Electronic Supplementary Material (ESI) for Soft Matter.

Electronic Supplementary Information

Tuning of optoelectronic properties of peptide appended core substituted naphthalenediimides: The role of self-assembly of two positional isomers

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Instrumentation:

NMR experiments

All NMR studies were carried out on a Bruker DPX400 MHz or Bruker DPX500 MHz spectrometer at 300 K. Concentrations were in the range 5–10 mmol in $CDCl_3$ or DMSO-d_6.

Mass spectrometry

Mass spectra were recorded on a Q-Tofmicro™ (Waters Corporation) mass spectrometer by positive mode electrospray ionization process.

MALDI-TOF MS

MALDI-TOF MS analysis was performed using an Applied Biosystems MALDI-TOF Analyzer with dithranol as a matrix.

Fourier Transform Infrared (FTIR) study

All FT-IR spectra were recorded in a Nicolet 380 FT-IR spectrophotometer (Thermo Scientific) in solution state (Chloroform and n-hexane).

Powder X-ray diffraction study (XRD) study

X-ray diffraction studies on the xerogels were carried out by placing the sample on a glass plate. Experiments were carried out using an X-ray diffractometer (Bruker AXS, Model D8 Advance). The instrument was operated at a 40 kV voltage and 40 mA current using Ni-filtered CuK_α radiation and the instrument was calibrated with a standard Al_2O_3 (corundum) sample before use. For scans over 2θ= 1°-5°, a scintillation counts detector was used with scan speed 2s and step size 0.02°. In another scan 2θ= 5°-50°, a Lynx Eye super speed detector was used with scan speed 0.3s and step size 0.02°.

Transmission electron microscopy (TEM)

TEM images were recorded on a JEM 2010 electron microscope at an accelerating voltage of 200 KV. A drop of dilute solution of the gel-phase material were placed on carbon coated copper

grids (300 mesh) and dried by slow evaporation. Each grid was then allowed to dry in a vacuum for one days and then images were taken.

UV/Vis spectroscopy

UV/Vis absorption spectra were recorded on a Hewlett-Packard (model 8453) UV/Vis spectrophotometer (Varian Carry 50.bio).

PL spectroscopy

Fluorescence studies of the gel were carried out in a Perkin Elmer LS55 Fluorescence Spectrometer instrument using the front face geometry. The sample was excited at 340 nm wavelength and emission scans were recorded from 350 to 750 nm.

Time-Correlated Single Photon Counting (TCSPC)

TCSPC measurements were performed by Horiba Jobin Yvon IBH instrument having MCP

PMT Hamamatsu R3809 detector.

Current-Voltage study (I-V)

I-V measurements For I-V measurements, the DC currents were measured using Keithley source meter (model 2410). The dark I-V characteristic has been performed after keeping the samples in dark for several hours. For photocurrent transient measurement, a xenon light source (model no. 66902; Newport Corp. USA) with power of 1 sun was used for the light illumination.

Experimental procedure

Synthesis procedure:

Synthesis of Boc-11-aminoundecanoic acid (Boc-AUDA-COOH):

2.01g (10 mmol) of 11-aminoundecanoic acid (AUDA) was taken in a 250 ml round bottom flask. 10 ml 1(N) NaOH and 20 ml dioxane was added to it and cooled to 0°C. 2.20 g (10.1mmol) di-tert-butyl dicarbonate (Boc anhydride) was added to the reaction mixture and stirred for 8 hours at room temperature. Then dioxane was removed by reduced pressure. The resulting mixture was acidified with saturated $KHSO_4$ solution and the aqueous layer was extracted with ethyl acetate (3 x 50 mL). The ethyl acetate extract was dried over anhydrous sodium sulfate and evaporated in vacuum to obtain the colorless sticky product.

Yield: 2.85g (9.5 mmol, 95%)

Synthesis of Boc-AUDA-Phe-OMe :

2.85 g (9.5 mmol) of Boc-AUDA-OH was dissolved in 10ml dry N,N-dimethyl formamide (DMF) and cooled in an ice bath. H_2N-Phe-OMe (15mmol) was obtained by neutralization with saturated Na_2CO_3 from its hydrochloride salt and subsequent extraction with ethyl acetate. The ethyl acetate solution was then concentrated to 20 ml and added to the DMF solution followed by 1.35 g (10 mmol) of HOBt and 2.06 g (10 mmol) of N,N dicylohexylcarbodiimide (DCC).The reaction mixture was allowed to come at room temperature and stirred for 24 hr. The reaction mixture was diluted with ethyl acetate and filtered to separate N,N- dicyclohexyl urea (DCU). The ethyl acetate layer was washed with brine (2 × 30 ml). The organic layer was dried over anhydrous sodium sulfate and evaporated to obtain the yellowish product. The product was purified through silica gel column chromatography using ethyl acetate: n-hexane (10-90) as eluent to obtain the pure product.

Yield: 3.24 g (7 mmol, 73.6 %).

^{1}H NMR (500 MHz, ($CDCl_3$), 25 °C): δ 7.08-7.29 (5H, m, aromatic proton), 5.85-5.87 (2H, d, NH), 4.88-4.92 (1H, m, α-CH of Phe), 4.49 (1H, br, NH), 3.73 (3H, s, -OMe), 3.07-3.17 (4H, m, β-CH_2 of Phe and α-CH_2 of AUDA), 2.15-2.18 (2H, t, J=7.5 Hz), 1.44-1.64 (25H, m). ^{13}C NMR(125 MHz, ($CDCl_3$, 25 °C): δ 172.80, 136.08, 129.42, 128.71, 127.27, 53.07, 52.44, 38.11, 36.72, 30.23, 29.61, 29.49, 29.41, 29.31, 28.60, 26.93, 25.67. HRMS (m/z): Calculated for $C_{26}H_{42}N_2O_5$ 462.62. Found: 463.45 (M+H)+, 485.42 (M+Na)+.

Synthesis of H_2N-AUDA-Phe-OMe (P):

To 2.31 g (5 mmol) of Boc-AUDA-Phe-OMe, 5 ml of 98% formic acid was added and the removal of the Boc group was monitored by TLC. After 6 h, formic acid was removed under vacuum. The residue was taken in water (8 ml) and pH of the aqueous solution was then adjusted to 8.0 with 30% aqueous NH_3. The aqueous portion was evaporated under vacuum. A white material was obtained, purified using basic alumina in and methanol chloroform (1:9) as eluent.

Yield: 1.70 g (4.7 mmol, 94%).

^{1}H NMR (500 MHz, $(CD_3)_2SO$, 25 °C): δ 7.97-7.99 (1H, d, NH), 7.13-7.28 (5H, m, aromatic proton), 5.57-5.59 (1H, m, α-CH of Phe), 4.06 (2H, br, NH_2), 3.59 (3H, s, -OMe), 2.84-3.04 (4H, m, β-CH_2 of Phe and α-CH_2 of AUDA), 2.01-2.04 (2H, t, J=7.5 Hz), 1.19-1.59 (16H, m, CH_2 of AUDA). ^{13}C NMR(125 MHz, ($(CD_3)_2SO$, 25 °C): δ 172.21, 172.17, 171.85, 171.13, 170.92, 156.57, 137.99, 137.29,129.38, 129.04, 128.95, 128.09, 127.84, 126.38, 126.03, 79.12, 53.80, 53.29, 51.69, 48.54, 47.46, 36.62, 35.13, 34.91, 33.29, 31.77, 28.91, 28.83, 28.75, 28.71, 28.59, 28.42, 28.38, 26.24, 25.27, 25.14, 25.07, 24.40. HRMS (m/z): Calculated for $C_{21}H_{34}N_2O_3$ 362.25. Found: 363.12 $(M+H)^+$.

Synthesis of 2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic dianhydride (Br_2NDA):

The synthesis of 2,6-dibromonaphthalene-1,4,5,8-tetracarboxylic dianhydride (Br_2NDA) was carried out by using a reported procedure. (*ACS Appl. Mater. Interfaces* 2016, **8**, 18584−18592.)

Synthesis of 2,6 dibromo, N,N'(didodecyl)-naphthalenediimide (A1):

The synthesis was carried out using a reported procedure (*RSC Adv.,* 2015**, 5**, 2147–2154)

^{1}H NMR (500 MHz, ($CDCl_3$), 25 °C): δ 8.99 (2H, s, naphthyl proton), 4.17-4.21 (4H, t, J=8Hz), 1.26-1.76 (40 H, m, chain CH_2), 0.87-0.89 (6H, t, J=7 Hz). ^{13}C NMR(125 MHz, ($CDCl_3$, 25 °C): δ 160.92, 160.29, 139.21, 129.51, 125.58, 124.32, 41.78, 37.28, 32.07, 29.85, 29.77, 29.72, 29.67, 29.48, 29.44, 28.08, 27.24, 27.15, 22.82, 14.23. HRMS (m/z): Calculated for $C_{38}H_{52}Br_2N_2O_4$ 758.229. Found: 781.574 $(M+Na)^+$

Synthesis of 2,6 dibromo, N,N'(AUDA-Phe-OMe)-naphthalenediimide (A2):

Br_2NDA (5mmol) and 20 ml acetic acid was taken in a 100ml round bottom flax. To the mixture 20 mmol H_2N-AUDA-Phe-OMe was added and the reaction mixture was stirred at 120°C under nitrogen atmosphere. After cool down to room temperature the reaction mixture was poured into the ice water. The precipitate was filtered and dried to obtained orange solid. It was purified by column chromatography using n-hexane:ethylacetate (98:2) as eluent.

Yield: 1.63 g (2.15 mmol, 43%).

^{1}H NMR (500 MHz, ($CDCl_3$), 25 °C): δ 8.99 (2H, s, naphthyl proton), 7.07-7.29 (10H, m, H of Phe), 5.82-5.84 (2H, d, NH), 4.89-4.91 (2H, m, α-CH of Phe), 4.17-4.20 (4H, t, J=8Hz), 3.73 (6H, s, -OMe), 3.09-3.14 (4H, m, β-CH_2 of Phe), 2.146-2.177 (2H, m), 1.27-1.75 (32H, m aliphatic proton) ^{13}C NMR(125 MHz, ($CDCl_3$, 25 °C): δ 172.76, 172.34, 160.93, 139.23, 136.08, 129.42, 128.71, 128.48, 127.27, 125.55, 124.30, 53.06, 52.44, 41.76, 38.12, 36.72, 29.57, 29.49, 29.40, 29.32, 28.06, 27.21, 25.68. HRMS (m/z): Calculated for $C_{56}H_{66}Br_2N_4O_{10}$ 1115.3159. Found: 1116.857 $(M+H)^+$, 1138.8514 $(M+Na)^+$.

Synthesis of N1:

H_2N-AUDA-Phe-OMe **(P)** (283 mg, 0.79 mmol) and 2,6 dibromo, N,N'(didodecyl)-naphthalenediimide (**A1**) (200 mg, 0.26 mmol) were placed in a round-bottomed flask along with dry DMF (15 ml) and the reaction mixture was stirred for 12 h at 120 °C under N_2 atmosphere. The heating was stopped and the solution was allowed to cool to room temperature and and added 50 ml diethyl ether and placed in the refrigerator for 30 min. Blue product came out as precipitate, which was filtered. The product was further purified by column chromatography using silica gel as stationary phase and ethyl acetate- n-hexane (1:9) as eluent. (Scheme S1)

Yield: 282 mg (0.21 mmol, 82%).

^{1}H NMR (400 MHz, ($CDCl_3$), 25 °C): δ 9.32-9.35 (2H, t, NH attached with NDI), 8.13 (2H, s, NDI proton), 7.07-7.30 (10H, m, C-H of phe), 5.84-5.86 (2H, d, NH), 4.88-4.92 (2H, m, α-CH of Phe), 4.14-4.17 (4H, t, J=8Hz), 3.73 (6H, s, -OMe), 3.45-3.50 (4H, m, α-CH of AUDA), 3.06-3.18 (4H, m, β-CH_2 of Phe), 2.15-2.19 (4H, t, J=8Hz), 1.25-1.52 (72H, m, chain proton), 0.85-0.89 (3H, t, J=6.8Hz). ^{13}C NMR (100 MHz, ($CDCl_3$, 25 °C): δ 172.78, 172.34, 166.40, 163.30, 149.39, 136.07, 129.41, 128.70, 127.26, 126.01, 121.33, 118.50, 102.03, 53.06, 52.42, 43.38, 40.62, 38.11, 36.71, 32.07, 29.80, 29.78, 29.74, 29.63, 29.56, 29.49, 29.45, 29.34, 28.30, 27.38,

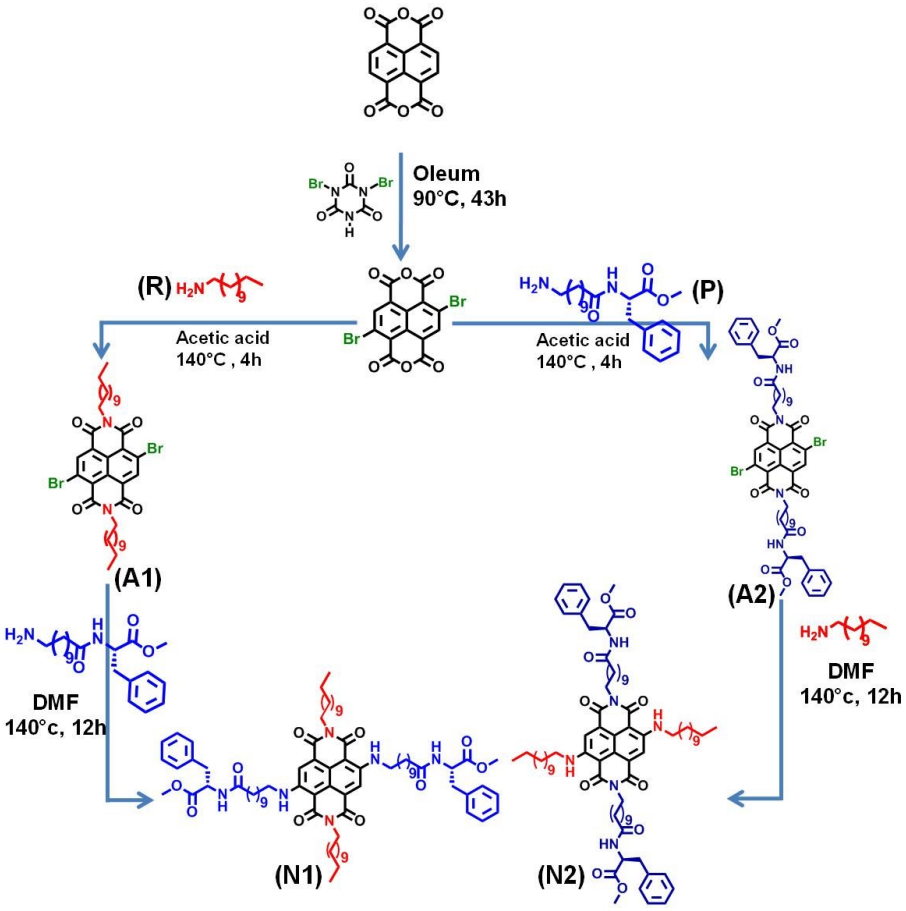
27.30, 25.68, 22.83, 14.24. MALDI-TOF MS (m/z): Calculated for $C_{80}H_{118}N_6O_{10}$ 1323.8271; observed 1324.616$[M+H]^+$, 1346.583$[M+Na]^+$. (Fig. S1-S3)

Synthesis of N2:

2,6 dibromo, N,N'(AUDA-Phe-OMe)-naphthalenediimide **(A2)** (100 mg, 0.089 mmol) and dodecyl amine (**R**) (66 mg, 0.356 mmol) were placed in a round-bottomed flask along with dry DMF (15 ml) and the reaction mixture was stirred for 12 h at 120 °C under N_2 atmosphere. The heating was stopped and the solution was allowed to cool to room temperature and and added 50 ml diethyl ether and placed in the refrigerator for 30 min. Blue product came out as precipitate, which was filtered. The product was further purified by column chromatography using silica gel as stationary phase and ethyl acetate- n-hexane (1:9) as eluent. (Scheme S1)

Yield: 82 mg (0.06 mmol, 70%).

^{1}H NMR (400 MHz, ($CDCl_3$), 25 °C): δ 9.32-9.34 (2H, t, NH attached with NDI), 8.13 (2H, s, NDI proton), 7.07-7.29 (10H, m, C-H of phe), 5.84-5.86 (2H, d, NH), 4.87-4.92 (2H, m, α-CH of Phe), 4.14-4.17 (4H, t, J=7.6 Hz), 3.73 (6H, s, -OMe), 3.45-3.50 (4H, m, α-CH of C_{12}), 3.06-3.18 (4H, m, β-CH_2 of Phe), 2.14-2.18 (4H, t, J=7.6Hz), 1.26-1.81 (72H, m, chain proton), 0.85-0.89 (3H, t, J=6.8Hz). ^{13}C NMR (100 MHz, ($CDCl_3$, 25 °C): δ 172.79, 172.34, 166.38, 163.30, 149.39, 136.05, 129.41, 128.70, 127.26, 125.99, 121.31, 118.51, 102.00, 53.05, 52.43, 43.38, 40.61, 38.09, 36.72, 32.07, 29.81, 29.79, 29.75, 29.68, 29.57, 29.49, 29.45, 29.34, 28.31, 27.38, 27.28, 25.69, 22.84, 14.26. MALDI-TOF MS (m/z): Calculated for $C_{80}H_{118}N_6O_{10}$ 1323.8271; observed 1324.609$[M+H]^+$. (Fig. S4-S6)



Scheme S1: Synthetic scheme core substituted NDI, N1 and N2.

Figures:

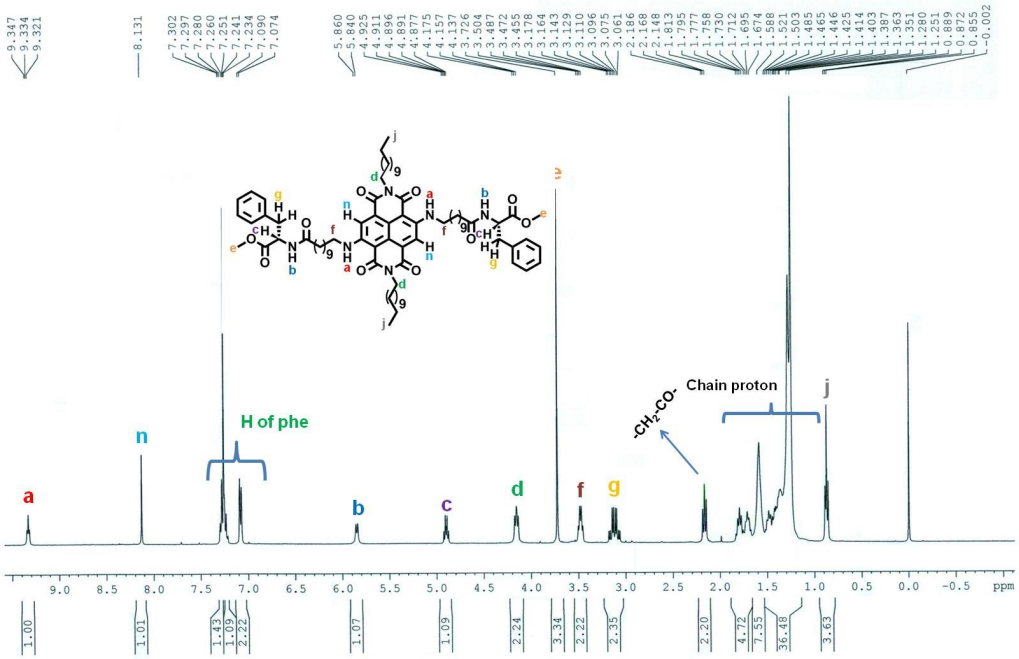


Fig. S1 400 MHz ^{1}H NMR spectra of N1

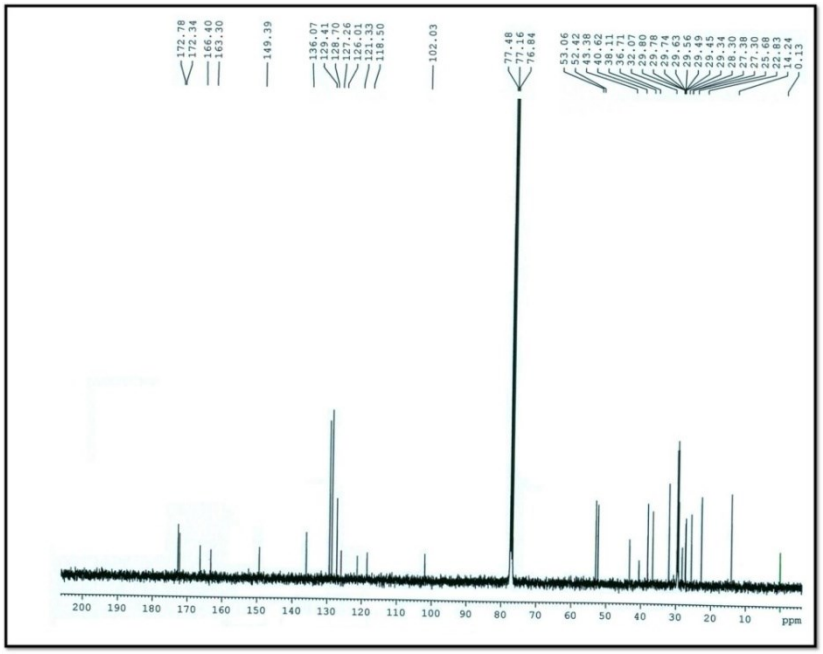


Fig. S2 ^{13}C NMR spectra of N1

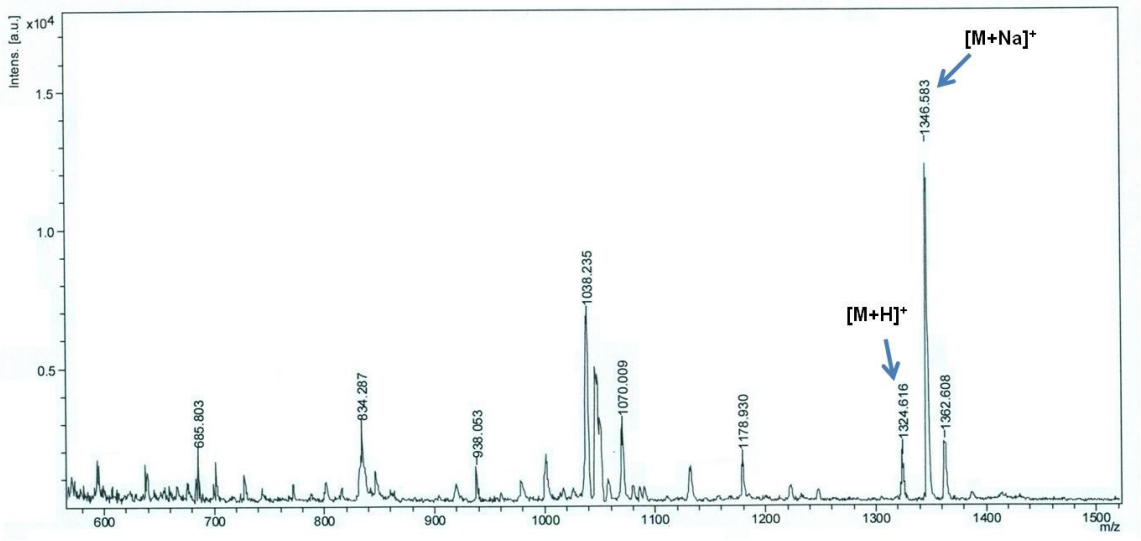


Fig. S3 MALDI-TOF mass spectra of N1

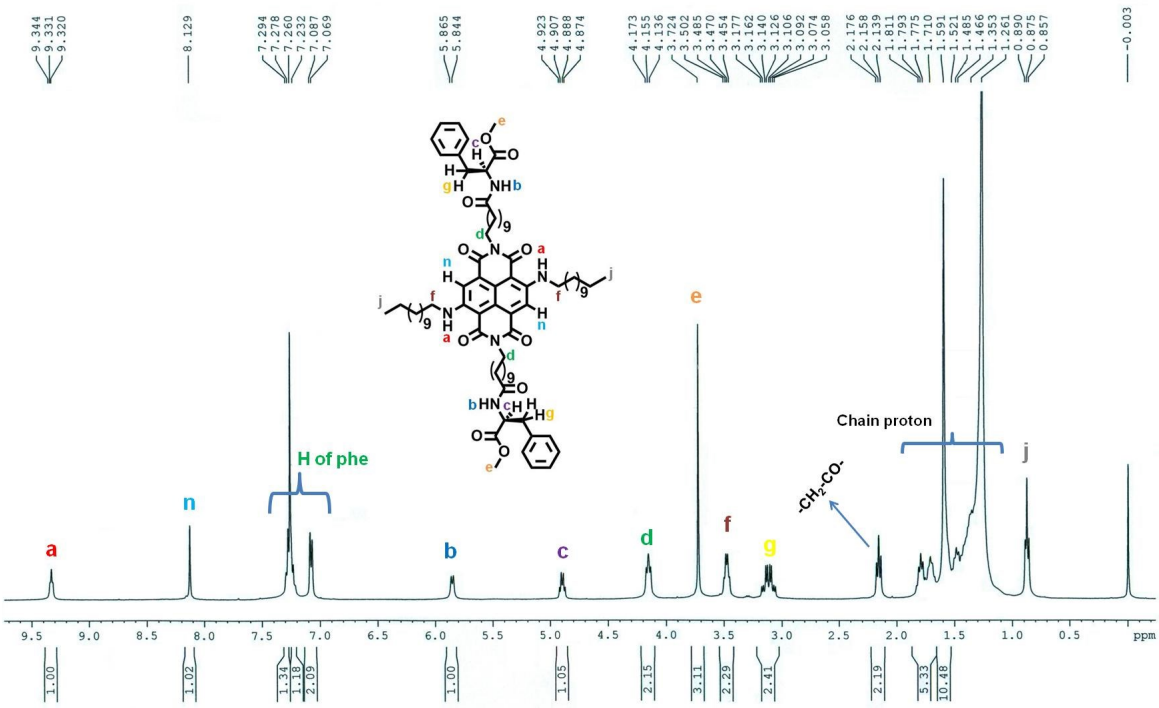


Fig. S4 400 MHz ^{1}H NMR spectra of N2

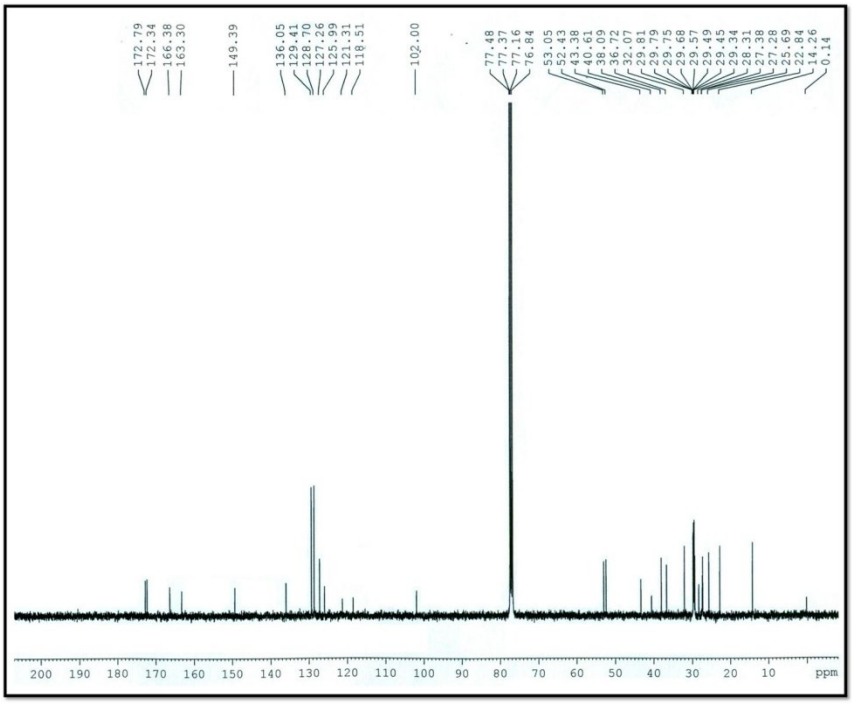


Fig. S5 ^{13}C NMR spectra of N2

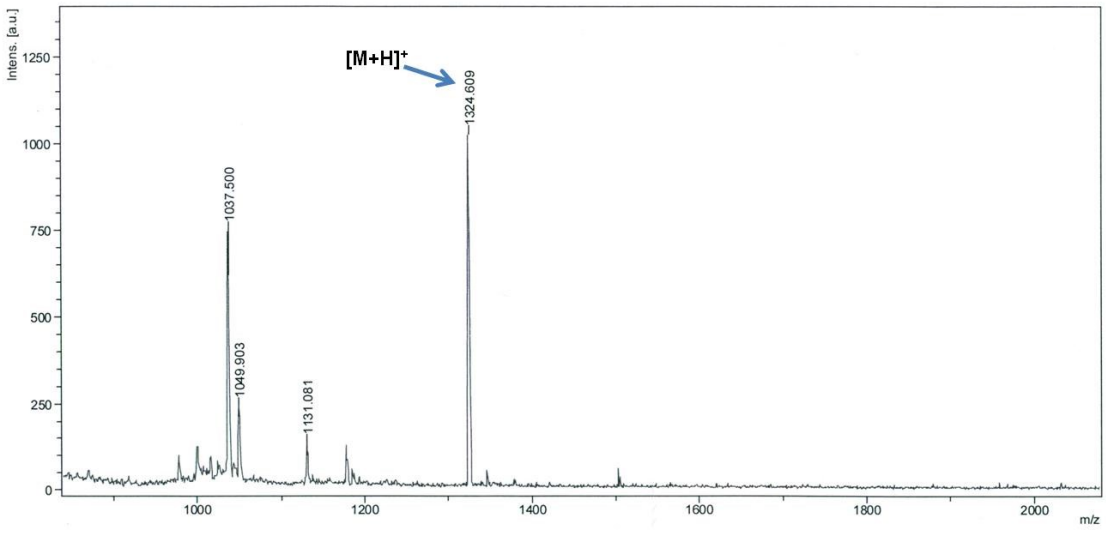


Fig. S6 MALDI-TOF mass spectra of N2

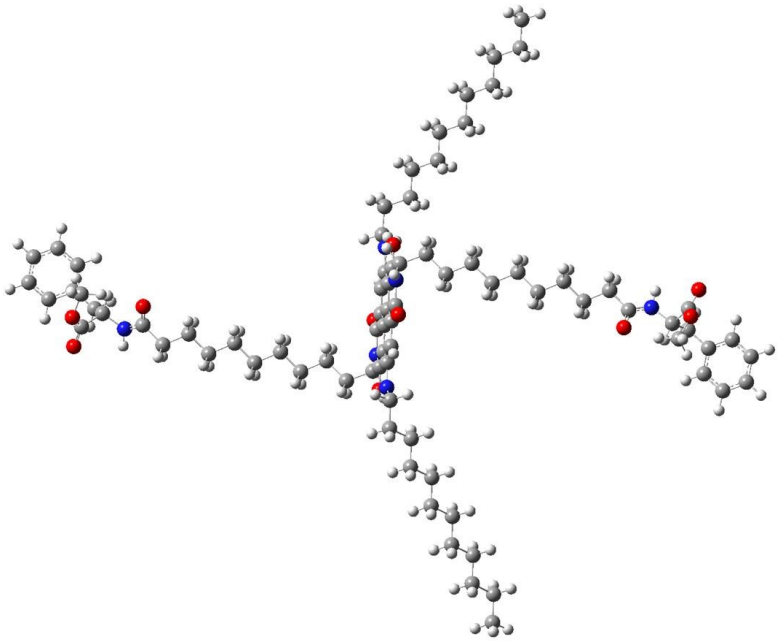


Fig. S7 Energy minimized 3D structure of N2.

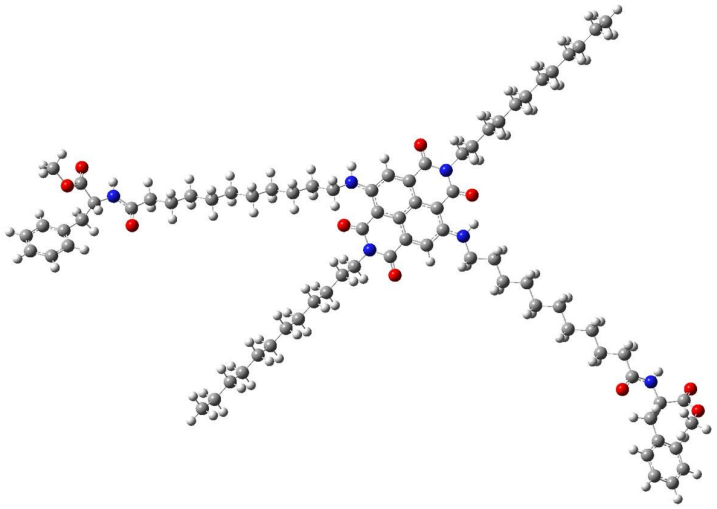


Fig. S8 Energy minimized 3D structure of N1.

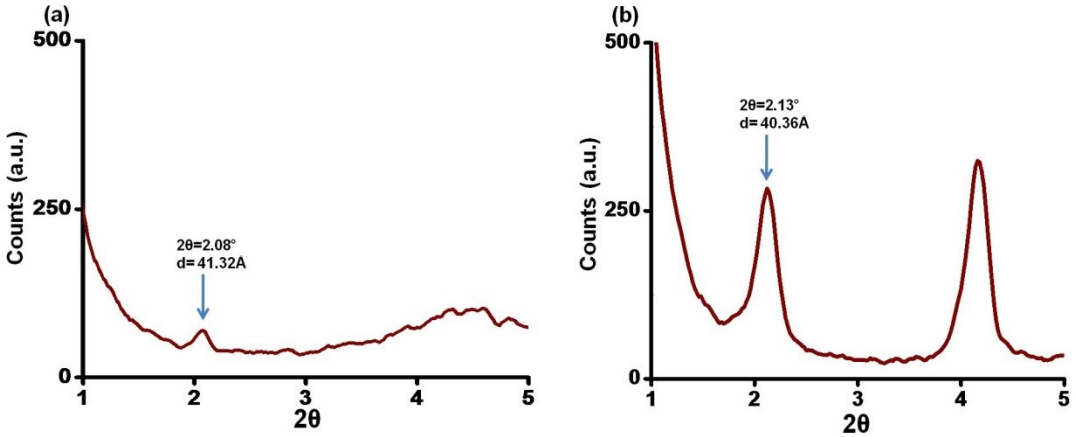


Fig. S9 Low angle powder X-ray diffraction spectra of (a) N1 and (b) N2.

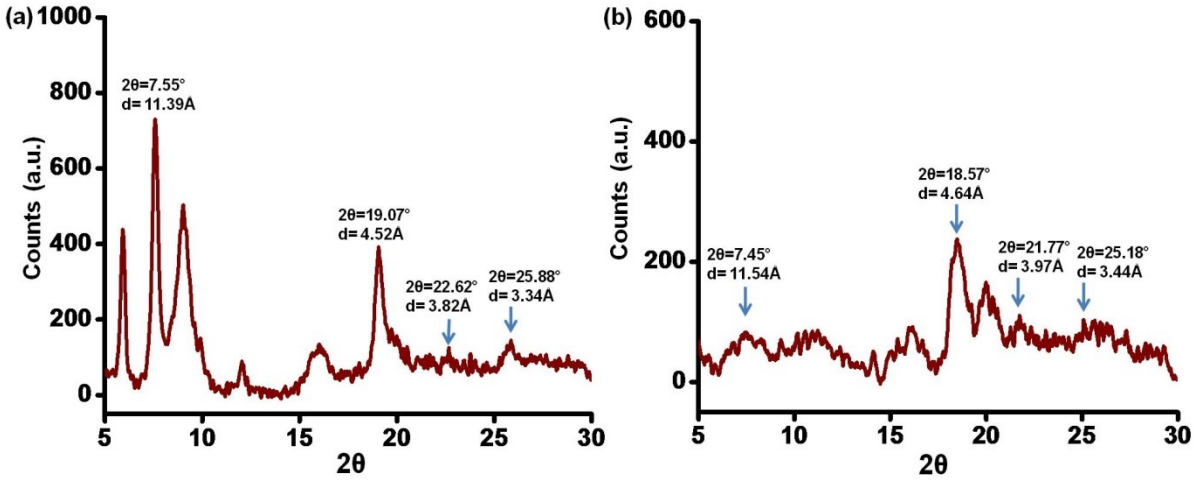


Fig. S10 Wide angle power X-ray diffraction (WPXRD) spectra of (a) N2 and (b) N1.

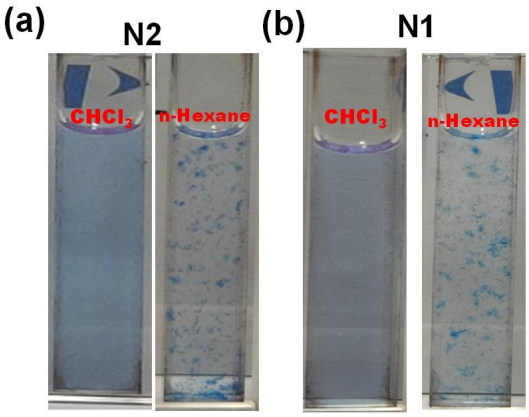


Fig. S11 Visual image in the monomeric state in chloroform and aggregated state in n-hexane (a) N2, (b) N1 (for both cases left side image is in chloroform and right side image in n-hexane).

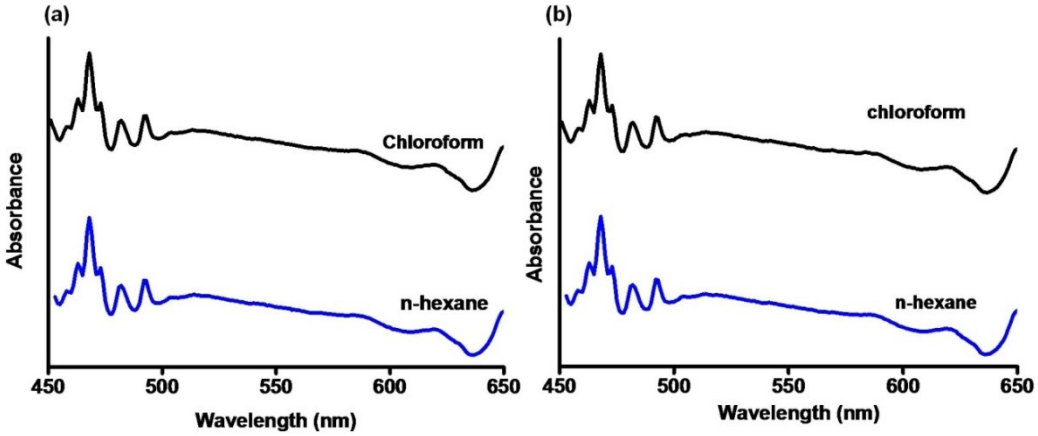


Fig. S12 Excitation spectra of (a) N1 and (b) N2 in the chloroform and n-hexane at the emission 620 nm.

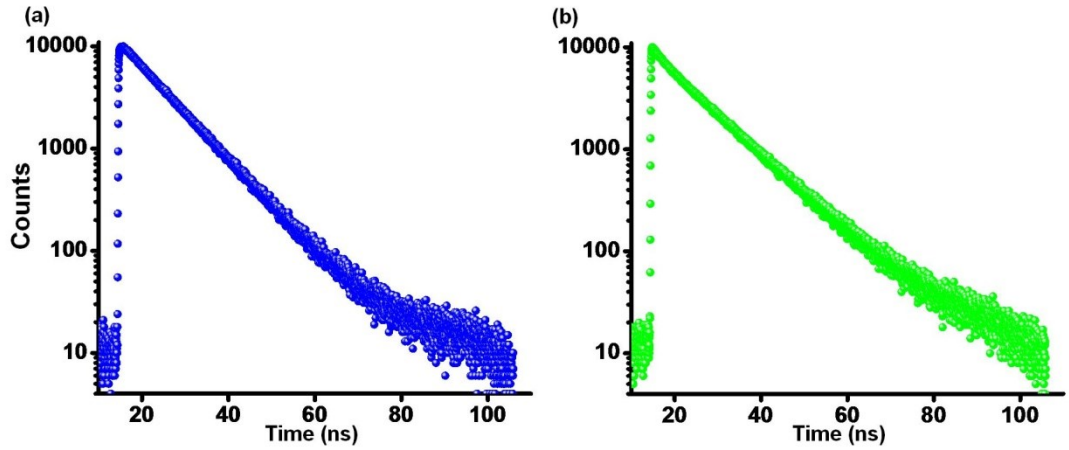


Fig. S13 Time-correlated Single Photon Counting (TCSPC) spectra of N1 in (a) monomeric state in chloroform and (b) aggregated state in n-hexane.

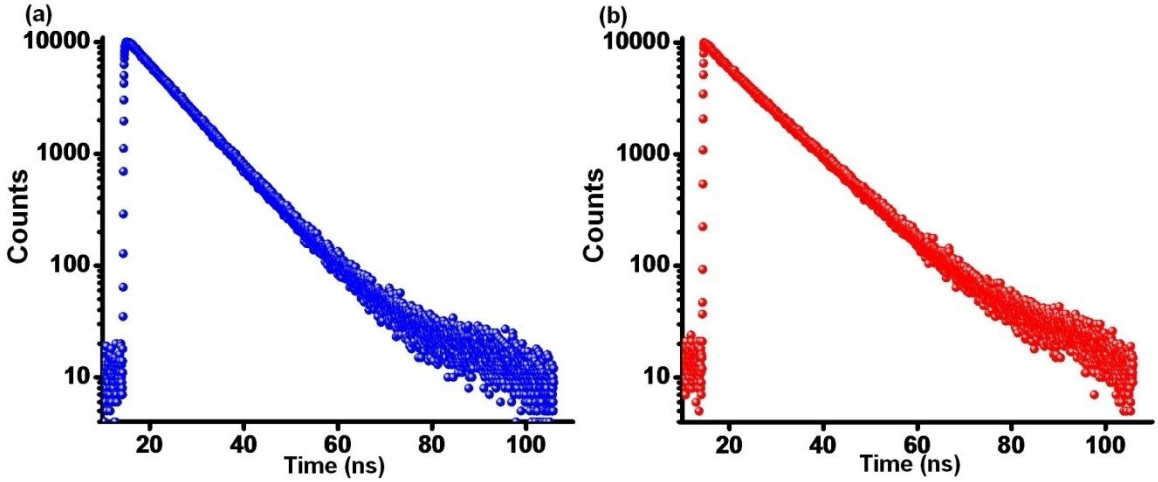


Fig. S14 Time-correlated Single Photon Counting (TCSPC) spectra of N2 in (a) monomeric state in chloroform and(b) aggregated state in n-hexane.