

Supporting Information for

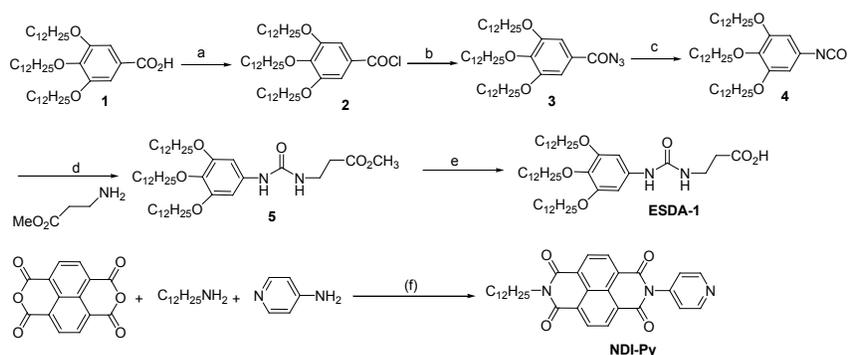
Two-component gelation and morphology-dependent conductivity of a naphthalene-diimide (NDI) π -system by orthogonal hydrogen-bonding

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Materials and methods: Reagents were received from Sigma Aldrich Chemical Co. and used without further purification. Solvents were purchased from commercial sources and purified by reported protocol.¹ Spectroscopic grade solvents were used for physical studies. ¹H NMR experiments were done on a Bruker DPX-300 MHz and 500 MHz NMR machine and all the data were calibrated against TMS. UV/visible absorption experiments were performed in a Perkin-Elmer Lambda 25 spectrometer. Photoluminescence studies were performed in a Horiba Fluoromax-3 spectrophotometer. Mass spectrometric data were acquired by an electron spray ionization (ESI) technique on a Q-tof-micro quadrupole mass spectrometer (Micro mass). Atomic force microscopy (AFM) experiments were done in an AUTOPROBE CP base unit, di CP-II instrument, (model no.AP-0100). Rheological studies were performed with an AR 2000 advanced Rheometer (TA instruments) by cone and plate method. FT-IR spectra were recorded in a Perkin Elmer Spectrum 100FT-IR spectrometer. XRD data was recorded on a Seifert XRD3000P diffractometer having a Cu K α radiation source (α =0.15406 nm) operating at a voltage and current of 40 kV and 30 mA, respectively.

Synthesis: Synthesis of ESDA-1 and NDI-Py is described in Scheme S1.



Reagents and conditions: (a) SOCl_2 , DCM, rt, 12h, 90%; (b) NaN_3 , THF/ H_2O , -5 °C to rt, 10h, 85%; (c) Benzene, 80°C, 7h; (d) DCM, triethyl amine, rt, 8h, 65%; (e) LiOH, THF/ H_2O , rt, 18h, 90%; (f) DMF, 130°C, 16h, 40%

Scheme S1: Synthetic route for ESDA-1 and NDI-Py

Compound 2: To a solution of compound **1** (0.40 gm, 0.59 mmol) in dry dichloromethane (20 ml), freshly distilled SOCl_2 (0.85 ml, 11.8 mmol) was added drop-wise under N_2 atmosphere. After the addition was over the reaction mixture was stirred at rt for 12 h and then excess SOCl_2 was removed via distillation to produce compound **2** as yellow semi-solid which was dried under vacuum for 6 h to remove trace of thionyl chloride and was used for the next step without further purification. Crude yield: 90 %

Compound 3: A solution of NaN_3 (0.69 gm, 10.6 mmol) in 2 ml water was cooled to $\sim 0^\circ\text{C}$ in an ice bath and to this a solution of compound **2** (0.37 gm, 0.53 mmol) in 15 ml THF was added slowly over a period of 30 minutes and the reaction mixture was stirred at rt for additional 10 h. Initially a yellow precipitate appeared which dissolved as the reaction progressed. After 10 h, THF was removed under reduced pressure and the product was extracted with dichloromethane (30 ml) and washed with water. Organic layer was passed through anhydrous Na_2SO_4 and the solvent was removed to get the product as yellow sticky solid (yield= 85 %) which was used for the next step without further purification.

Compound 5: Compound **3** (0.31 gm, 0.45 mmol) was dissolved in dry benzene (18 ml) and the solution was refluxed for 7 h and cooled to rt. Then to this, a solution of methyl ester of β -alanine (0.06 gm, 0.67 mmol) in dichloromethane (8 ml) and tri-ethylamine (0.8 ml) were added and the reaction mixture was stirred at rt under N_2 atmosphere for 8 h. After that the volatiles were removed under reduced pressure and the product was re-dissolved in dichloromethane (30 ml), washed with water and the solution was passed through anhydrous Na_2SO_4 and the solvent was removed to get the crude product as light brown solid. It was purified by column chromatography using silica gel (60-120 mesh) as stationary phase and 10% EtOAc in DCM as eluent to get the desired product as sticky white material (yield =65%). ^1H NMR (CDCl_3 , 500 MHz, TMS): δ (ppm) = 6.47(2H, s), 6.17 (1H, s), 5.31 (1H, t, $J = 6$ Hz), 3.94-3.88 (6H, m), 3.67 (3H, s), 3.52-3.49 (2H, m), 2.57 (2H, t, $J=6$), 1.80-1.70(6H, m), 1.44-1.36(6H, m), 1.32-1.25(48H, m), 0.89-0.84 (9H,m); HRMS (ESI): m/z calc for $\text{C}_{47}\text{H}_{86}\text{N}_2\text{O}_6$ $[\text{M} + \text{Na}]^+$: 797.6384; found: 797.6384.

ESDA-1: To a solution of compound **5** (0.25 gm, 0.33 mmol) in 10 ml H_2O , a solution of LiOH (0.46 gm, 19.3 mmol) in 10 ml THF was added and the reaction mixture was stirred for 18 h at rt. The stirring was stopped, THF was removed under reduced pressure and the aqueous solution was acidified with 3 ml 1N HCl while solid precipitate came out which was extracted by dichloromethane (40 ml) and passed through anhydrous Na_2SO_4 then solvent was removed under reduced pressure to get the final product as white sticky solid (yield = 90%). ^1H NMR (CDCl_3 , 500 MHz, TMS): δ (ppm) = 6.50 (2H, s), 3.93-3.89 (6H, m), 3.50 (2H, t, $J=5.5$ Hz), 2.59 (2H, t, $J=5.5$ Hz), 1.79-1.70 (6H, m), 1.44-1.41(6H, m), 1.33-1.20 (48H, m), 0.88 (9H, t, $J = 6.5$ Hz). ^{13}C NMR(CDCl_3) δ (ppm) = 176.65, 153.62, 101.54, 73.81, 69.37, 35.99, 34.76, 32.08, 31.58, 30.45, 30.36, 29.92, 29.88, 29.84, 29.64, 29.55, 29.26, 26.29, 24.90, 22.84,

14.24; FTIR (KBr, cm^{-1}) 3335 (N-H stretching), 1632 (urea carbonyl symmetric stretching), 1601 (urea carbonyl asymmetric stretching); UV-visible (CH_2Cl_2): $\lambda_{\text{max}}(\epsilon) = 228 (15,300), 248 (12,200 \text{ M}^{-1}\text{cm}^{-1})$

NDI-Py: Commercially available Naphthalene dianhydride (0.54 gm, 2.02 mmol), 4- amino pyridine (0.19 gm, 2.02 mmol) and dodecyl amine (0.37gm, 2.02 mmol) were dissolved in 25 ml dry DMF and the reaction mixture was stirred at 130 °C for 16 h under N_2 atmosphere. Heating was stopped; the reaction mixture was cooled to rt and placed in the refrigerator for 2 h. A light yellow precipitate came out of the solution which was filtered and the solid obtained was washed several times with methanol to get the crude product. It was purified by column chromatography using silica gel (60-120 mesh) as stationary phase and 2% methanol in DCM as eluent to get the desired product as light yellow solid. Yield=40%. ^1H NMR (CDCl_3 , 300 MHz, TMS): δ (ppm) = 8.84 (2H, d, $J=13\text{Hz}$), 8.76 (4H, s), 7.32 (2H, d, $J=6 \text{ Hz}$), 4.21 (2H, t, $J = 6$), 1.78-1.71 (2H, m), 1.41-1.25 (16H, m), 0.87 (3H, t, $J = 6.0$); ^{13}C NMR (CDCl_3) δ (ppm) = 162.68, 162.35, 150.06, 131.86, 131.20, 127.57, 127.20, 127.01, 126.14, 124.60, 41.29, 32.05, 30.33, 29.83, 29.77, 29.75, 29.72, 29.66, 29.47, 29.45, 28.21, 27.22, 22.82, 14.24 ; FTIR (KBr, cm^{-1}) 1717,1702 (imide carbonyl symmetric stretching) ;1657,1659 (imide carbonyl asymmetric stretching), 1580 (C=N of pyridine ring); UV/visible (CH_2Cl_2): $\lambda_{\text{max}}(\epsilon) = 237 (11300), 341 (3900), 359(6700), 379 (8400 \text{ M}^{-1} \text{ cm}^{-1})$. HRMS (ESI): m/z calc for $\text{C}_{31}\text{H}_{33}\text{N}_3\text{O}_4$ $[\text{M}+\text{H}]^+$: 512.2578; found: 512.2578.

Gelation Test: For testing ESDA induced gelation ability stock solution of the particular ESDA (0.20 wt%) and NDI-Py (0.13 wt %) were made in CHCl_3 and from each stock solution 100 μl aliquots were placed in a small screw capped sample vial to produce a solution of ESDA + NDI-Py (1:1) and the solvent was removed by gentle heating to get a thin film of the mixture. To this measured amount of a non-polar solvent was added and the contents were heated in closed condition with a hot air gun until the entire solid dissolved. The solution was allowed to stand at rt for ~ 30 minutes before gelation ability was checked by standard “stable-to-inversion of a vial” method. To determine the critical gelation concentration the gel was made at relatively higher concentration and gradually diluted with measured amount of the same solvent. In each occasion after addition of solvent the mixture was heated till it became homogeneous solution and allowed to stand at rt for 30 min before conclusions were made about its gelation ability. The concentration below which no gelation was observed was noted as the critical gelation concentration.

Rheological Measurements: Stress-amplitude sweep measurement was carried out with 1.0 wt % (w/w) gel (measurements were done 3 h after the gel was prepared) in methyl cyclohexane using an Advanced Rheometer AR 2000 (TA Instrument) with the cone diameter, cone angle and truncation of 40 mm, 4° 0'

22” and 121 μM , respectively. The runs were conducted at 25 $^{\circ}\text{C}$ with a constant oscillation frequency of 1Hz.

AFM Studies: A diluted gel/sol (0.05 wt %) in 95:5 MCH / CHCl_3 was drop casted on a glass slide and the sample was allowed to stand at ambient temperature for 24 h before taking the AFM images.

Uv-Vis and Photoluminescence Studies of Gel/Sol: ESDA-1 + NDI-Py (1:1) gel (0.3 wt %) in MCH was placed in a cuvette with 0.1 cm path length for UV/vis studies. For temperature-variable experiments, the same sample was heated from lower to higher temperature using an external temperature control while spectra were recorded with 5 $^{\circ}\text{C}$ interval. Before each measurement 10 min equilibrium time was allowed after the desired temperature was reached. For comparing the data in the solution state, spectrum was recorded with the same composition of sample in good solvent like CHCl_3 at dilute concentration (5×10^{-3} mM). Steady state PL spectra were recorded for the same gel and sol sample with $\lambda_{\text{ex}} = 338$ nm and 340 nm, respectively.

Powder X-Ray diffraction studies: ESDA-1+NDI-Py (1:1) gel in MCH (0.3 wt%) was drop-casted repeatedly on a glass slide to make a thick film and it was then air dried for 12 h. Data was recorded with this sample from 1 $^{\circ}$ to 30 $^{\circ}$ with sampling interval of 0.02 \AA per state.

FT-IR studies: For FT-IR studies gel/sol of a particular material in a given solvent (concentration is mentioned in the figure captions of the individual experiments) was placed between two NaCl windows (path length = 0.2 mm) and spectral measurements were carried out in the absorbance mode. Scan range = 4000-600 cm^{-1} , resolution = 0.5 cm^{-1} , number of scans = 30, T = 25 $^{\circ}\text{C}$.

Current (*I*)-Voltage (*V*) Measurements: 0.3 wt % gel/sol in MCH was drop casted on indium tin oxide (ITO) coated glass surface and dried at ambient atmosphere for 12 h. It was then sandwiched with another similar plate and Cu electrodes were connected to it using silver paste. *I-V* profile of this device was checked in a Keithley 617 programmable electrometer instrument and conductivity (σ) was calculated equation 1.²

$$\sigma = 1 / (V/I) \times \pi t / \ln 2 \quad (1)$$

Where t = film thickness estimated by ellipsometry (30 and 40 μm for ESDA-1 + NDI-Py and ESDA-2 + NDI-Py).

Additional Figures:

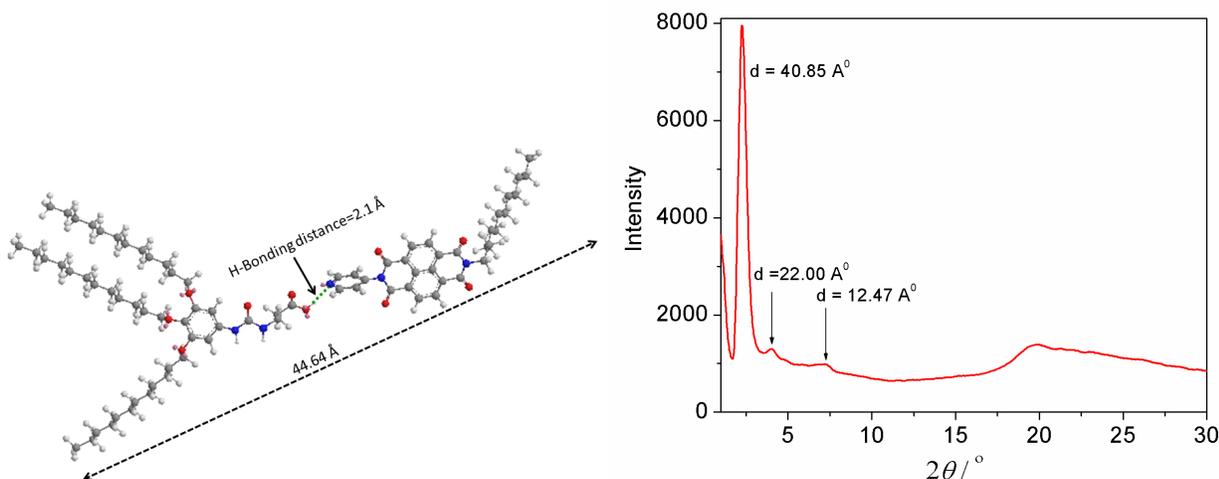


Fig. S1: *Left-* energy minimized structure of H-bonded complex of ESDA-1 + NDI-Py obtained by molecular modelling done in Chem 3D-ultra 8.0 using MM₂ for energy minimization; *Right-* XRD pattern of the xerogel of ESDA-1 + NDI-Py (1:1) in MCH.

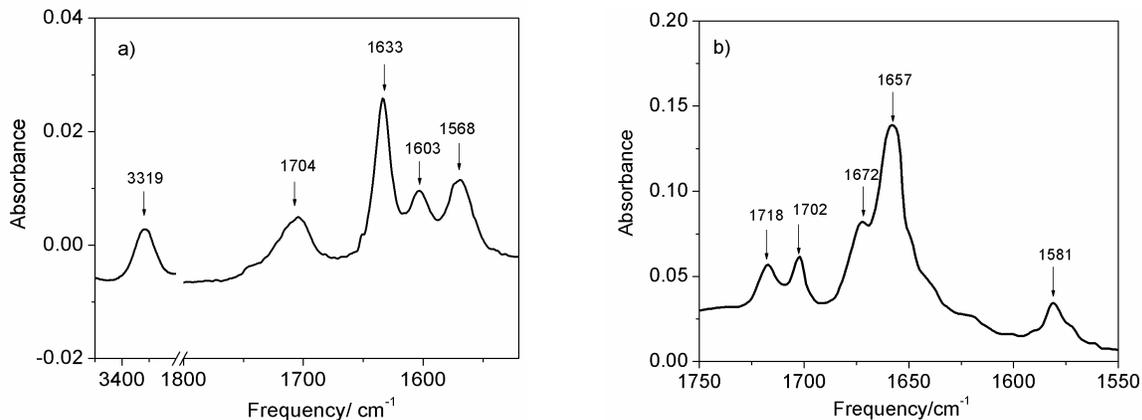


Fig. S2: Selected region of FT-IR spectra of ESDA-1 (a) and NDI-Py (b) in CHCl₃ (concentration = 0.5 wt %).

Note: FT-IR spectra of ESDA-1 and NDI-Py (1:1) were recorded in CHCl₃ solution and compared with that of the mixed gel (Fig 1b) in MCH. For NDI-Py the peaks at (1718, 1702) and (1672, 1657) cm⁻¹ in CHCl₃ (Fig S2b) can be attributed to symmetric and asymmetric stretching of the two types of imide carbonyls in the NDI ring. These peaks appeared almost in the same position in the gel state (Fig 1b). On the other hand the peak at 1581 cm⁻¹ (Fig S2b) corresponding to the C=N of pyridine ring appeared at

1599 cm^{-1} in the gel state (Fig 1b) suggesting non H-bonded to H-bonded state going from sol to gel.³ The FT-IR spectrum of ESDA-1 in CHCl_3 (Fig S2a) showed a peak at 3319 cm^{-1} corresponding to NH stretching of the urea group which appeared at 3299 cm^{-1} in the gel state (Fig 1b) suggesting stronger H-bonding in the gel state as envisaged in non-polar medium. The peak at 1704 cm^{-1} (Fig S2a) corresponding to the carbonyl stretching of the carboxylic acid group appeared almost in the similar position in gel (Fig 1b) which is expected because the carbonyl is not involved in H-bonding in the proposed model (Fig 1a). Carbonyl stretching of the urea functional groups appear at 1633 and 1603 cm^{-1} in CHCl_3 compared to 1630 and 1581 cm^{-1} in gel (Fig 1b) suggesting stronger H-bonding in MCH. However existence of H-bonding among the urea groups cannot be eliminated even in CHCl_3 since FT-IR measurements had to be carried out at reasonably high concentration (0.5 wt %) to achieve good quality spectra. The peak 1568 cm^{-1} (Fig S2a) possibly appears due to aromatics.

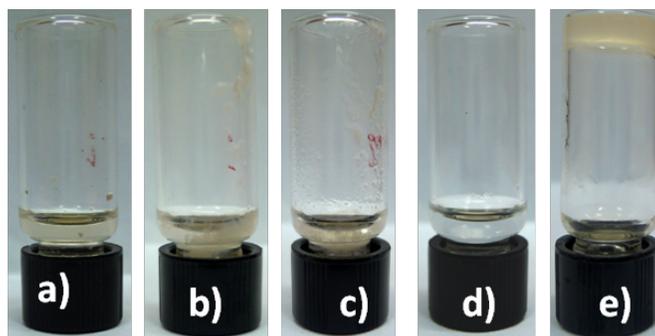


Fig. S3: Images showing results of gelation test for ESDA-1 + NDI-Py (1:1) (concentration = 0.5 wt %) in CCl_4 (a), *n*-octane (b), *n*-decane (c), benzene (d) and cyclohexane (e). Gelation was noticed only for cyclohexane, while gel-like precipitation was observed in *n*-octane and *n*-decane. In benzene and CCl_4 the solution remained clear even after prolonged waiting at rt.

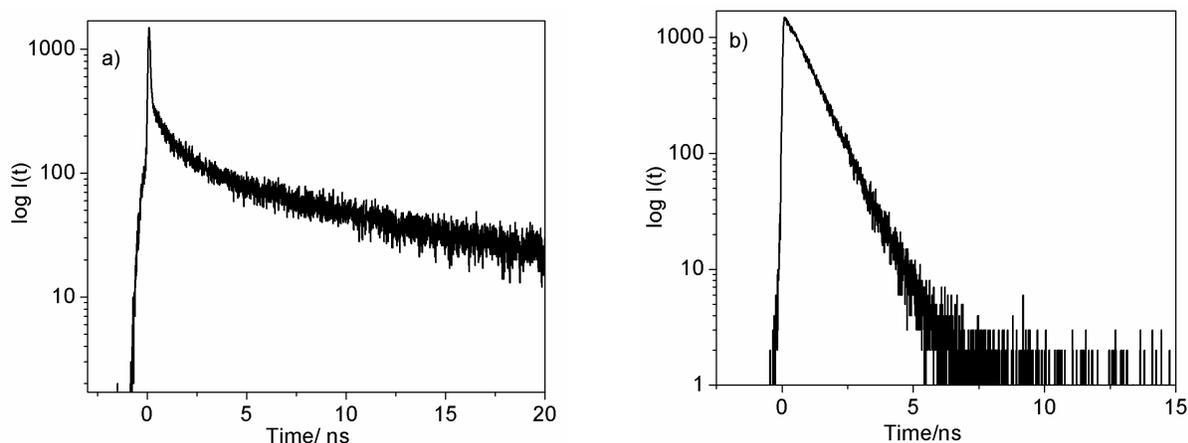


Fig S4: Time resolved fluorescence decay of NDI-Py+ESDA-1 (1:1) in (a) gel state (0.3 wt% in MCH, $\lambda_{\text{ex}} = 375 \text{ nm}$, $\lambda_{\text{em}} = 425 \text{ nm}$) and (b) sol state ($5 \times 10^{-3} \text{ mM}$ in CHCl_3 , $\lambda_{\text{ex}} = 375 \text{ nm}$, $\lambda_{\text{em}} = 410 \text{ nm}$)

Table S1: Fluorescence lifetime data for NDI-Py+ESDA-1 (1:1) in (a) gel state (0.3 wt% in MCH, $\lambda_{\text{ex}} = 375 \text{ nm}$, $\lambda_{\text{em}} = 425 \text{ nm}$) and (b) sol state ($5 \times 10^{-3} \text{ mM}$ in CHCl_3 , $\lambda_{\text{ex}} = 375 \text{ nm}$, $\lambda_{\text{em}} = 410 \text{ nm}$)

Sample	Component Lifetimes (ps) ^a		
	τ_1	τ_2	τ_{avg}
Gel	70 (95 %)	4200 (5 %)	3206
Sol	36 (36 %)	860 (64 %)	841

^aValues in parenthesis shows the decay contribution in each life times. Average life time was calculated using the following equation:⁴ $\tau_{\text{avg}} = (a_1\tau_1^2 + a_2\tau_2^2) / (a_1\tau_1 + a_2\tau_2)$

References:

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