

Supplementary Information

Golf ball-like architecture fabricated by supramolecular self-assembly of naphthalene diimide

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Materials and methods

Naphthalene tetracarboxylic dianhydride, chloroform (CHCl₃), hexane were purchased from Sigma-Aldrich, Bangalore, Karnataka, India and used without purification, unless otherwise specified. ¹H NMR and ¹³C-NMR spectra were recorded on a Bruker spectrometer using CDCl₃ as solvent and tetramethylsilane as an internal standard. Mass spectrometric data were acquired by an electron spray ionization (ESI) technique on a Q-tof-micro quadrupole mass spectrometer (Micro mass). FTIR spectra were recorded in a Perkin Elmer Spectrum FTIR spectrometer. UV-vis absorption spectra were recorded in a UV-1800 Shimadzu spectrophotometer. Fluorescence measurements were performed in a Cary eclipse fluorescence spectrophotometer Agilent technologies. The solvents for spectroscopic studies were of spectroscopic grade and used without further purification.

Sample preparation: Stock solutions of **NDI-S** ($c = 1 \times 10^{-4}$ M) was prepared in chloroform. A 0.2 mL aliquot of the stock solution of **NDI-S** was transferred separately to different volumetric flasks, and made up to 2 mL volume with respective solvents. The solutions were allowed to equilibrate for 2 h prior to the Scanning Electron Microscopy (SEM) measurements.

UV-Visible Measurements: UV-vis spectrometer in 1cm path length cuvette. The solutions were allowed to equilibrate at room temp for 2 h before spectral measurements.

Fluorescence Measurements: Fluorescence measurements were performed on a Cary eclipse fluorescence spectrophotometer. All experiments were performed in a quartz cell with a 1 cm path length.

Sample preparation: The stock solutions were prepared in CHCl_3 in a similar manner as for the UV-vis absorption study. The solutions were allowed to equilibrate for 2 h at room temperature.

Scanning Electron Microscopy Measurements: SEM Samples were prepared by solvent evaporation on a silicon wafer and then sputter coated with gold for 10 s at 0.016 mA Ar plasma (SPI, West Chester, USA) for SEM imaging using a FEI Nova NanoSEM (Hillsboro, USA) operating at high vacuum.

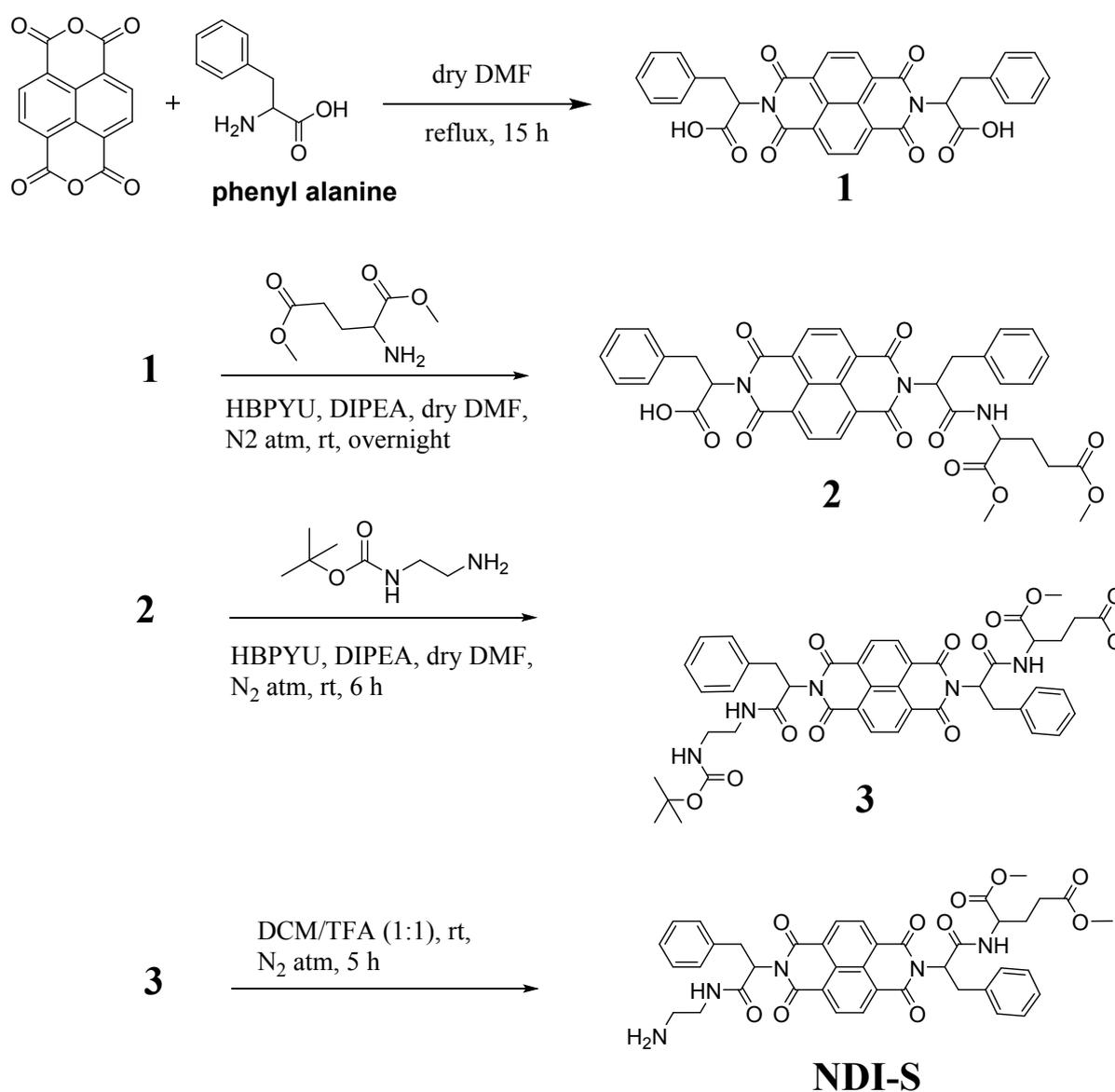


Fig. S1 Synthetic scheme of NDI-S.

Synthesis of 1.¹ 1,4,5,8 Naphthalene tetracarboxylic dianhydride (0.5g, 1.8 mmol) and L-phenylalanine (0.6 g, 1.8 mmol) were suspended in 20 mL of dry DMF. To this suspension Et₃N (0.2 mL) was added and allowed to reflux for 15 h. After cooling the reaction mixture to room temperature, the precipitate was filtered and recrystallised from ethanol resulted into formation of **1** (600 mg, 57%). **M.P.**- 323 °C; **FTIR (KBr) cm⁻¹** 1706 (acid C=O), 1670 (NDI C=O); **¹H NMR (300 MHz, DMSO-*d*₆)** δ : 8.60 (4H, s), 7.14-7.05 (10H, m), 5.93-5.88 (2H, q), 3.69-3.63 (4H, m) ppm ; **MS (ESI) *m/z*** found: 563[M+H]⁺; **HRMS (ESI) *m/z***: calculated for C₃₂H₂₃O₈N₂ 563.14489, found 563.14518.

Synthesis of 2. In a 25 mL round bottomed flask compound **1** (100 mg, 0.18 mmol), HBPYU (43 mg, 0.1mmol) was added to a 10 mL dry DMF under nitrogen atmospheric condition. The reaction mixture was stirred for half an hour at 0 °C. Glutamic dimethyl ester (19 mg, 0.09 mmol) and DIPEA (19 mg, 0.1mmol) were added to the reaction mixture, the resulting reaction mixture was stirred for overnight at room temperature. After completion of the reaction (monitored by TLC) solvent was removed by rotary evaporator under reduced pressure. Water was added to the reaction mixture and pH maintained at 3. The reaction mixture was extracted with dichloromethane (20 mL) and washed with aqueous 10% w/v NaHCO₃ solution (2 x 20 mL), followed by water (20 mL) and brine (20 mL). The resultant organic solvent was dried over anhydrous sodium sulphate, filtered and reduced under vacuum. The residue was purified by silica gel column chromatography eluting with 3% methanol: dichloromethane solution to afford **2** as orange colour solid (60 mg, 47%). **FTIR (KBr) cm⁻¹**: 3311 (O-H) 3089, 2933, 2924, 2853, 1709 (Acid C=O) 1670, 1580, 1531; **¹H NMR (500 MHz, CDCl₃)** δ : 8.64-8.62 (2H, *J* = 7.6 Hz, d), 8.62-8.60 (2H, *J* = 7.6 Hz, d), 7.20-7.18 (2H, *J* = 7.12 Hz, d), 7.15-7.09 (6H, , d), 7.08-7.04 (2H, m), 6.94-6.93 (2H, *J* = 7.1 Hz, d), 6.05-6.01(2H, m), 4.68-4.64 (1H, m), 3.76 (3H, s), 3.73-3.67 (2H, m), 3.56-3.50 (2H, m), 3.40 (3H, s), 2.34-2.25 (2H, m), 2.15-2.18 (1H, m), 1.97-1.92 (1H, m) ppm; **¹³C NMR (125 MHz, CDCl₃)** δ : 173.60, 171.83, 168.35, 162.27, 136.46, 136.39, 130.97, 130.87, 128.80, 128.74, 128.36, 128.14, 126.68, 126.51, 126.40, 126.27, 126.13,

125.72, 55.61, 54.18, 52.38, 51.86, 51.45, 36.46, 34.34, 34.14, 29.44, 26.45 ppm ; **MS (ESI) m/z** : 720 [M+H]⁺; **HRMS (ESI) m/z** : calculated for C₃₉H₃₄O₁₁N₃ 720.2187, found 720.2201.

Synthesis of 3. To a 10 mL of dry DMF under nitrogen were added successively (100 mg, 0.14 mmol) of compound **2** followed by (0.86 mg, 0.20 mmol) of O-(Benzotriazol-1-yl)-N,N,N',N'-bis(tetramethylene) uronium hexafluorophosphate (HBPYU) at 0 °C resulting mixture was stirred for 30 minutes. Mono Boc protected ethylene diamine (22 mg, 0.14 mmol) and (0.03 mL, 0.2 mmol) of DIEPA were added to reaction mixture, the resulting mixture was stirred for 6 h at room temperature. After completion of reaction solvent was removed by rotary evaporator under reduced pressure. Water was added to the reaction mixture and pH maintained at 7. The reaction mixture was extracted with dichloromethane (20 mL) and washed with aqueous 10% w/v NaHCO₃ solution (2 x 20 mL), followed by water (20 mL) and brine (20 mL). The resultant organic solvent was dried over anhydrous sodium sulphate, filtered and reduced under vacuum. The residue was purified by silica gel column chromatography eluting with 2% methanol: dichloromethane solution to afford **3** as light yellow colour solid (80 mg, 67%). **FTIR (KBr) cm⁻¹**: 3313, 3087, 2937, 1748, 1709, 1673; **¹H NMR (500 MHz, CDCl₃) δ**: 8.61 (4H, s), 7.20-7.19 (2H, $J = 7.32$ Hz, d), 7.15-7.09 (8H, m), 6.92-6.91 (1H, $J = 7.0$ Hz, d), 6.05-6.02 (1H, q), 5.99-5.96 (1H, q), 4.92 (1H, br), 4.66-4.63 (1H, q), 3.75 (3H, s), 3.72-3.66 (2H, m), 3.58-3.53 (2H, m), 3.37 (3H, s), 3.35-3.27 (2H, m), 3.26-3.16 (2H, m), 2.36-2.23 (2H, m), 2.17-2.0 (1H, m), 1.98-1.91 (1H, m), 1.12 (9H, s); **¹³C NMR (125 MHz, CDCl₃) δ**: 173.80, 161.99, 163.39, 167.46, 162.58, 136.72, 131.01, 128.57, 126.17, 52.08, 52.56, 42.33, 40.18, 34.38, 29.72, 27.97, 26.71; **MS (ESI) m/z** : 862 [M+H]⁺; **HRMS (ESI) m/z** : calculated for C₄₆H₄₈O₁₂N₅ 862.3325 found 862.3294.

Synthesis of NDI-S. In 10 mL of dry DCM take a 100 mg of compound **3** add 4 mL of TFA at 0 °C, the resulting mixture was stirred for 5 h. The solvent was removed under vacuum afforded

compound **NDI-S** as pale yellow solid (75 mg, 85%). **FTIR (KBr) cm^{-1}** 3429, 2929, 2739, 2675, 2491, 1703, 1660, 1339; **^1H NMR (500 MHz, CDCl_3) δ :** 8.54 (4H, s), 8.11(1H, br), 7.71 (2H, br) 7.15-7.14 (2H, $J = 6.56$ Hz, d), 7.11-7.08 (2H, $J = 6.8$ Hz, t), 7.05-6.99 (6H, m), 6.01-5.96 (2H, m), 4.59 (1H, br), 3.7 (3H, s), 3.65-3.58 (2H, m), 3.52-3.47 (2H, m), 3.44 (3H, s), 3.42-3.25 (2H, m), 2.7 (2H, m), 2.28 (2H, m), 2.06 (1H, m), 1.87 (1H, m); **^{13}C NMR (CDCl_3 , 125 MHz) δ :** 173.96, 172.22, 169.37, 163.13, 162.26, 136.50, 136.40, 131.11, 128.95, 126.64, 126.05, 123.46, 59.87, 55.81, 52.65, 51.81, 29.38, 26.49. **MS (ESI) m/z :** 762 $[\text{M}+\text{H}]^+$; **HRMS (ESI) m/z :** calculated for $\text{C}_{41}\text{H}_{40}\text{O}_{10}\text{N}_5$ 762.2813, found 762.2769.

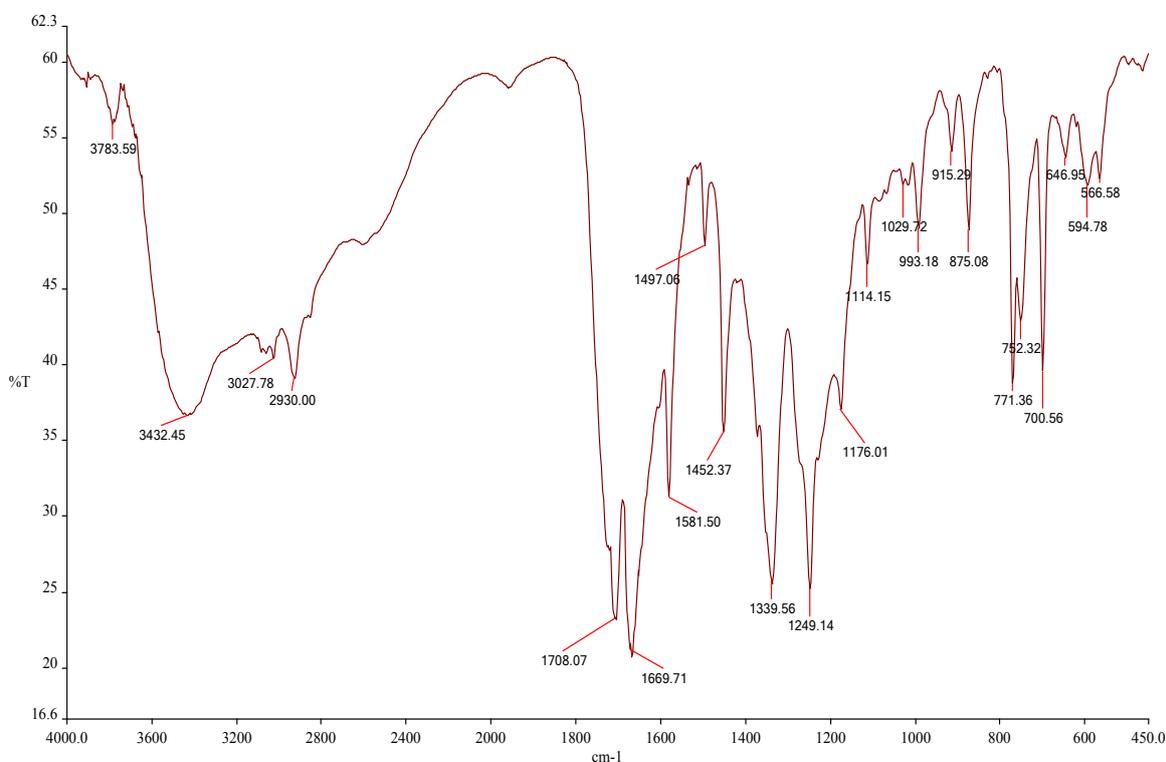


Fig. S2 FT-IR spectrum of **1**.

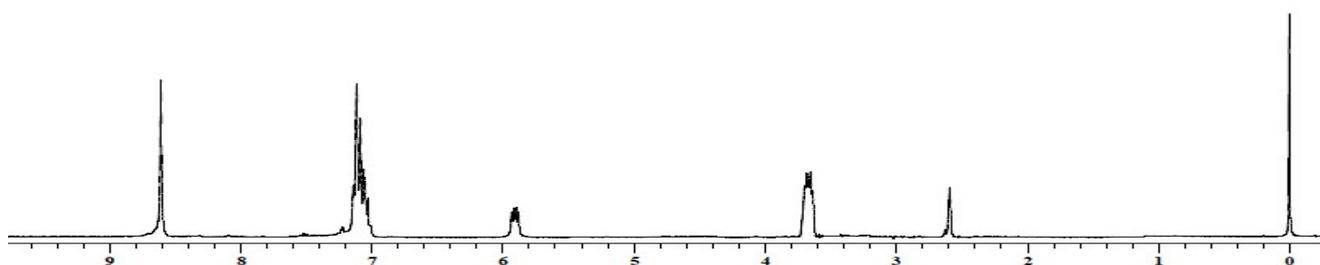


Fig. S3 ^1H NMR spectrum of **1**.

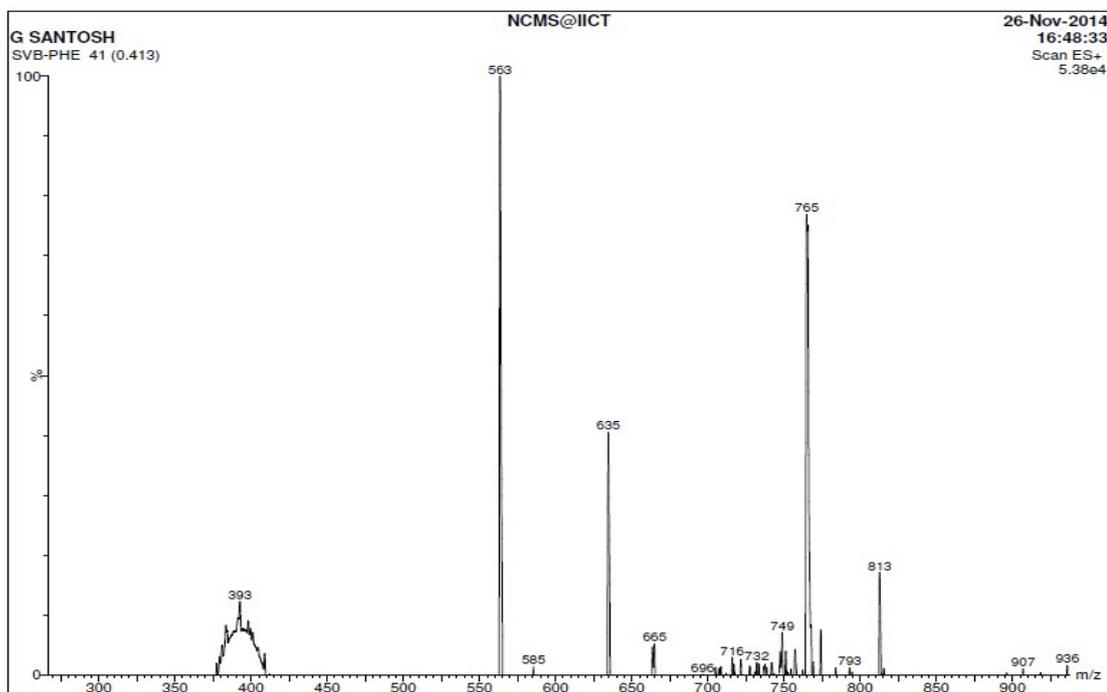


Fig. S4 Mass spectrum of **1**.

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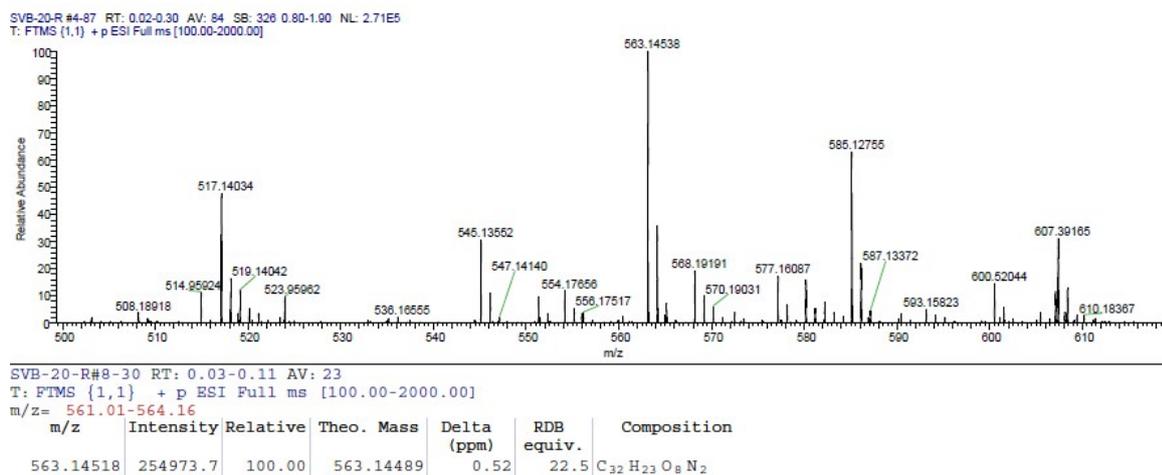


Fig. S5 HRMS spectrum of **1**.

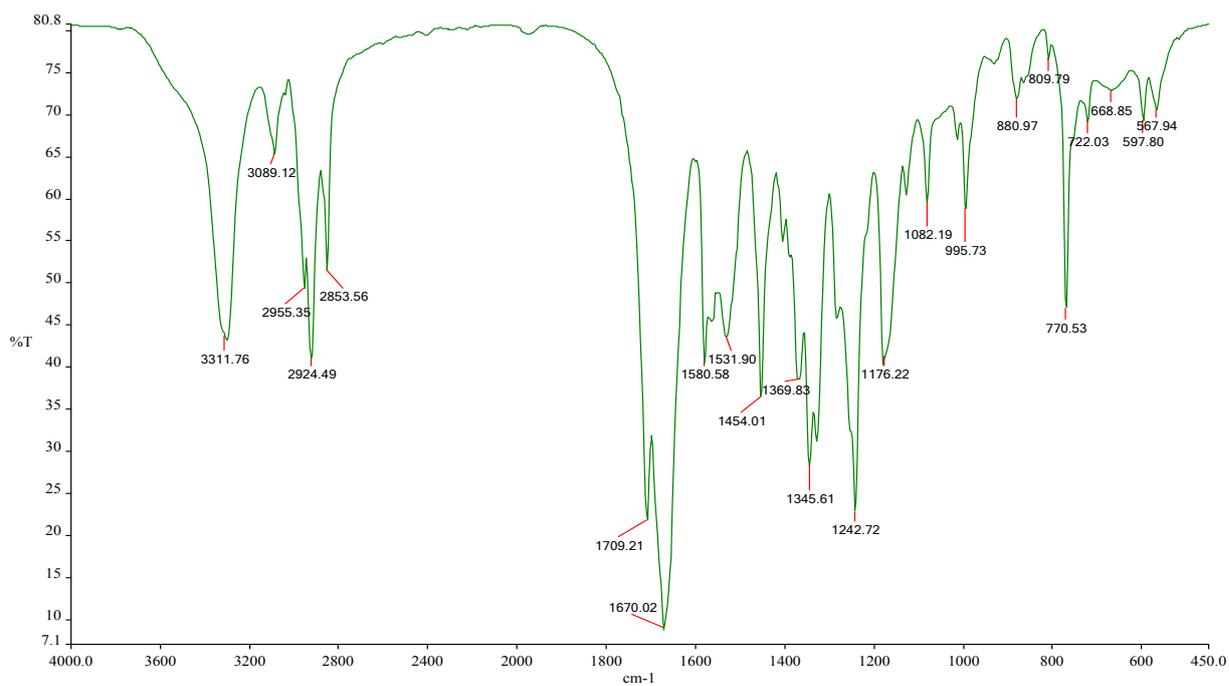


Fig. S6 FT-IR spectrum of **2**.

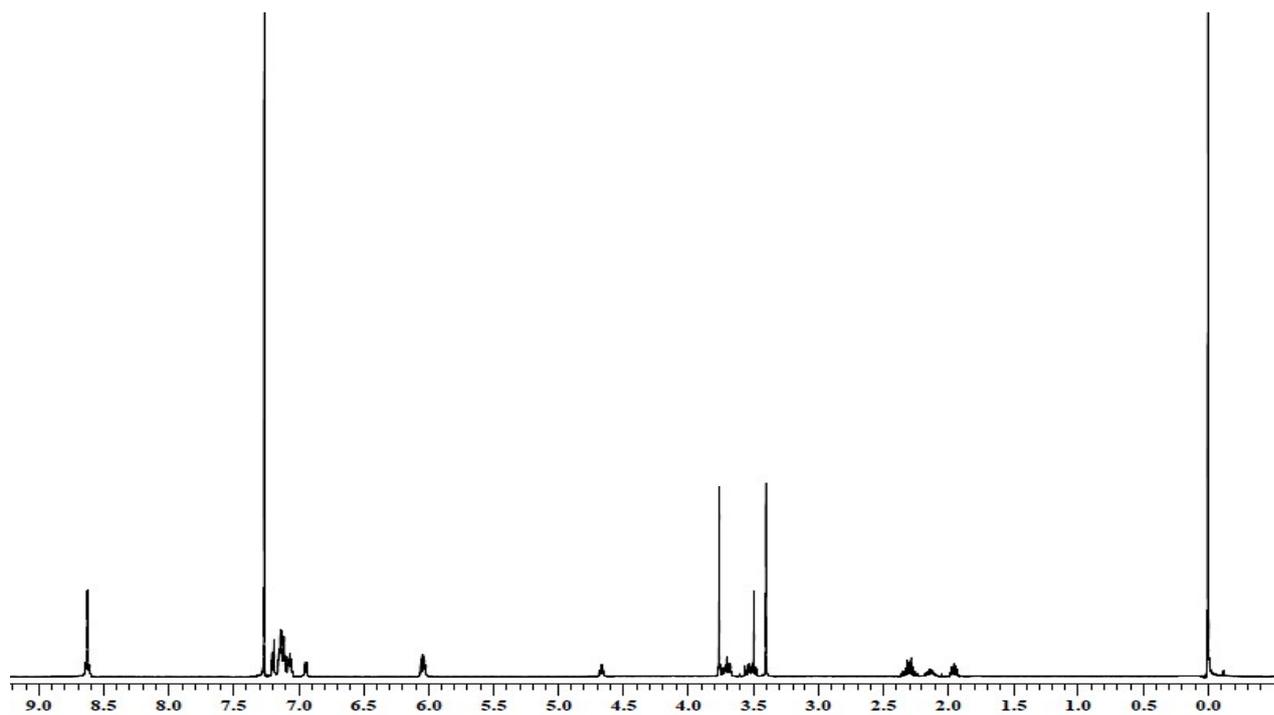


Fig. S7 ¹H NMR spectrum of **2**.

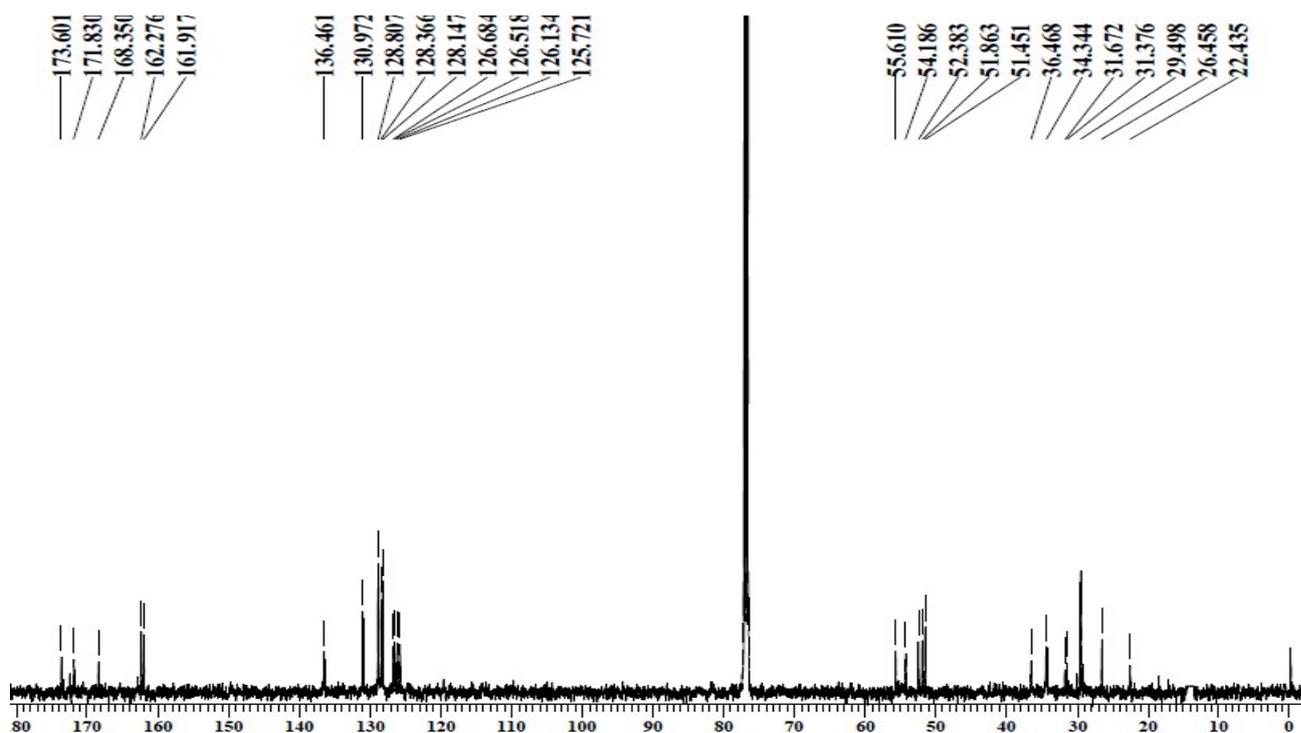


Fig. S8 ^{13}C NMR spectrum of **2**.

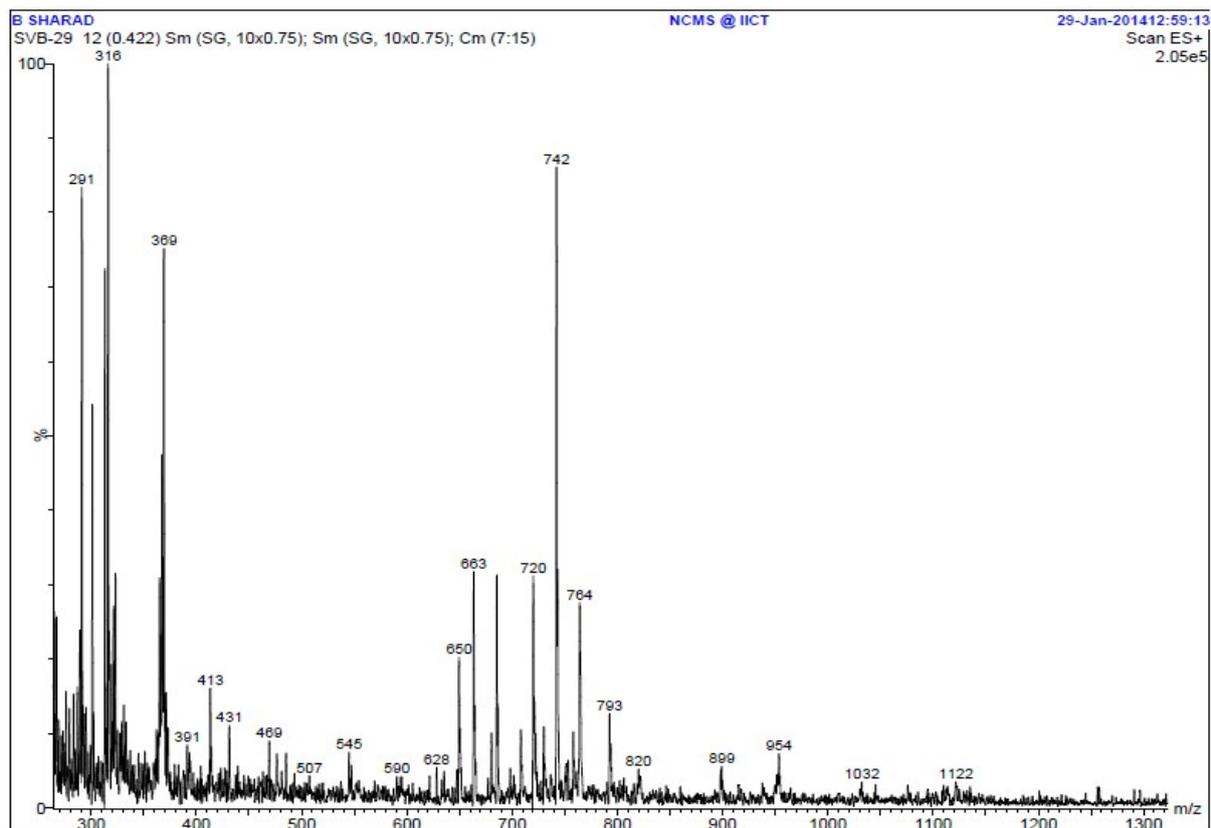
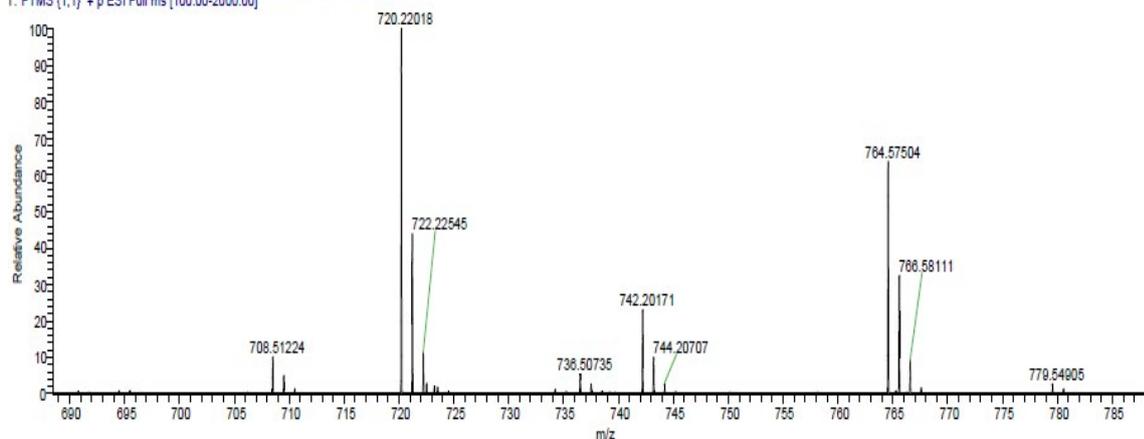


Fig. S9 Mass spectrum of **2**.

File Name C:\IICT-HRMS\11.02.2014\SVB-29
 Sample Name SHARAD
 Sample ID A:1
 Date and Time 13-02-14 13:37:10

SVB-29#4-87 RT: 0.02-0.30 AV: 84 SB: 327 0.80-1.90 NL: 4.74E8
 T: FTMS (1,1) + p ESI Full ms [100.00-2000.00]



SVB-29#8-30 RT: 0.03-0.11 AV: 23

T: FTMS {1,1} + p ESI Full ms [100.00-2000.00]

m/z= 717.41-723.42

m/z	Intensity	Relative	Theo. Mass	Delta (ppm)	RDB equiv.	Composition
720.22011	6835904.5	100.00	720.21879	1.84	24.5	C ₃₉ H ₃₄ O ₁₁ N ₃

Fig. S10 HRMS spectrum of 2.

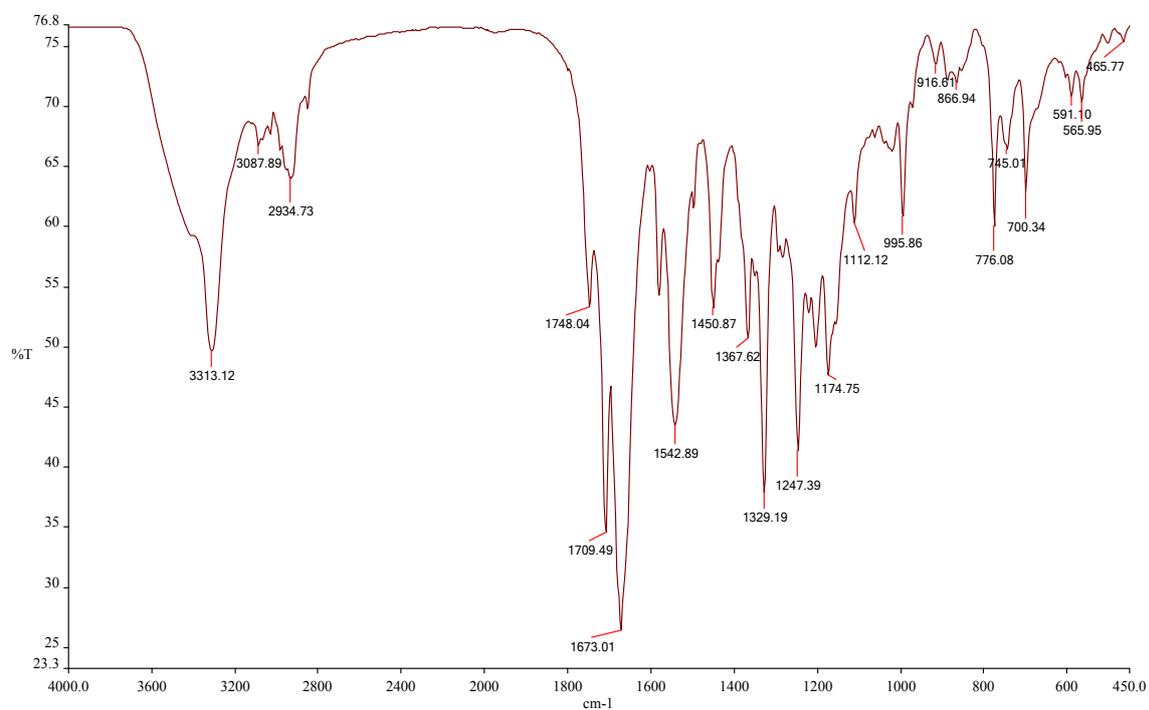


Fig. S11 FT-IR spectrum of 3.

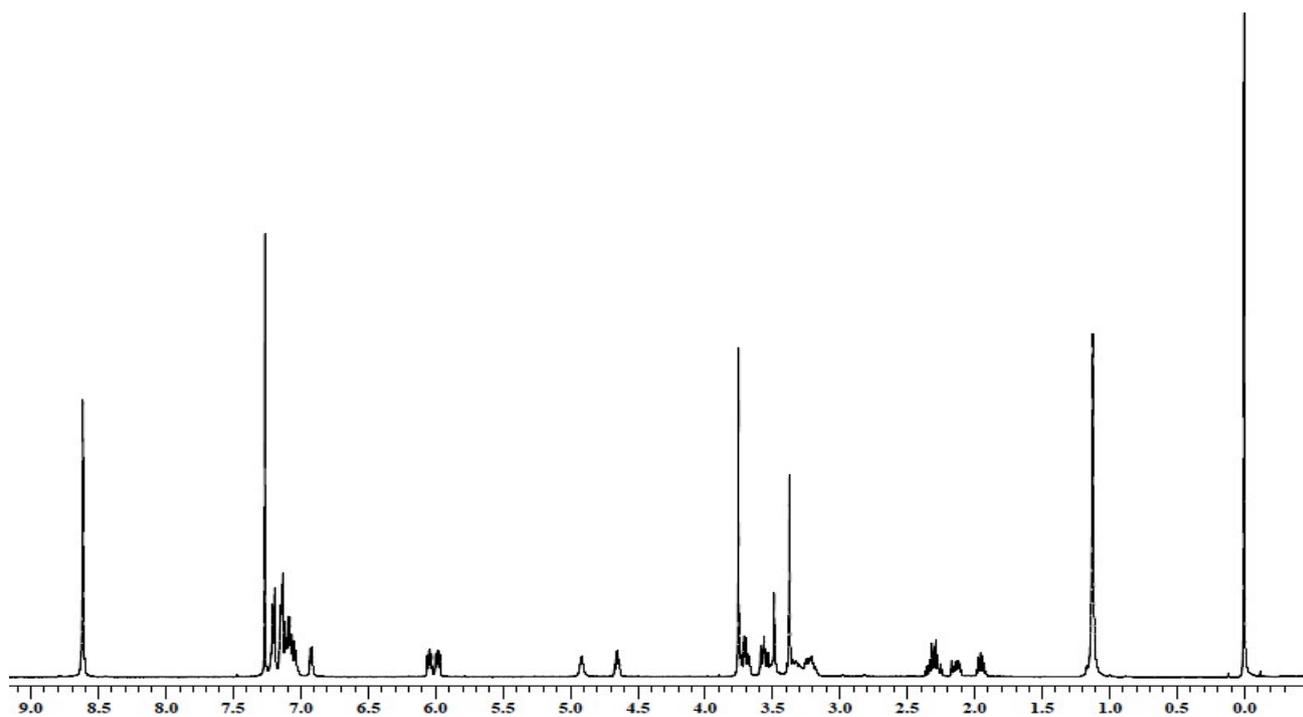


Fig. S12 ^1H NMR spectrum of **3**.

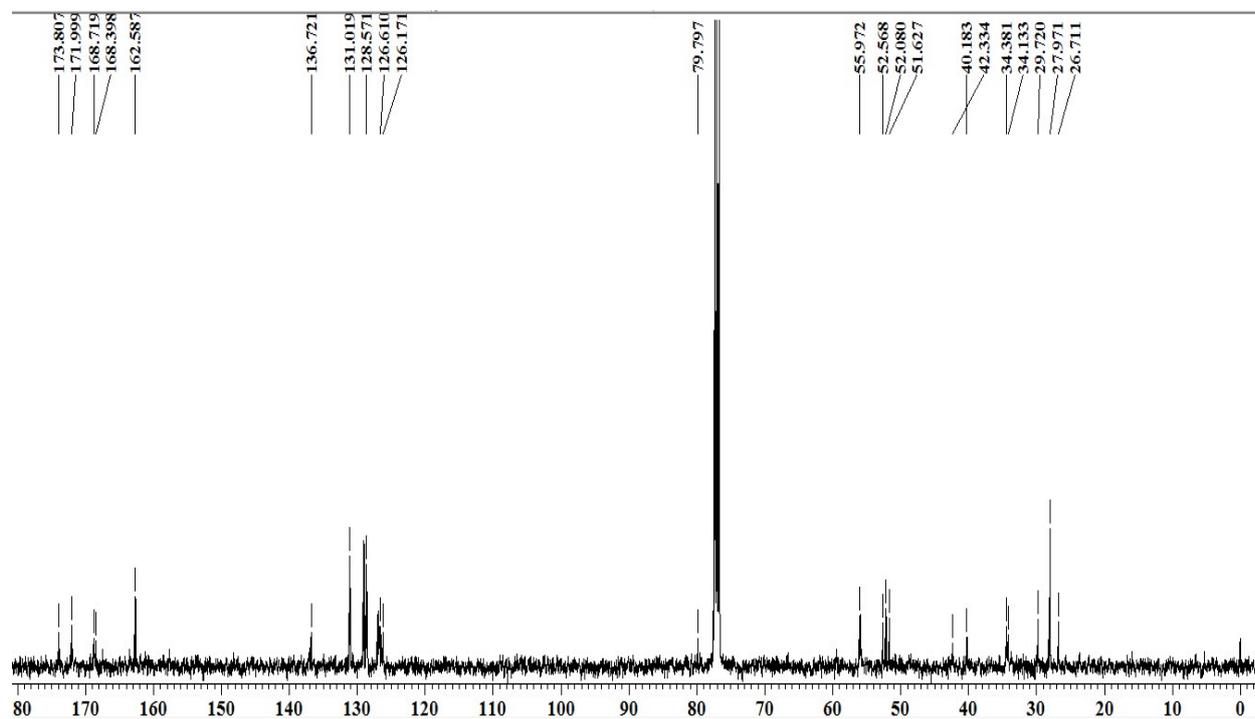


Fig. S13 ^{13}C NMR spectrum of **3**.

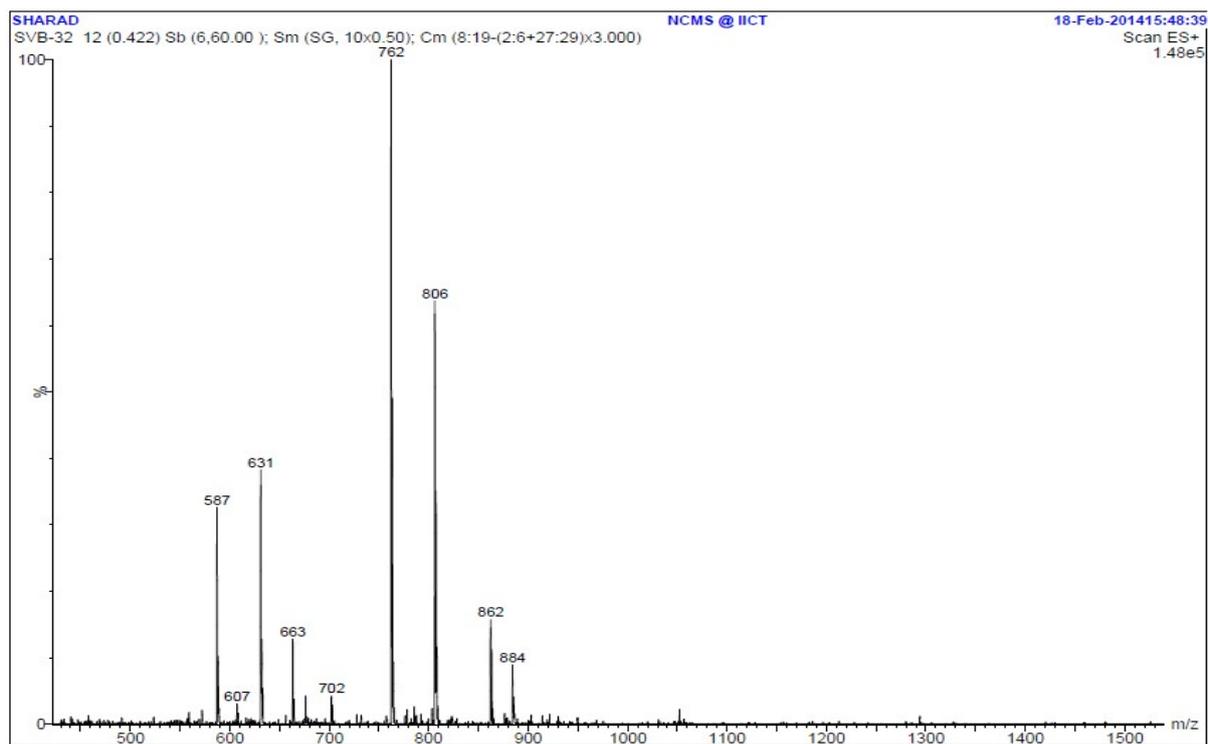


Fig. S14 Mass spectrum of 3.

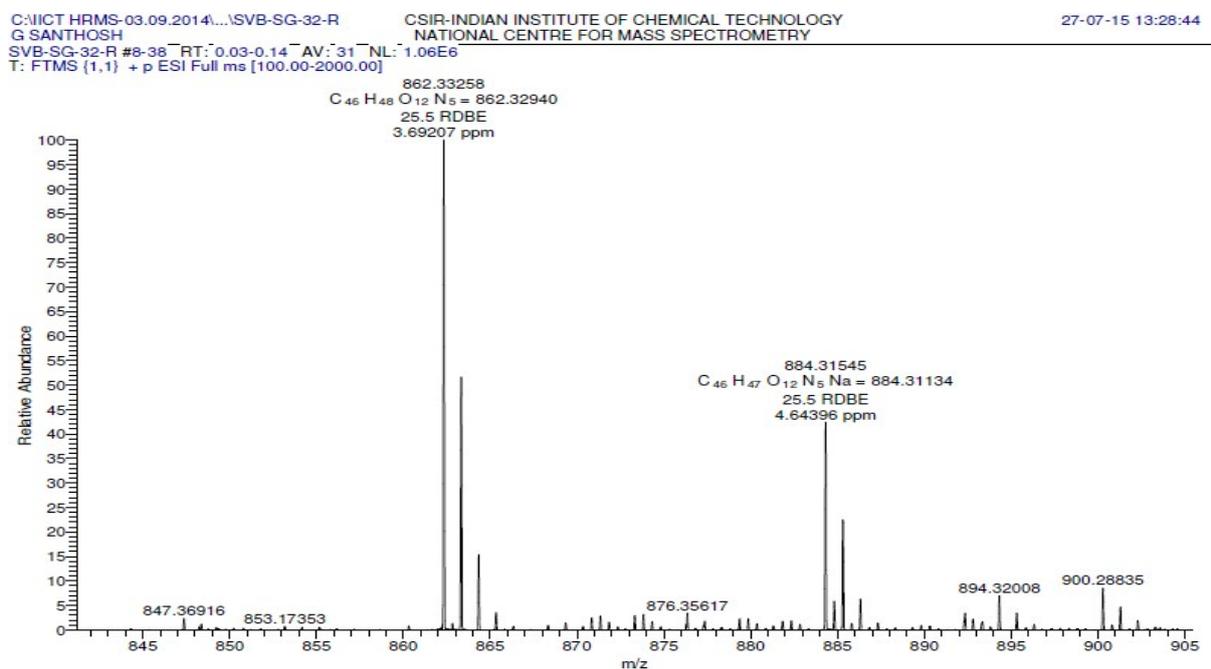


Fig. S15 HRMS spectrum of 3.

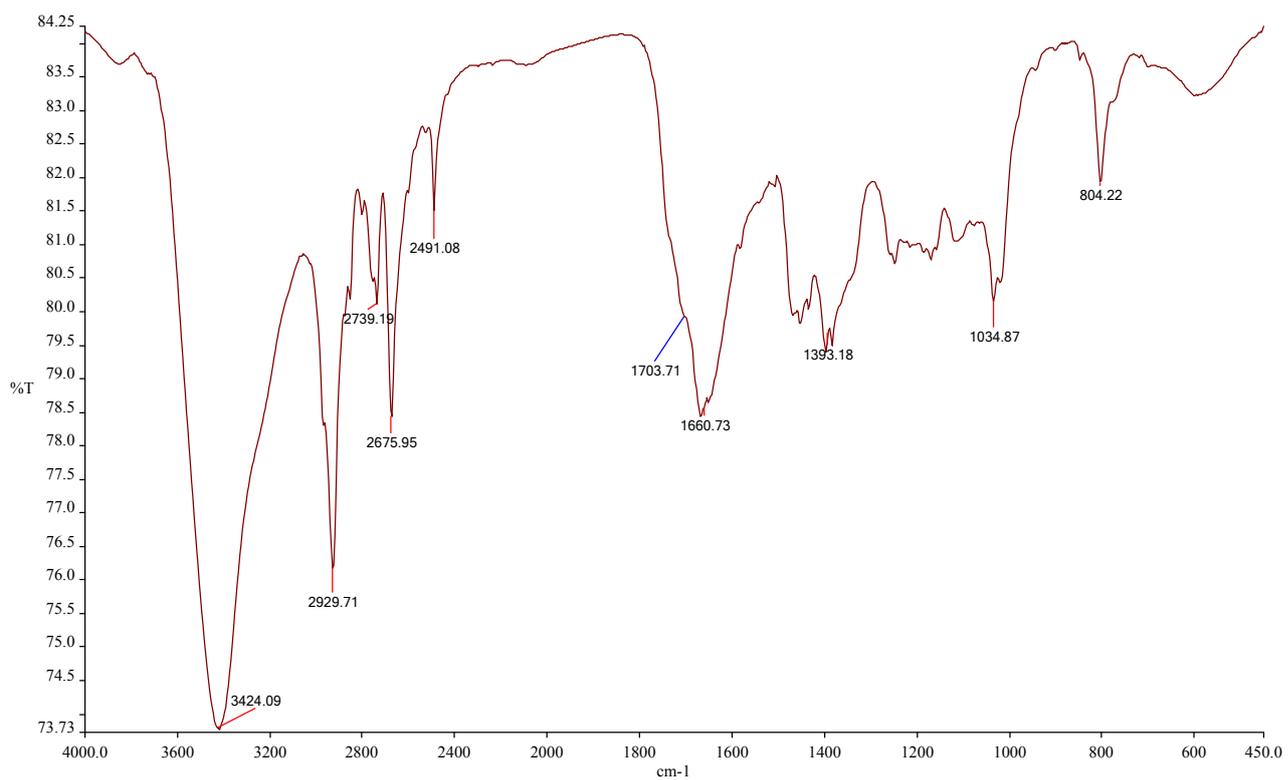


Fig. S16 FT-IR spectrum of NDI-S.

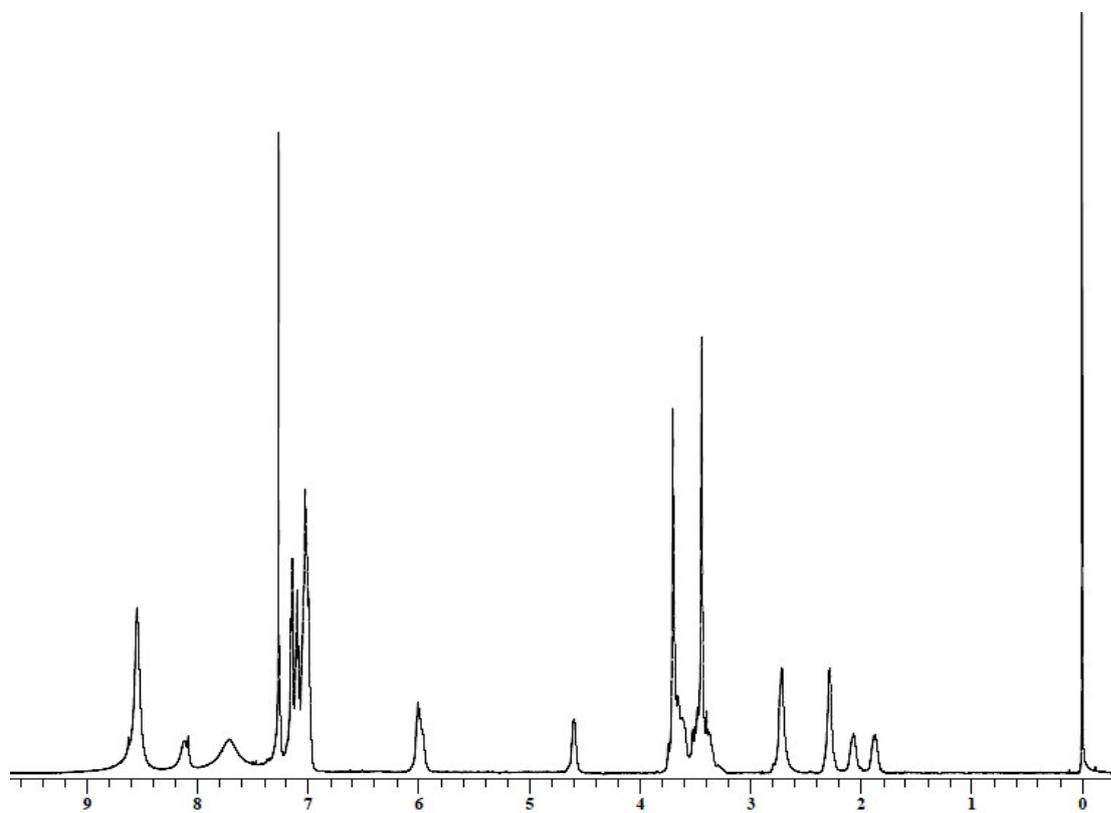


Fig. S17 ¹H NMR spectrum of NDI-S.

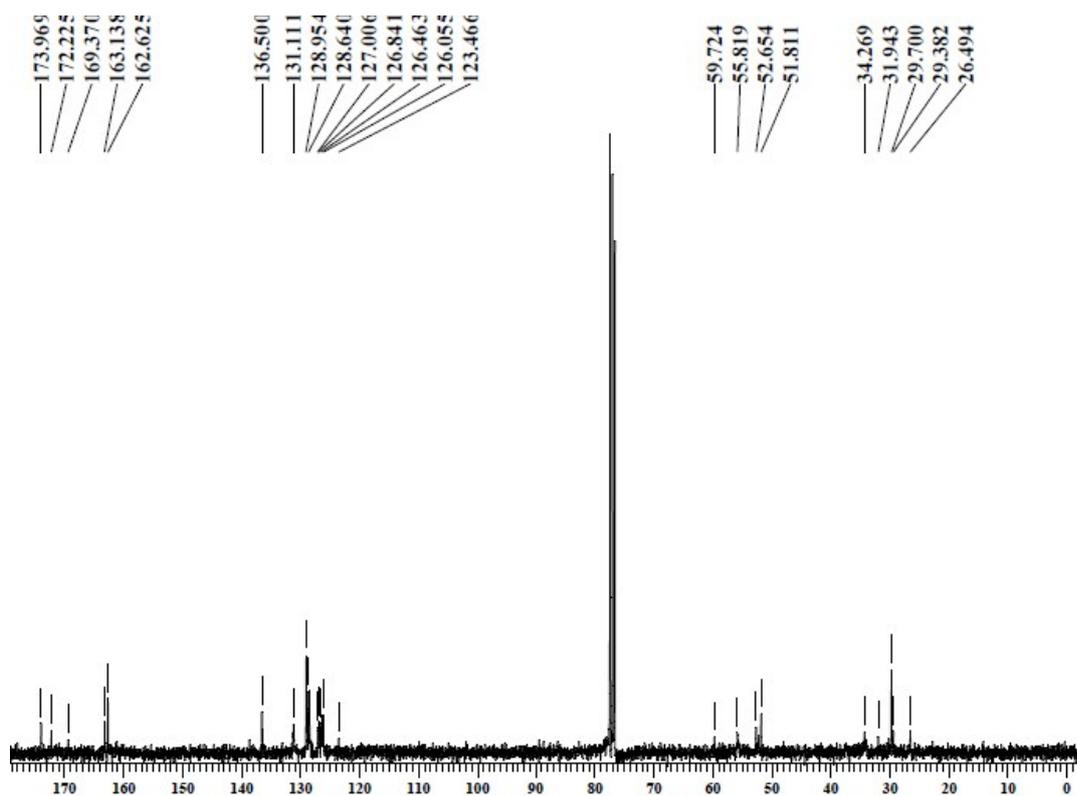


Fig. S18 ^{13}C NMR spectrum of NDI-S.

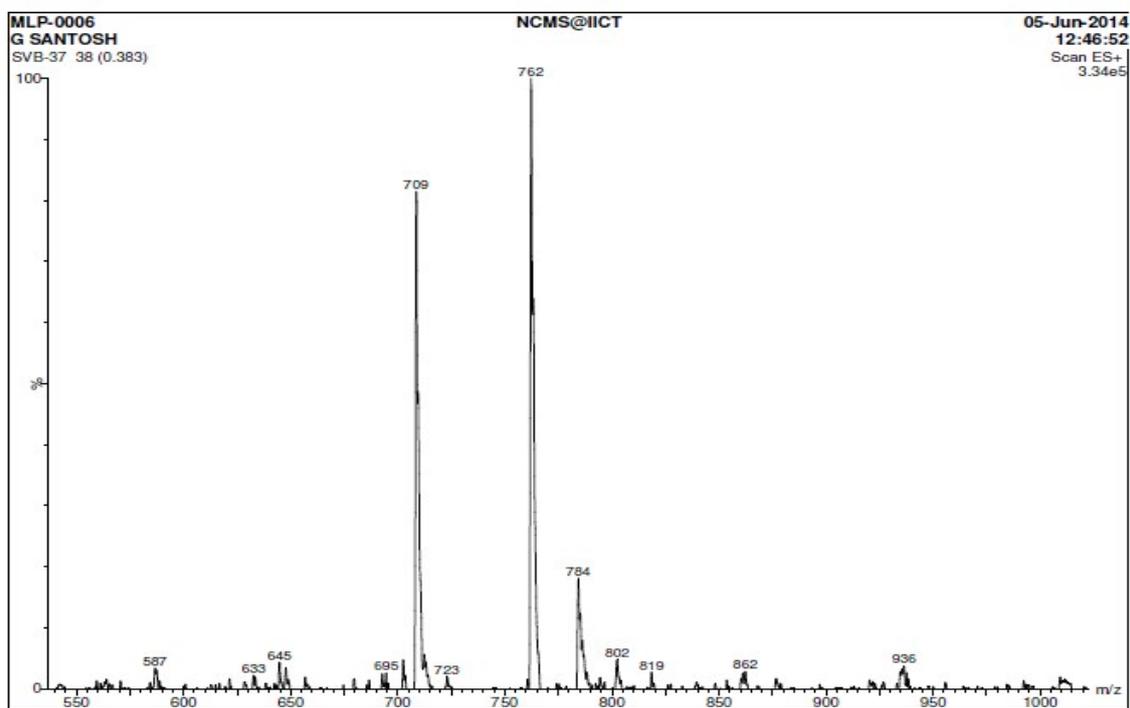


Fig. S19 ESI-Mass spectrum of NDI-S.

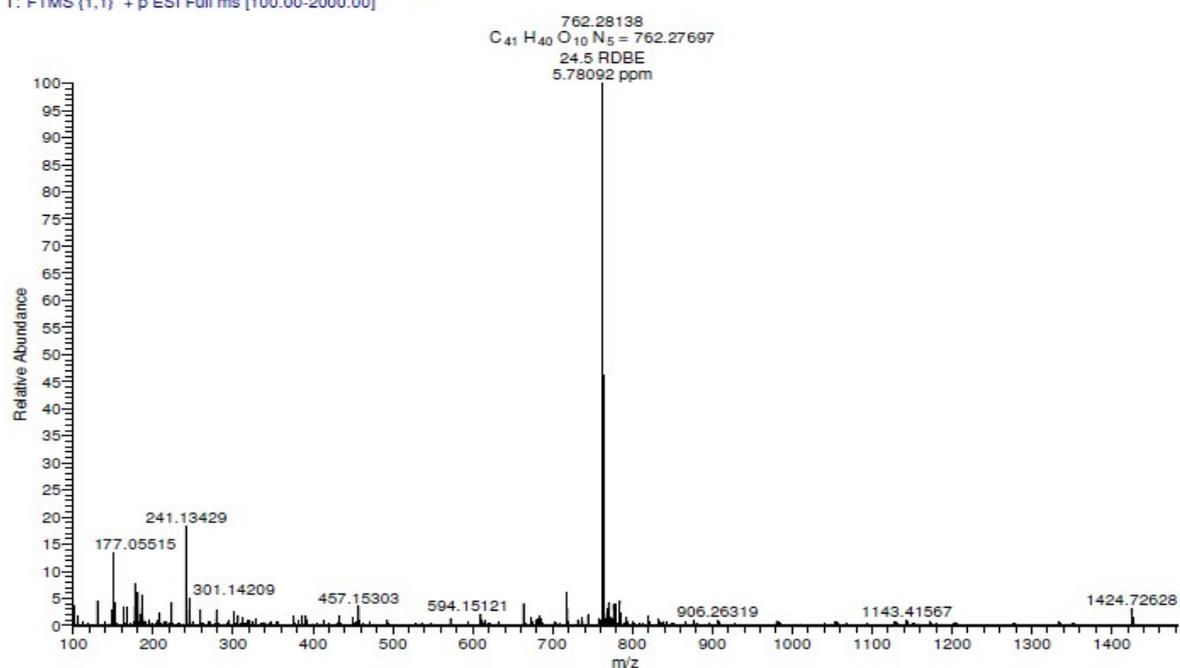


Fig. S20 HRMS spectrum of NDI-S.

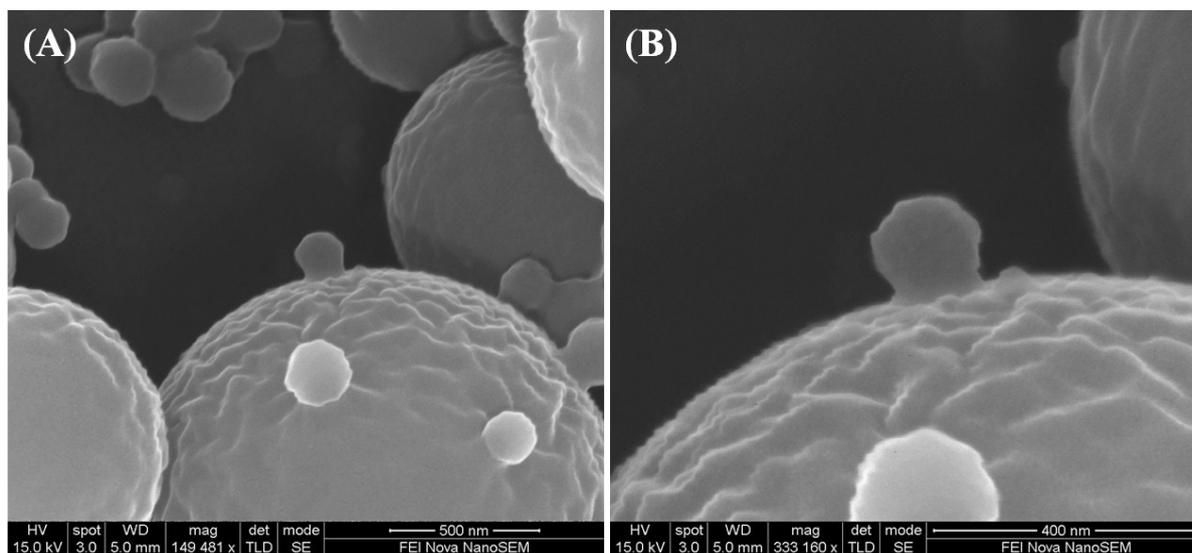


Fig. S21 A zoomed SEM image showing wrinkle surface of golf ball-like microspheres along with dents.

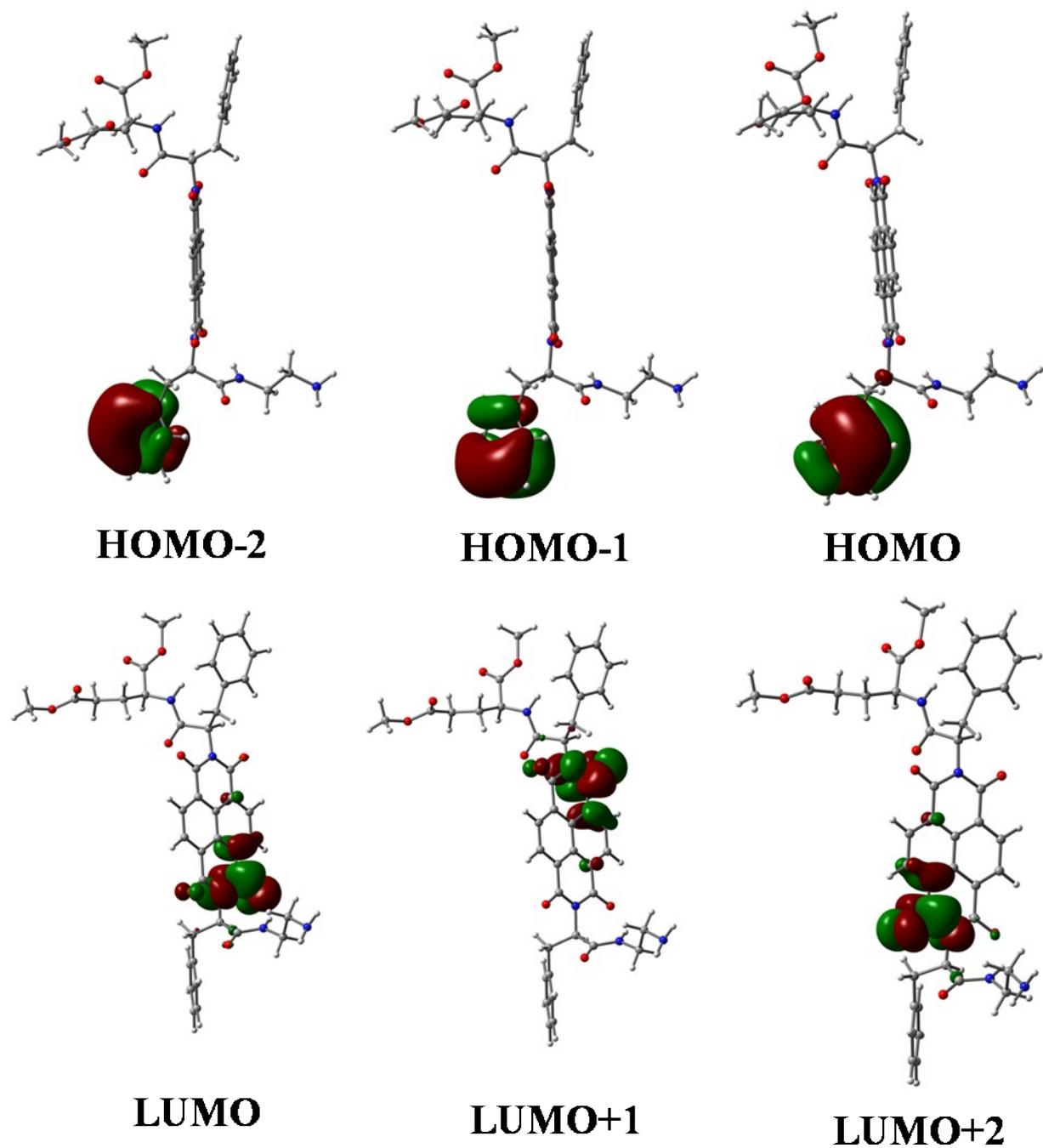


Fig. S22 The electron density distribution of HOMO-2, HOMO-1, HOMO, LUMO, LUMO+1, LUMO+2 molecular orbitals of NDI-S.

Reference

- 1 M. Pandeewar, H. Khare, S. Ramakumar and T. Govindaraju, *RSC Adv.*, 2014, **4**, 20154-20163.