

Supporting Information for

J-aggregation of a Sulfur-Substituted Naphthalenediimide (NDI) with Remarkably Bright Fluorescence

Haridas Kar and Suhrit Ghosh *

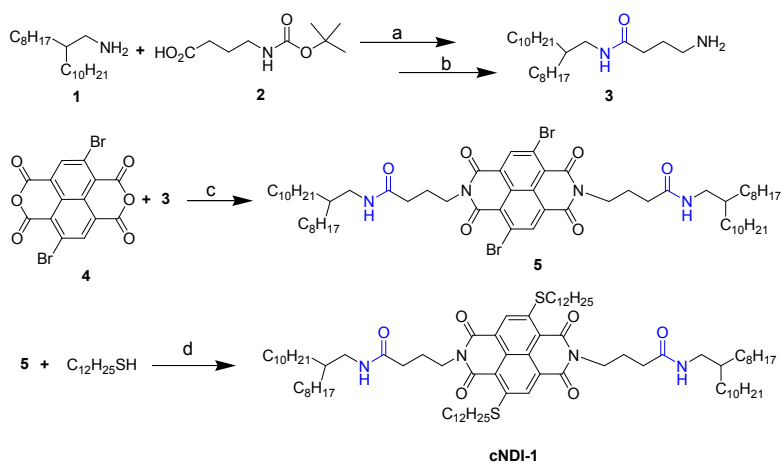
Indian Association for the Cultivation of Science, Polymer Science Unit, 2A & 2B Raja S. C. Mullick

**Corresponding author's email: psusg2@iacs.res.in*

Materials and Methods:

All reagents were procured from Sigma Aldrich Chemical Co. and used without further purification. Solvents were purchased from commercial sources and purified by reported protocol.¹ Spectroscopy grade solvents were used for physical studies. ¹H NMR and ¹³C NMR experiments were done on a Bruker DPX-300 MHz and 500 MHz NMR machine and all the data were calibrated against TMS. UV/Vis absorption experiments were performed in a Perkin-Elmer Lambda 25 spectrometer. Mass spectrometry data were acquired by an electron spray ionization (ESI) technique on a Q-tof-micro quadrupole mass spectrometer (Micro mass). Photoluminescence studies were performed in a Horiba FluoroMax-3 spectrophotometer. FT-IR spectra were recorded in a Perkin Elmer Spectrum 100FT-IR spectrometer. AFM was done in Bruker-Innova instrument in tapping mode. TCSPC. XRD data was recorded on a Seifert XRD3000P diffractometer having a Cu K α radiation source (λ = 0.15406 nm) operating at a voltage and current of 40 kV and 30 mA, respectively.

Synthesis:



Reagents and conditions: a) EDC, DMAP, CHCl_3 , ice cold to RT, 12h, 80% b) 4 M HCl in dioxane/ H_2O , 30 min; K_2CO_3 , CHCl_3 , 3h, 85% c) Acetic Acid, 3h, 90°C, 50% d) K_2CO_3 , CHCl_3 , 12h, 50°C, 70%

Scheme 1: Synthesis of cNDI-1

Compound 3: Compound 2 (1.6 gm, 7.87 mmol) was dissolved in chloroform (15 ml) and placed in an ice bath. To this cold solution, compound 1 (1.95 gm, 6.56 mmol),² DMAP (0.24 gm, 1.96 mmol) and EDC (1.22 gm, 7.87 mmol) were added sequentially and the reaction mixture was stirred at rt under nitrogen atmosphere for 12 h. Subsequently the crude product was diluted with CHCl_3 (10 ml) and washed with water (2 x 50 ml). The organic layer was dried over anhydrous sodium sulphate and then solvent was removed to get the crude product as a waxy material. It was dissolved in 4.0 (M) HCl in dioxane / H_2O (5/4 ml) and stirred for 30 min at rt. After that dioxane was removed under reduced pressure and the crude product was dissolved in CHCl_3 (10 ml) and potassium carbonate (3.2 gm, 23.3 mmol) was added and stirred for 3h at rt. Then, the reaction mixture was poured into excess water and the organic layer was separated out, passed through sodium sulphate and solvent was removed under reduced pressure. The desired product was obtained as light yellow oil in 68% yield. ^1H NMR (CDCl_3 , 500 MHz, TMS): δ (ppm) = 5.91 (1H, broad), 3.16 (2H, t, $J = 5.5$ Hz), 2.74 (2H, t, $J = 7.0$ Hz), 2.23 (2H, t, $J = 7.5$ Hz) 1.77-1.73 (3H, m), 1.28-1.24 (32H, m), 0.89-0.86 (6H, t, $J = 6.5$ Hz)

Compound 5: Dibromo-NDA 4 (0.22 gm, 0.52 mmol) was prepared following reported procedure³. It was taken together with compound 3 (1.0 gm, 2.61 mmol) in acetic acid (10 ml) and the suspension was refluxed for 3h under argon atmosphere while it became a clear solution. Then, the solution was allowed to cool to rt and precipitated out in water (40 ml) to get a yellow sticky solid which was washed with methanol (2 x 30 ml) and taken to the next step without further purification. Yield: 0.35 gm, 58%. ^1H NMR (CDCl_3 , 400 MHz, TMS): δ (ppm) = 8.96 (2H, s), 5.74 (2H, s), 4.27 (4H, t, $J = 6.4$ Hz), 3.15 (4H, t, $J = 5.6$ Hz), 2.32 (4H, t, $J = 7.2$ Hz), 2.14-2.11 (6H, m), 1.42-1.21 (64H, m), 0.88-0.86 (12H, t, $J = 5.6$ Hz).

cNDI-1: To a solution of compound 5 (0.32 gm, 0.27 mmol) in CHCl₃ (12 ml), dodecane thiol (1.12 gm, 5.53 mmol) and potassium carbonate (0.76 gm, 5.53 mmol) were added and refluxed for 12h under argon atmosphere. Then, the reaction mixture was allowed to cool to rt and diluted with CHCl₃(10 ml). The organic layer was washed with water (3 x 50 ml) and dried over anhydrous sodium sulfate. Then excess solvent was removed to get the crude product as a red solid. It was further purified by column chromatography where silica gel (100-200 mesh) was used as stationary phase and DCM: MeOH (99:1) was used as eluent to get the pure product as red solid in 90 % yield. ¹HNMR (CDCl₃, 500 MHz, TMS): δ (ppm) = 8.62 (2H, s), 5.94 (2H, s), 4.25 (4H, t, J = 6.5 Hz), 3.17 (8H, t, J = 5.5 Hz), 2.31 (4H, t, J =6.0 Hz), 2.12 (4H, t, J =7.0 Hz), 1.86 (4H, t, J =7.5 Hz), 1.58 (4H, t, J =7.5 Hz), 1.26-1.22 (98H, m), 0.89-0.83(18H, m); ¹³C NMR (CDCl₃) δ (ppm) =172.2, 163.6, 162.6, 149.1, 128.4, 125.0, 123.7, 119.4, 43.0, 40.5, 38.0, 34.4, 32.5, 32.0, 30.2, 29.8, 29.7, 29.6, 29.5, 29.4, 28.1, 26.8, 24.4, 22.8, 14.2 HRMS (ESI): m/z calc for C₈₆H₁₄₈N₄O₆S₂ [M + 2H]⁺: 1399.085; found: 1399.093.; M.P: 172 $\pm$ 3 °C ; UV/ Vis: extinction coefficient (ϵ) in DCM : 11000 (350 nm) , 13900 (367 nm), 12100 (487 nm), 19900 (520 nm) M⁻¹ cm⁻¹; FT-IR (KBr) : 3320, 2958, 2924, 2873, 2854, 1700, 1693, 1648, 1581.

Analysis of temperature dependent UV/ Vis absorption data by nucleation-elongation model: We have attempted to fit the cooling curves (Fig 3d) by nucleation-elongation model which is also known as cooperative model, proposed by Meijer and co-workers.⁴ In MATLAB R2009 a software, all data were fitted using the following equations.

$$\alpha_{agg} = \frac{A(T) - A_{mon}}{A_{agg} - A_{mon}} \text{-----(1)}$$

$$\alpha_{agg} = \alpha_{const} \left[1 - \exp\left(\frac{-h_e}{RT_e^2}(T - T_e)\right) \right] \text{-----(2)}$$

$$\alpha_{agg} = \alpha_{const} \left[\sqrt[3]{K_a} \exp\left[\left(\frac{2}{3\sqrt[3]{K_a}} - 1\right) \frac{-h_e}{RT_e^2}(T - T_e)\right] \right] \text{-----(3)}$$

$$\langle N_n(T_e) \rangle = \frac{1}{\sqrt[3]{K_a}} \text{-----(4)}$$

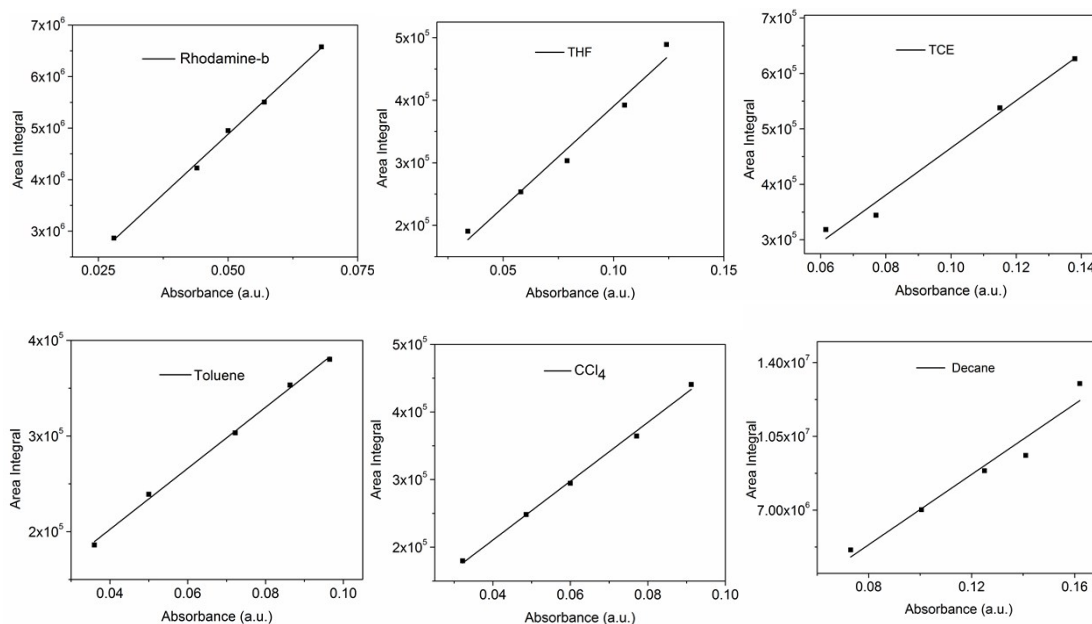
A (T) is absorbance at different temperature, A_{mon} is absorbance in monomeric state, A_{agg} is absorbance in aggregated state. α_{const} is the parameter which ensures $\alpha_{agg}/\alpha_{const}$ does not exceed unity, h_e is the molecular enthalpy released owing to non covalent interaction during elongation, T is absolute temperature, T_e is elongation temperature, R is ideal gas constant, K_a is the dimensionless equilibrium constant of the activation step at T_e, $\langle N_n(T_e) \rangle$ is average length of the stack averaged over the nucleated species at the T_e.

Determination of quantum yield: To determine fluorescence quantum yield⁵ of cNDI-1 in different solvents (TCE, Toluene, CCl₄, Decane, THF), we have used emission of Rhodamine-B in water as a standard. First, we have prepared stock solution of cNDI-1 at different concentration in various solvents and recorded absorption spectra where intensity is less than 0.10. After that we have recorded emission spectra and calculated area integral for each spectrum using Origin 8.0. The area integral was further plotted against absorbance maxima and by linear fitting of the data, the gradient was calculated (shown

below). Similarly, the gradient of standard was also calculated. Quantum yield was then calculated using equation 5.

$$\phi_X = \phi_{ST} \left(\frac{Grad_X}{Grad_{ST}} \right) \left(\frac{\eta_X^2}{\eta_{ST}^2} \right) \text{-----} (5)$$

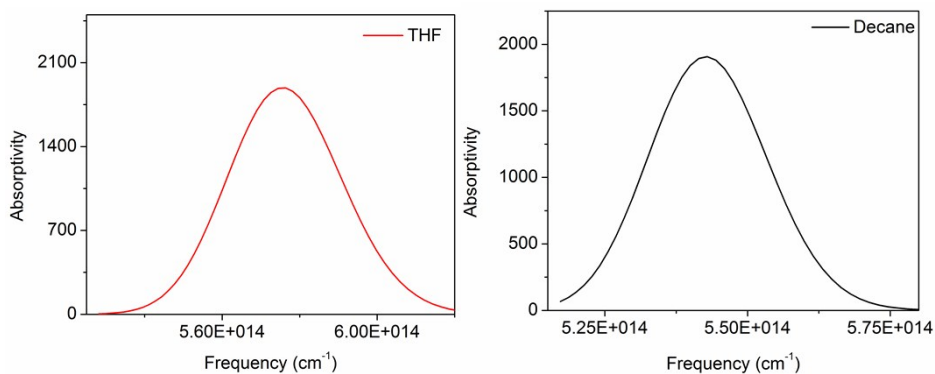
Where ST and X represents standard and test, respectively; η is refractive index; Grad is the gradient from the plot of area integral of fluorescence spectrum vs corresponding absorbance. The excitation wavelength was 480 nm and quantum yield of standard (ϕ_{ST}) = 0.31.



Calculation of oscillator strength: Oscillator strength⁵ in THF and decane were estimated from deconvoluted S₀-S₁ transition band (shown below). We have thus calculated $\nu_{\max}$ and Einstein coefficient (B₁₂). Then using equation 6, we have determined corresponding oscillator strength.

$$f = \frac{4\epsilon_0 m_e h \nu}{e^2} B_{12} \text{-----} (6)$$

Where f = oscillator strength, ϵ_0 = vacuum permittivity, m_e = mass of the electron, h = plank constant, ν = frequency, e = charge of the electron, B₁₂ = Einstein coefficient. Calculation is done in SI unit.



Additional Figures:

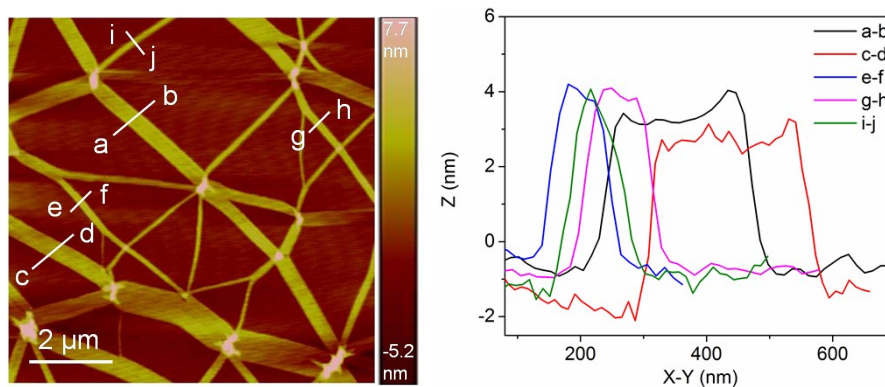


Fig S1: *Left*, AFM image of diluted gel of cNDI-1; *right*, cross section analysis of selected regions.

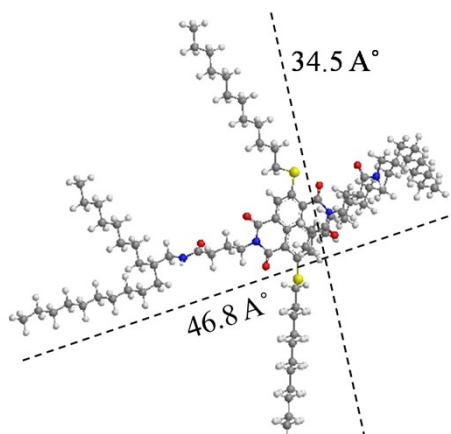


Fig S2: Energy minimized structure of the cNDI-1. Molecular modeling was done in Chem3D Ultra 8.0 using MM2 for energy minimization.

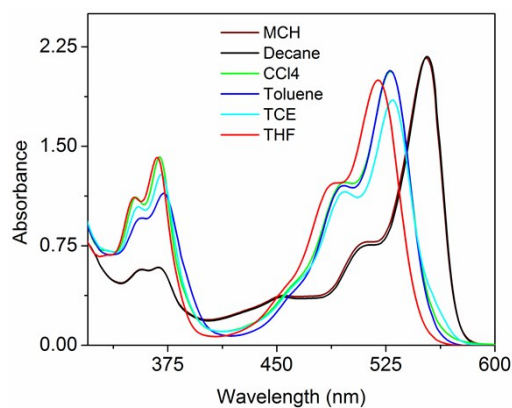


Fig S3: Solvent dependent UV/Vis study of cNDI-1. Where $c=0.1$ mM, $l=1$ cm, $T=25^{\circ}\text{C}$

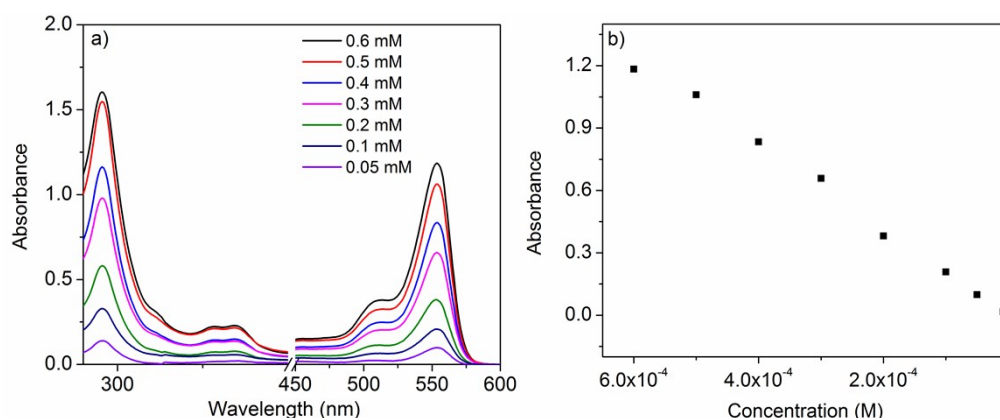


Fig S4: a) Concentration dependent UV-Vis study of cNDI-1; $l=0.1$ cm, $T=25^{\circ}\text{C}$. b) Absorbance vs concentration plot for the band at 552 nm.

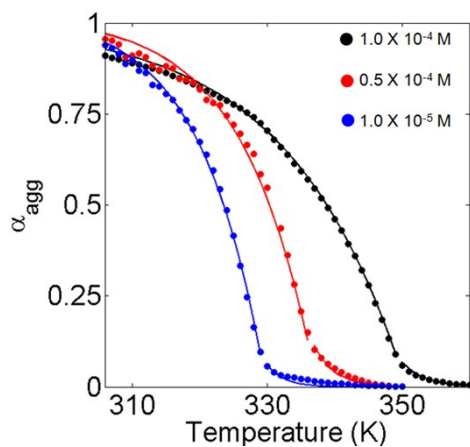


Fig S5: α_{agg} (equation 1) vs temperature data (Fig 3d) were fitted by nucleation and elongation model using MATLAB 2009a software. Elongation and nucleation regimes were independently fitted with equation 2 and 3, respectively.

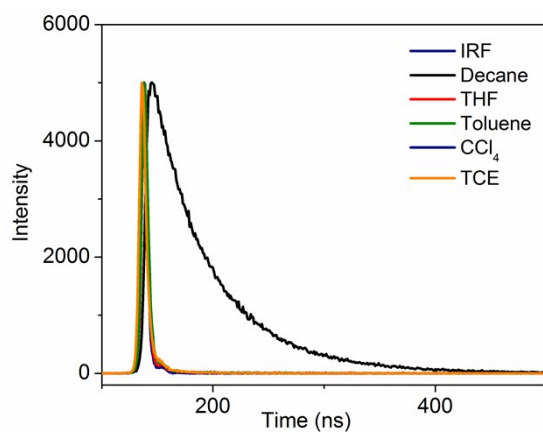


Fig S6: Time resolved fluorescence decay of cNDI-1 in different solvents. Where $\lambda_{\text{ex}}=440$ nm, $c=0.1$ mM.

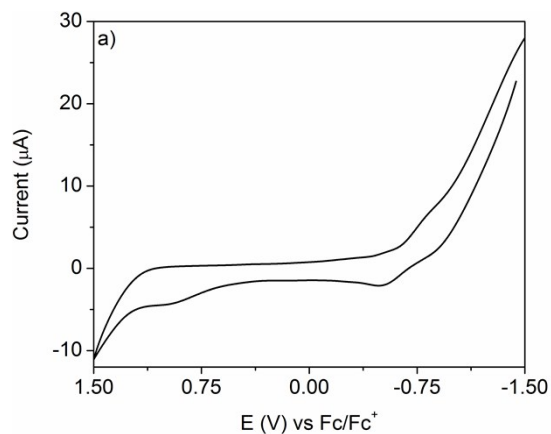


Fig S7: Cyclic voltammogram of cNDI-1 against Fc/Fc^+ ; scanning rate: 100 mV/s; $T = 298$ K. Tetrabutyl ammonium chloride was used as an internal standard. The LUMO energy level was calculated using the following equation: $E_{\text{LUMO}} = -e (E_{1/2(\text{redox})} - E_{\text{Fc}} + 4.8)$ where $E_{\text{Fc}} = 0.39$ V (versus Ag/AgCl).

Table S1: Results of gelation test in few organic solvents ($c=3\text{mM}$)

THF	CHCl_3	Decane	TCE	CCl_4	MCH	Toluene	Dioxane
Solution	Solution	Gel	Solution	Solution	Gel	Solution	Solution

Table S2: Thermodynamic parameters extracted from the fitted data shown in Fig S5

Concentration	α_{const}	h_e	K_a	T_e	$N_n(T_e)$
1.0×10^{-4} M	1.001	-60.2	0.0013	350.7 K	9
0.5×10^{-4} M	1.021	-90.0	0.0025	337.4 K	8
1.0×10^{-5} M	1.030	-95.4	0.0030	329.9 K	7

References:

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2. T. Mondal, D. Basak, A. Al Ouahabi, M. Schmutz, P. Mésini, S. Ghosh, *Chem. Commun.*, 2015,**51**, 5040.
3. M. Sasikumar, Y. V. Suseela, T. Govindaraju, *Asian J. Org. Chem.*, 2013, **2**, 779.
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5. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy* (2nd ed.) Kluwer Academic/Plenum Publishers: New York 1999.