C, D) UV-Vis absorbance and emission spectra of naphthalene 1,5-diamine (B1) in 100% THF and THF: water mixtures (THF : water = 7 : 3, 4 : 6 and 1 : 9)

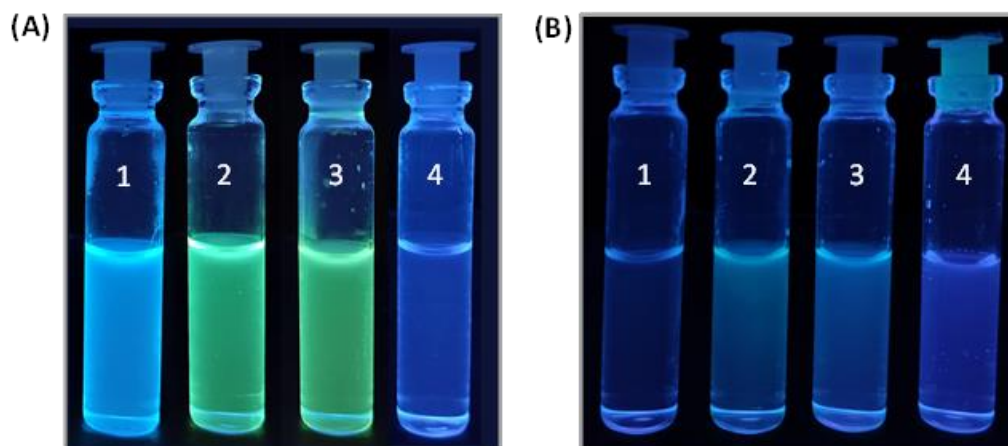


Figure S8. Photographs showing the different fluorescence colours of Aldehyde (A1) and 1,5-diamine (B1) in THF and THF-water mixer solvent medium. (1 = 100% THF, 2 = THF : water = 7 : 3, 3 = THF : water = 4 : 6, and 4 = THF : water = 1 : 9)

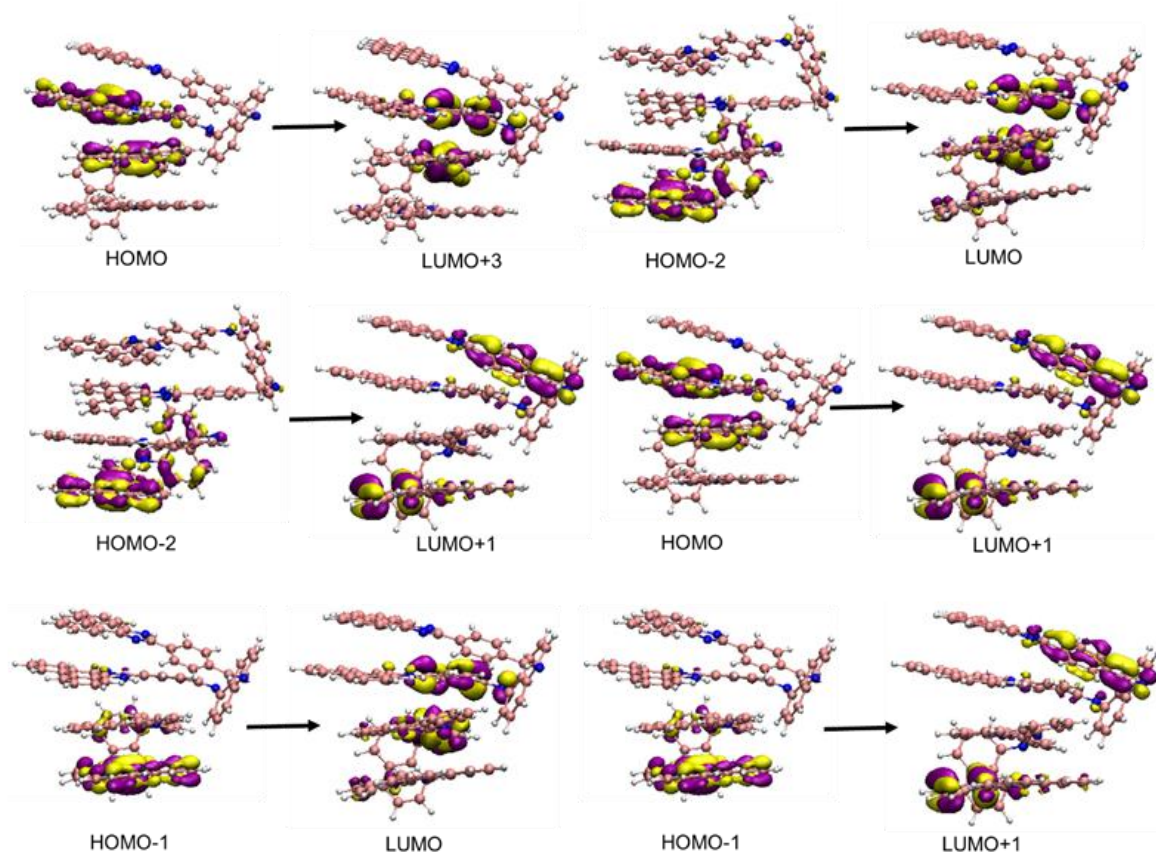


Figure S9. Frontier molecular orbitals of the calculated minima structure of S2-dimer involved in the main absorption peak at wB97XD/def2-TZVPP in THF solvent. [C: pink, N: blue, H: grey] The density of molecular orbitals is shown in yellow and violet colour with isosurface value of 0.03.

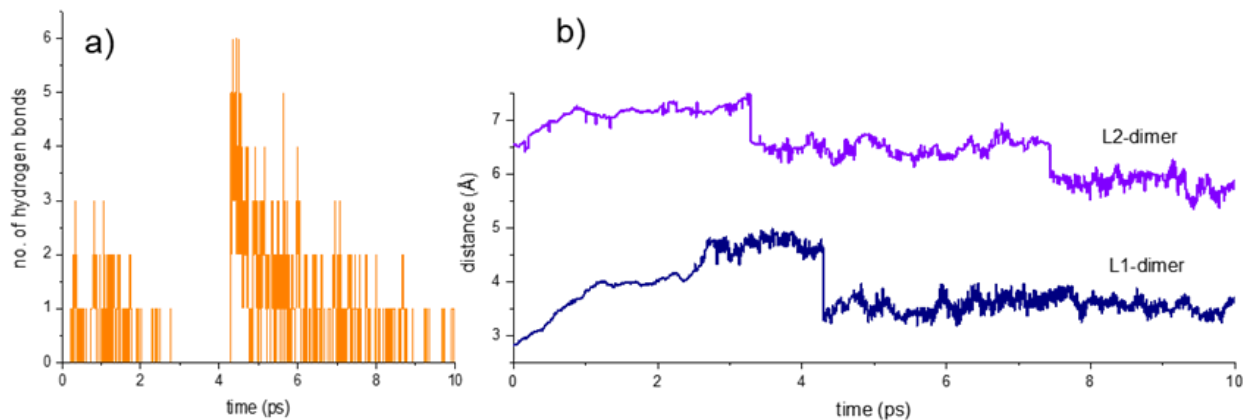


Figure S10 a) The no. of hydrogen bonds formed between S1-dimeric form of **L1** with explicit water molecules during the simulation time of 10 ps. b) The variation of the bond length between the center of mass of S1 and S2 monomers with time.

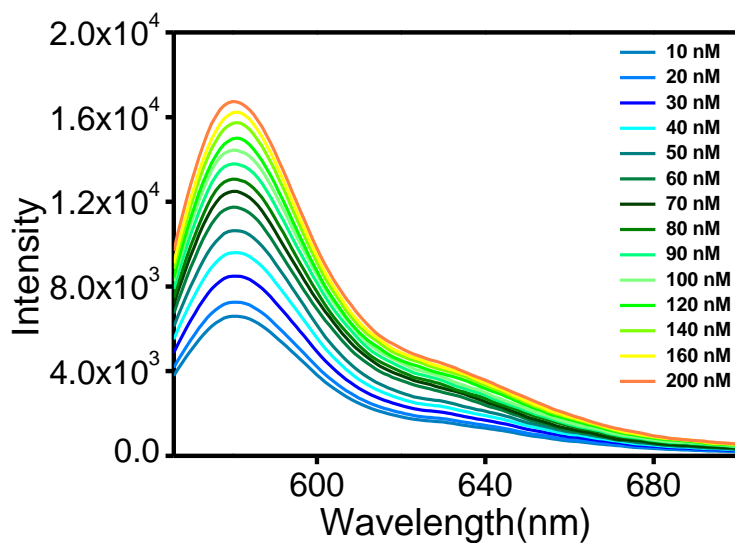


Figure S11 The emission spectra of RhB at varying concentration without the donor **L1** ($\lambda_{\text{ext}} = 560$ nm).

We have performed the antenna effect measurements using a fixed concentration of donor **L1** at 20 μM , while varying the RhB concentrations from 10 nM to 200 nM in a THF : water = 1 : 1 solvent mixture. Specifically, we quantified the antenna effect of this light harvesting system at varying RhB concentrations of 20 nM, 80 nM, 120 nM, and 200 nM in presence and absence of the donor moiety, which exhibited antenna effects of 6, 17, 39, and 51, respectively using the following equation 2

$$AE = F_{A(382\text{ nm})} / F_{A(560\text{ nm})} \dots\dots\dots (2)$$

Where $F_{A(382\text{ nm})}$ is the emission intensity of the acceptor RhB at corresponding emission maxima in presence of donor ($\lambda_{\text{ext}}=382\text{ nm}$). $F_{A(560\text{ nm})}$ is the emission intensity of the acceptor RhB at corresponding emission maxima in absence of donor ($\lambda_{\text{ext}}=560\text{ nm}$)

Table S1. Antenna effect with different donor/acceptor concentrations of L1/RhB.

Samples	Concentration, respectively	Antenna Effect
L1+RhB	[L1] = 20×10^{-6} M [RhB] = 20×10^{-9} M	6
L1+RhB	[L1] = 20×10^{-6} M [RhB] = 80×10^{-9} M	17
L1+RhB	[L1] = 20×10^{-6} M [RhB] = 120×10^{-9} M	39
L1+RhB	[L1] = 20×10^{-6} M [RhB] = 200×10^{-9} M	51