

## Supplementary Information

### **Influences of number of 2-ethylhexylamine chain substituents on electron transport characteristics of core-substituted naphthalene diimide analogues**

Shailesh S. Birajdar,<sup>a,e†</sup> Samya Naqvi,<sup>b†</sup> Kerba S. More,<sup>c</sup> Avinash L. Puyad,<sup>d</sup> Rachana

Kumar,<sup>b,e,\*</sup> Sidhanath V. Bhosale,<sup>a,e,\*</sup> Sheshanath V. Bhosale<sup>c,\*</sup>

<sup>a</sup>Polymers and Functional Materials Division, CSIR-Indian Institute of Chemical Technology, Hyderabad-500007, Telangana, India.

<sup>b</sup>Advanced Materials and Devices Metrology Division, Photovoltaic Metrology Group, CSIR-National Physical Laboratory, Dr. K. S. Krishnan Marg, New Delhi 110012, India

<sup>c</sup>School of Chemical Sciences, Goa University, Taleigao Plateau, Goa-403206, India

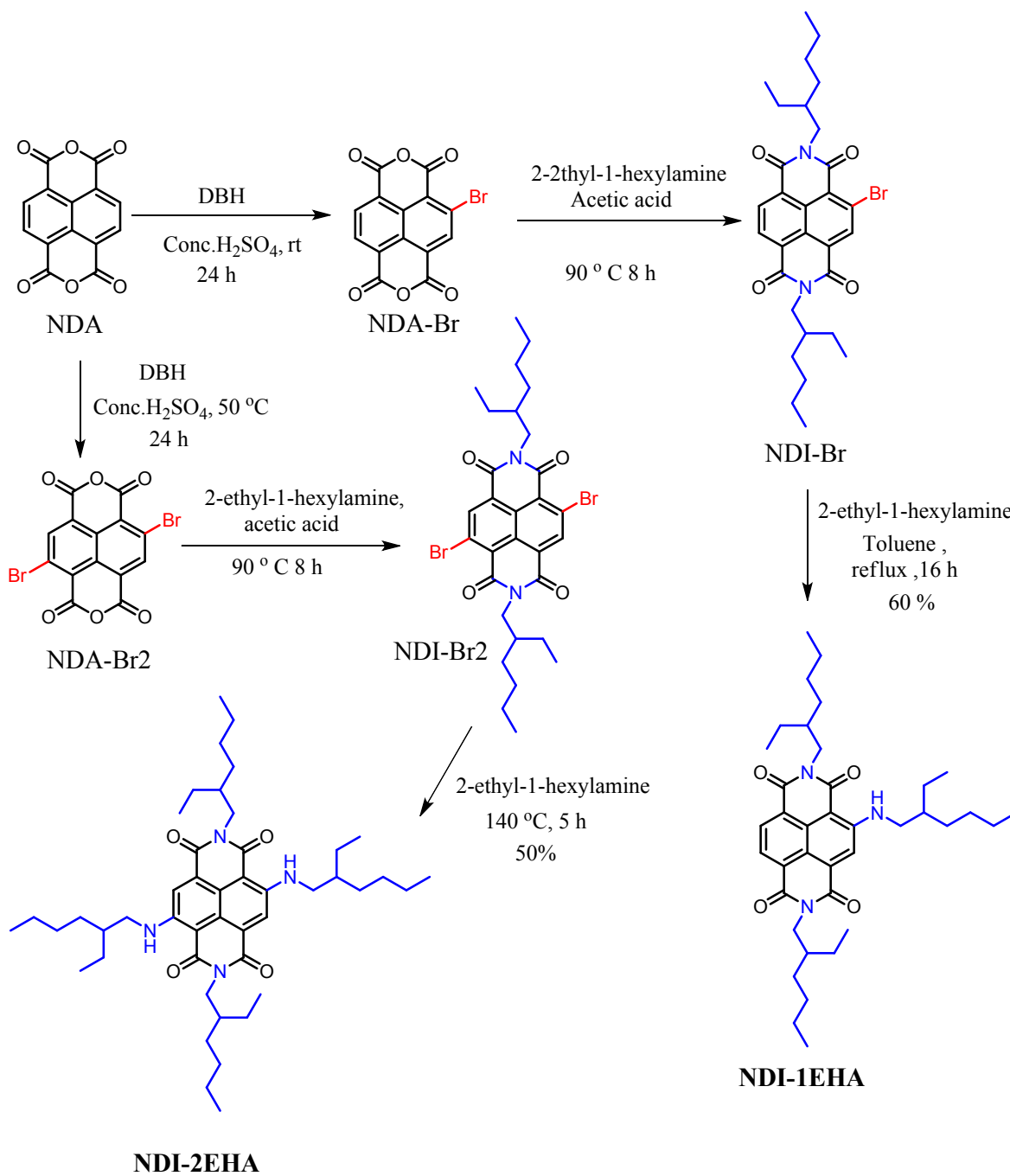
<sup>d</sup>School of Chemical Sciences, Swami Ramanand Teerth Marathwada University, Nanded 431606, Maharashtra, India.

<sup>e</sup>Academy of Scientific and Innovative Research (AcSIR), Ghaziabad- 201002, Uttar Pradesh, India

<sup>†</sup>These authors contributed equally

\*Corresponding Authors:

E-mail    bhosale@iict.res.in;    rachanak.npl@nic.in;    rachanasinghchem@gmail.com,  
svbhosale@unigoa.ac.in



**Scheme S1.** Synthesis of NDI-Br,<sup>S1</sup> NDI-1EHA, NDI-Br2<sup>S1</sup> and NDI-2EHA, respectively.

## S1 General Materials and methods

All the materials made available from commercial sources and used for reaction without further purification. The required solvents for the reactions were dried using reported procedures. The brominated naphthalene diimide derivatives were prepared using conventional procedures.<sup>S1</sup> The completion of reactions were monitored using thin-layer chromatography. The obtained compounds were purified by column chromatography on silica gel. The NMR studies were performed on Bruker at 400 MHz (<sup>1</sup>H) or 300 MHz (<sup>1</sup>H) and at 125 MHz (<sup>13</sup>C) or 100 MHz (<sup>13</sup>C) respectively using TMS as an internal standard and the chemical shifts ( $\delta$ ) in CDCl<sub>3</sub> as a solvent. The UV-vis absorption spectra were recorded in a 1 cm path length quartz cell using Shimadzu UV-1800 spectrophotometer. FT-IR spectra were measured on a Thermo Nicolet Nexus 670 spectrometer using KBr pellets. Matrix-assisted laser desorption/ionization (MALDI-TOF) were performed on Shimadzu Biotech Axima Performance Spectroscopic instrument.

## S2 Synthetic procedures

**S2.1. 4,5,9,10-tetrabromo-2,7-bis(2-ethylhexyl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8 (2H,7H)-tetraone (NDI-3Br and NDI-4Br):** In an oven dried 250 mL round bottom flask, NDA (1 g, 4 mmol) and sulphuric acid (35 mL) were stirred at room temperature for half an h. Then DBH (3.088 g, 12 mmol) was added to the reaction mixture in four portions within 1 h. After completion of DBH addition, the reaction mixture was stirred for half an hour at r.t. Then temperature of the reaction mixture was raised to 80 °C. The reaction was carried out for 24 h. After completion of reaction, bromine was evaporated very slowly at r.t. The obtained reaction mixture was poured into the ice water. The obtained precipitate was filtered on Buckner funnel and washed with water (3 - 4 times) followed by methanol (3 - 4 times). The mixture of NDA-3Br and NDA-4Br (1.6 g) as yellow solid was collected and dried it in oven.

The obtained mixture of NDA-3Br and NDA-4Br was used in next step without further purification.

In an oven 250 mL of round bottom flask, the mixture of NDA-3Br and NDA-4Br (1.6 g, 2.7 mmol) and acetic acid 60 mL were added and the reaction mixture was stirred for 30 min. at r.t. To this homogeneous mixture 2-ethyl-1-hexylamine (1.34 mL, 8.2 mmole) was added and the reaction mixture was heated at 100 °C for 14 h. The heating was stopped and cooled to room temperature. Then it was poured into ice water. The precipitate formation takes place. The precipitate was filtered on buckner funnel and washed with water (3 – 4 times). The obtained precipitate was dried over anhydrous magnesium sulphate followed by in oven. The obtained yellow colored crude naphthalene derivative (3 g) was utilized in next step without further purification.

The yellow colored crude naphthalene derivative (3 g) mixture was taken in an oven dried 250 mL round bottom flask containing dry toluene (30 mL). The reaction mixture was stirred at room temperature for 10 min. Then PBr<sub>3</sub> (0.8 mL, 8.90 mmol) was added to the reaction mixture. The reaction mixture was refluxed at 110 °C for 16 h. The progress of reaction was monitored by TLC. After completion of reaction, the reaction mixture was extracted with toluene (3×60 mL). The obtained solid was washed with methanol and dried over anhydrous sodium sulfate. Then purification of the compound was performed using column chromatography (silica gel, 100-200 mesh, DCM:hexane 1:1, v/v ratio), which in turn yielded NDI-3Br (20%) as golden yellow solid and NDI-4Br (60%) as dark yellow solid.

**Note:** Herein, the column chromatography was performed with slow elution with freshly prepared solvent mixture (DCM:hexane 1:1, v/v ratio run). The column chromatography yielded at first NDI-3Br (20%) followed by 20% mixture of NDI-3Br and NDI-4Br and finally NDI-4Br (60%).

**S2.1.1. Spectroscopic data for NDI-3Br:** FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3400, 3200, 2959.99, 2930.57, 2860.63, 1713.58, 1655.53, 1440.37, 1310.32, 122.5, 864.91;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  9.00 (s, 1H), 4.70 – 3.42 (m, 4H), 2.12 – 1.79 (m, 2H), 1.49 – 1.11 (m, 16H), 1.08 – 0.77 (m, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  161.24, 161.07, 139.20, 128.40, 127.78, 125.31, 124.11, 45.18, 37.79, 30.65, 28.56, 24.00, 23.10, 14.11, 10.60, 7.53.

**S2.1.2 Spectroscopic data for NDI-4Br:** FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3400, 2959.86, 2930, 1712.55, 1664.47, 1436.44, 1282.63, 1195.17, 785.05, 721.65;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.18 (d,  $J = 7.3$  Hz, 4H), 1.94 – 1.77 (m, 2H), 1.43 – 1.24 (m, 16H), 1.01 – 0.82 (m,  $J = 13.8, 7.2$  Hz, 12H).

**S2.2 Synthesis of 2,7-bis(2-ethylhexyl)-4-((2-ethylhexyl)amino)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (cNDI-1EHA):**<sup>S1</sup> NDI-1Br (150 mg, 0.26 mmol) and 10 mL dry toluene were taken in an oven dried 50 mL round bottom flask. The reaction mixture was stirred for 15 min at room temperature. Then 2-ethyl-1-hexylamine (64  $\mu\text{L}$ , 0.39599 mmol) was added to the reaction mixture. The reaction temperature was raised up to 90  $^\circ\text{C}$  and the heating was continued for 16 h. The completion of reaction was monitored by using TLC. The completion of reaction was also confirmed by the change in color from pale yellow into orange. The solvent was evaporated on rotary evaporator and washed with 0.1 N HCl ( $3 \times 100$  mL) and extracted with dichloromethane (DCM), dried over anhydrous sodium sulfate. The obtained residue was purified by column chromatography (DCM: hexane, 7:3), afforded orange solid as NDI-1EHA in 60% yield. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3463, 2957, 2854, 1638, 1589, 1520, 1456, 1391, 1323, 1276, 1192, 1131, 789, 564;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 10.22 (s, 1H), 8.63 (d,  $J = 10.7$  Hz, 1H), 8.32 (d,  $J = 9.3$  Hz, 1H), 8.22 (s, 1H), 4.21–4.04 (m, 4H), 3.50 (t,  $J = 5.8$  Hz, 2H), 1.98–1.88 (m, 2H), 1.79 (d,  $J = 18.7$  Hz, 1H),

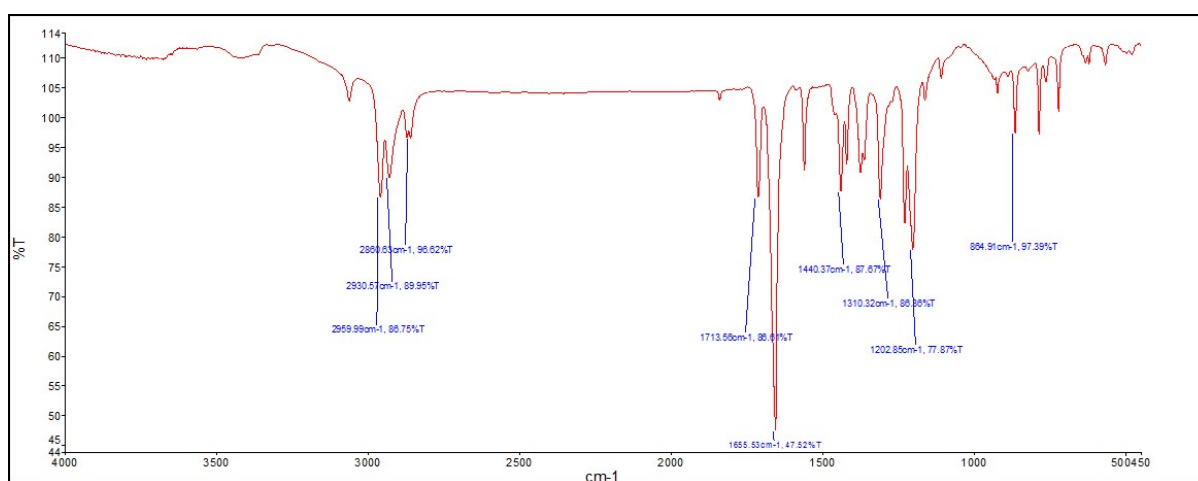
1.50–1.22 (m, 24H), 1.02–0.84 (m, 18H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 166.60, 163.84, 163.51, 163.47, 152.64, 131.35, 129.63, 127.87, 126.11, 124.44, 123.55, 120.05, 119.44, 99.84, 46.45, 44.54, 43.97, 39.37, 38.00, 37.79, 31.16, 30.77, 30.69, 29.73, 28.83, 28.71, 28.59, 24.54, 24.09, 23.07, 23.00, 14.11, 10.97, 10.87, 10.71; MALDI-TOF: (m/z) calculated for  $\text{C}_{38}\text{H}_{55}\text{N}_3\text{O}_4$  is 617.42; found = 618.55  $[\text{M}+\text{H}]^+$ .

**S2.3. Synthesis of 2,7-bis(2-ethylhexyl)-4-((2-ethylhexyl)amino)-9-(octan-3-ylamino)benzo[lmn][3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (cNDI-2EHA):** In a dried 50 mL round bottom flask NDI-2Br<sup>S1</sup> (300 mg, 0.46 mmol) and 2-ethyl-1-hexylamine (2 mL) were added under argon atmosphere. The reaction mixture was stirred for 15 min at room temperature. Then the temperature of the reaction mixture was raised up to 140 °C. Then the reaction was further heated at 140 °C for 2 h. The reaction mixture turns from yellow to dark blue color. The completion of reaction was confirmed by using TLC. Then the reaction mixture was quenched with  $\text{CH}_3\text{OH}/\text{HCl}$  (10:1 v/v), which in turn lead to the formation of precipitate. The obtained precipitate was washed with  $\text{CH}_3\text{OH}$  and dried over anhydrous sodium sulfate followed by in oven. This residue was purified by column chromatography (DCM:hexane 1:1) yields NDI-2EHA as indigo blue solid in 50%. FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3451.49, 3287.67, 2969.86, 2927.20, 2864.79, 2728.77, 2652.05, 1680.24, 1632.31, 1589.04, 1478.05, 1313.98, 1204.59, 1143.93, 1008.22, 885.85, 786.73;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$ : 9.44 (s, 2H), 8.18 (s, 2H), 4.54–3.77 (m, 4H), 3.41 (t,  $J = 5.7$  Hz, 4H), 2.02–1.86 (m, 2H), 1.87–1.68 (m, 2H), 1.54–1.24 (m, 16H), 1.00–0.87 (m, 12H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 166.59, 163.59, 149.45, 125.74, 121.18, 118.45, 101.84, 46.34, 43.98, 39.20, 37.86, 31.25, 30.73, 28.85, 28.63, 24.60, 24.09, 23.04, 14.07, 10.98, 10.74; MALDI-TOF: (m/z) calculated for  $\text{C}_{46}\text{H}_{72}\text{N}_4\text{O}_4$  is 744.56; Found = 745.61  $[\text{M}+\text{H}]^+$ .

**S2.4. Synthesis of 2,7-bis(2-ethylhexyl)-4,5,9-tris((2-ethylhexyl) amino) benzo [lmn][3,8] phenanthroline-1,3,6,8(2H,7H)-tetraone (NDI-3EHA):** To an oven dried 50 mL round bottom flask, NDI-Br3 (300 mg, 0.37 mmol) and an excess amount of 2-ethyl-1-hexylamine (3 mL) were added under N<sub>2</sub> atmosphere. The reaction mixture was stirred for 15 min. at room temperature. Then the temperature of reaction mixture was raised up to 100 °C. then the reaction was heated at 100 °C for 10 h. The product formation was confirmed by using TLC. After conversion of starting material into product the reaction mixture turns to dark red. Then the reaction mixture was quenched with CH<sub>3</sub>OH/HCl (10:1 v/v), which in turn lead to the formation of precipitate. The obtained precipitate was washed with CH<sub>3</sub>OH and dried over anhydrous sodium sulfate followed by in oven. This obtained sticky crude reaction mixture was purified by column chromatography (DCM-Hexane 1:2) to yield NDI-3EHA as bloodred sticky liquid in 40 %. FT-IR (KBr, v, cm<sup>-1</sup>): 3450.38, 2925.32, 2864.43, 2090.64, 1637.77, 1456.58, 1281.25, 1200.70, 1126.64, 1032.64, 759.26, 590.78; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ: 10.38 (s, 1H), 9.64 (s, 1H), 9.34 (s, 1H), 7.77 (s, 1H), 4.54–3.90 (m, 4H), 3.61 (s, 2H), 3.43–3.15 (m, 4H), 2.02–1.85 (m, 2H), 1.84–1.70 (m, 1H), 1.51–1.17 (m, 42H), 0.99–0.77 (m, 30H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ: 166.83, 166.20, 164.10, 152.66, 150.48, 147.08, 126.25, 125.00, 112.65, 110.07, 107.28, 104.71, 101.99, 48.53, 48.30, 46.39, 44.04, 43.50, 41.63, 41.44, 39.03, 37.93, 37.69, 31.34, 30.99, 30.73, 28.77, 24.67, 24.39, 24.07, 14.14, 13.99, 10.96, 10.77; MALDI-TOF: (m/z) calculated for C<sub>54</sub>H<sub>89</sub>N<sub>5</sub>O<sub>4</sub> is 871.69 [M]<sup>+</sup>; found = 871.56 [M]<sup>+</sup> and 872.61[M+H]<sup>+</sup>.

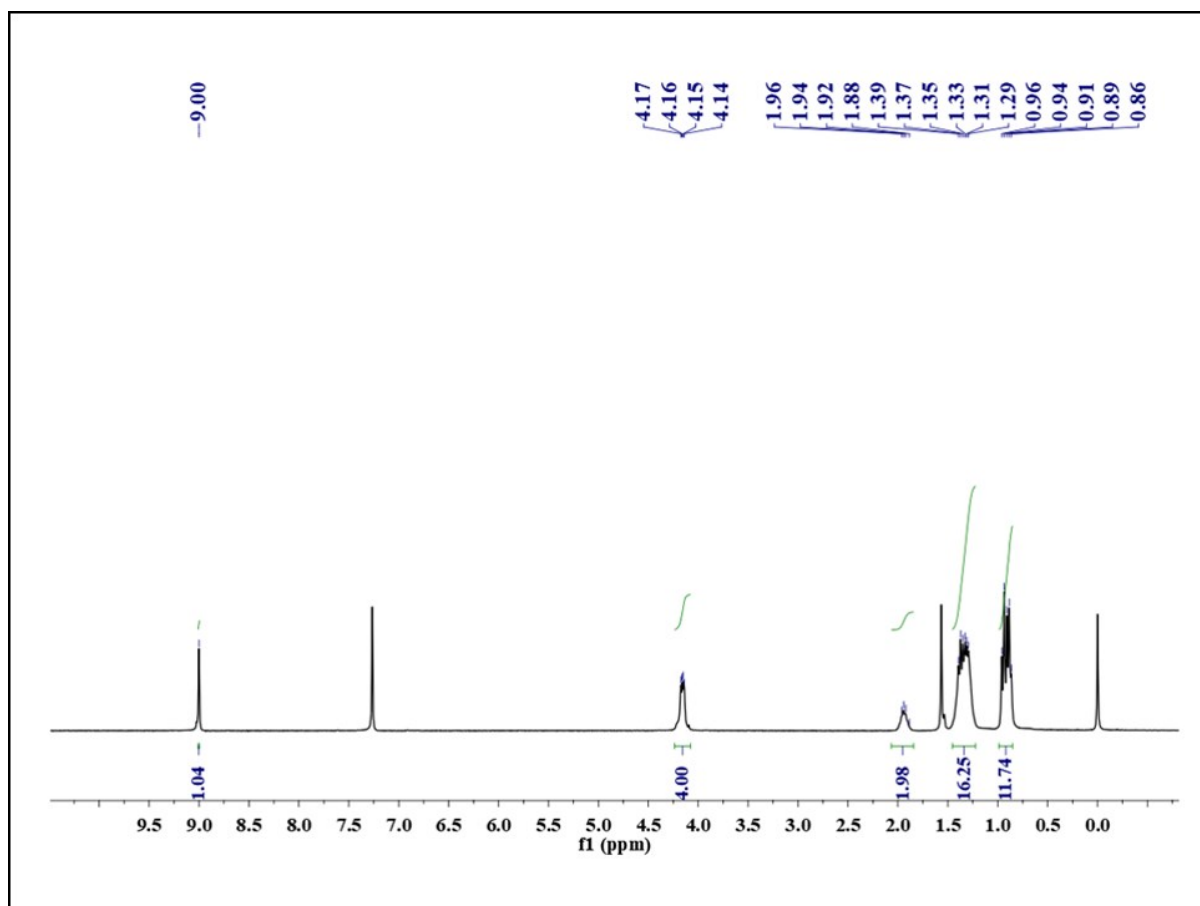
**S2.5. Synthesis of 2,7-bis(2-ethylhexyl)-4,5,9,10-tetrakis((2-ethylhexyl)amino)benzo[lmn][3,8] phenanthroline-1,3,6,8(2H,7H)-tetraone (cNDI-4EHA):** Synthesis of NDI-3EHA was performed following the procedure for the synthesis of NDI-3EHA as above. Column chromatography was performed using silica gel (100-200 mesh) in (DCM-

hexane 1:3) to yield dark green sticky liquid as NDI-4EHA (50%). FT-IR (KBr,  $\nu$ ,  $\text{cm}^{-1}$ ): 3450.38, 2925.32, 2864.43, 2092.64, 1637.77, 1456.58, 1281.25, 1200.70, 1126.64, 1032.64, 759.26, 590.78;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.42 (s, 4H), 4.18–4.03 (m, 4H), 3.31 (t,  $J = 5.5$  Hz, 8H), 1.91–1.81 (m, 2H), 1.24 (m, 9.3 Hz, 52H), 0.87–0.70 (m, 36H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$ : 166.21, 147.24, 116.83, 107.45, 53.45, 47.95, 43.60, 41.19, 37.80, 31.05, 30.88, 28.78, 24.45, 24.13, 23.12, 14.15, 13.99, 10.95, 10.79; MALDI-TOF: ( $m/z$ ) calculated for  $\text{C}_{62}\text{H}_{106}\text{N}_6\text{O}_4$  is 998.83  $[\text{M}]^+$ ; found = 998.61  $[\text{M}]^+$ .

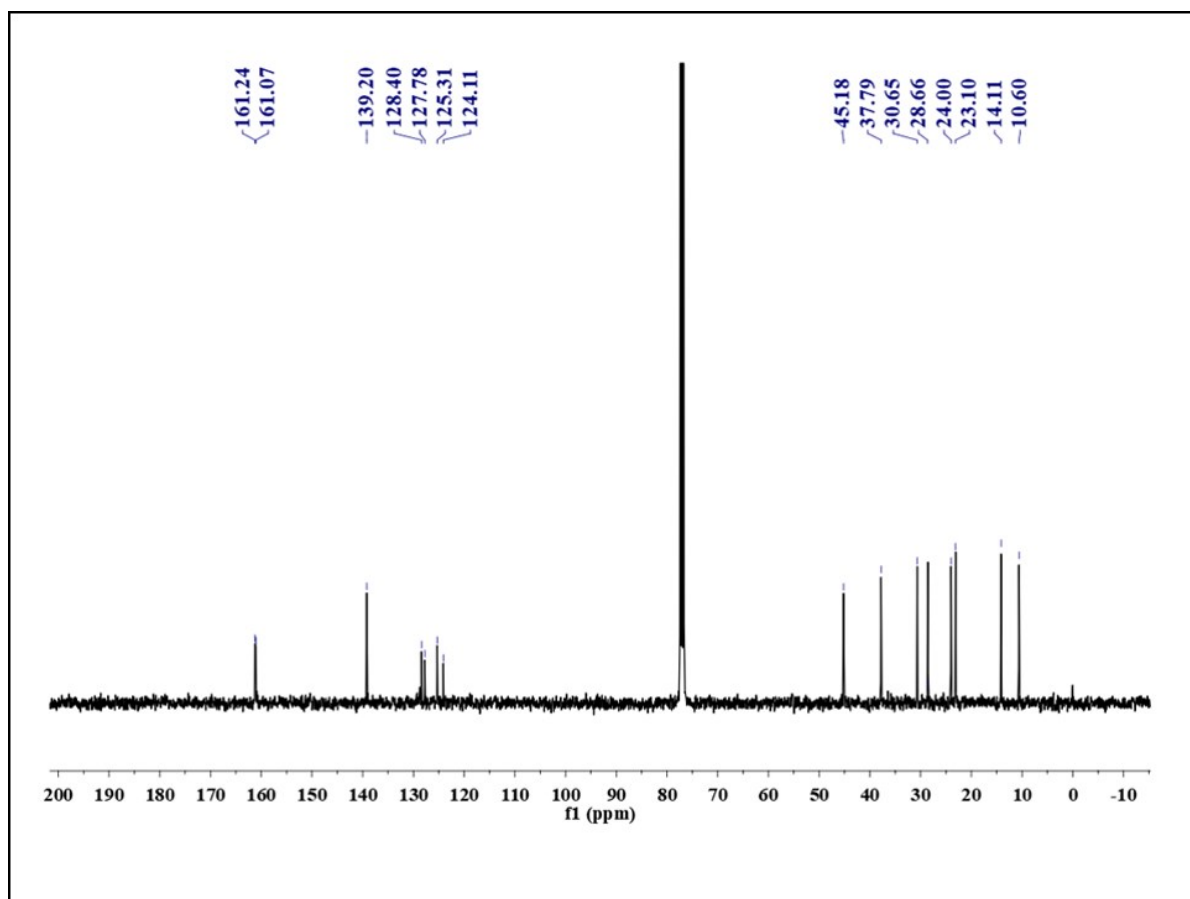


**Fig. S1** FT-IR spectra of NDI-3Br

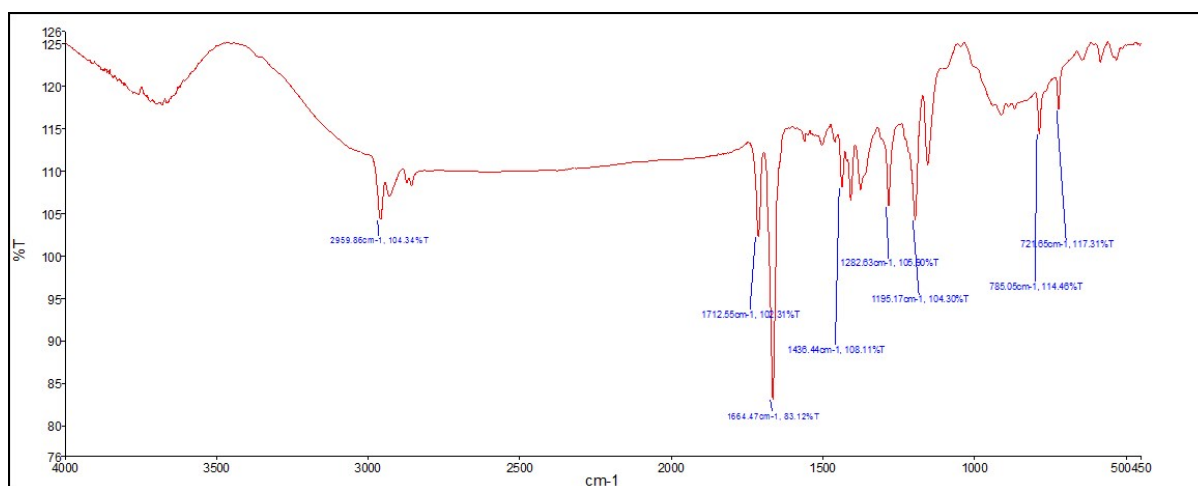




**Fig. S2**  $^1\text{H}$  NMR spectra of NDI-3Br



**Fig. S3**  $^{13}\text{C}$  NMR spectra of NDI-3Br



**Fig. S4** FT-IR spectra of NDI-4Br

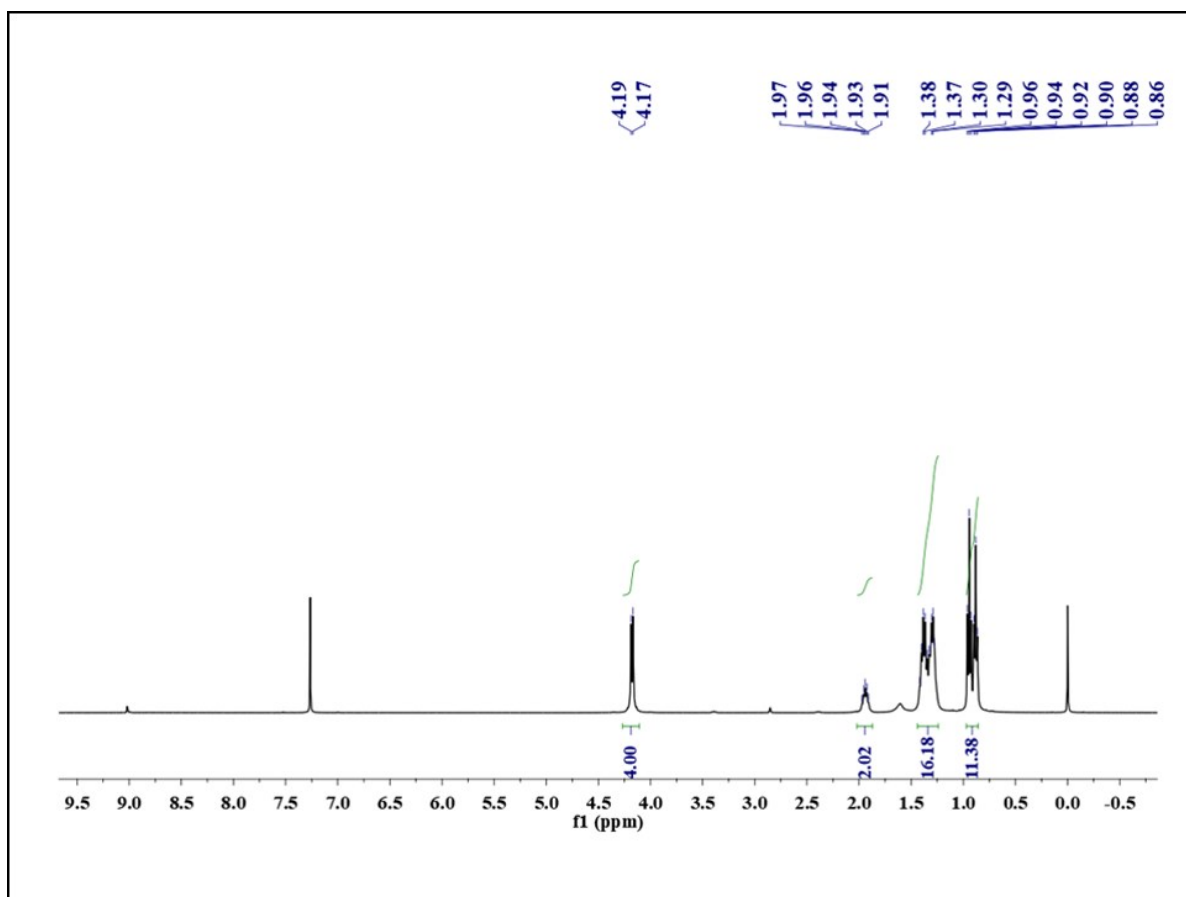


Fig. S5 <sup>1</sup>H NMR spectra of NDI-4Br

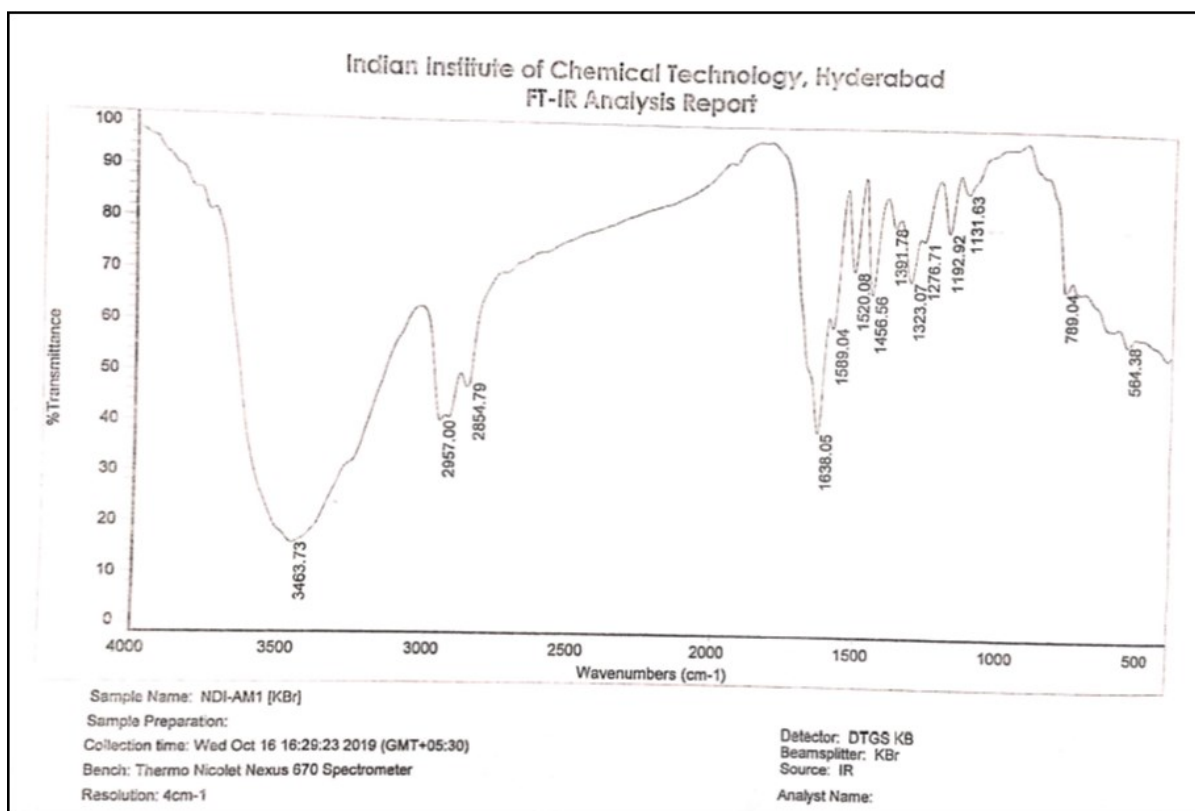


Fig. S6 FT-IR spectra of cNDI-1EHA

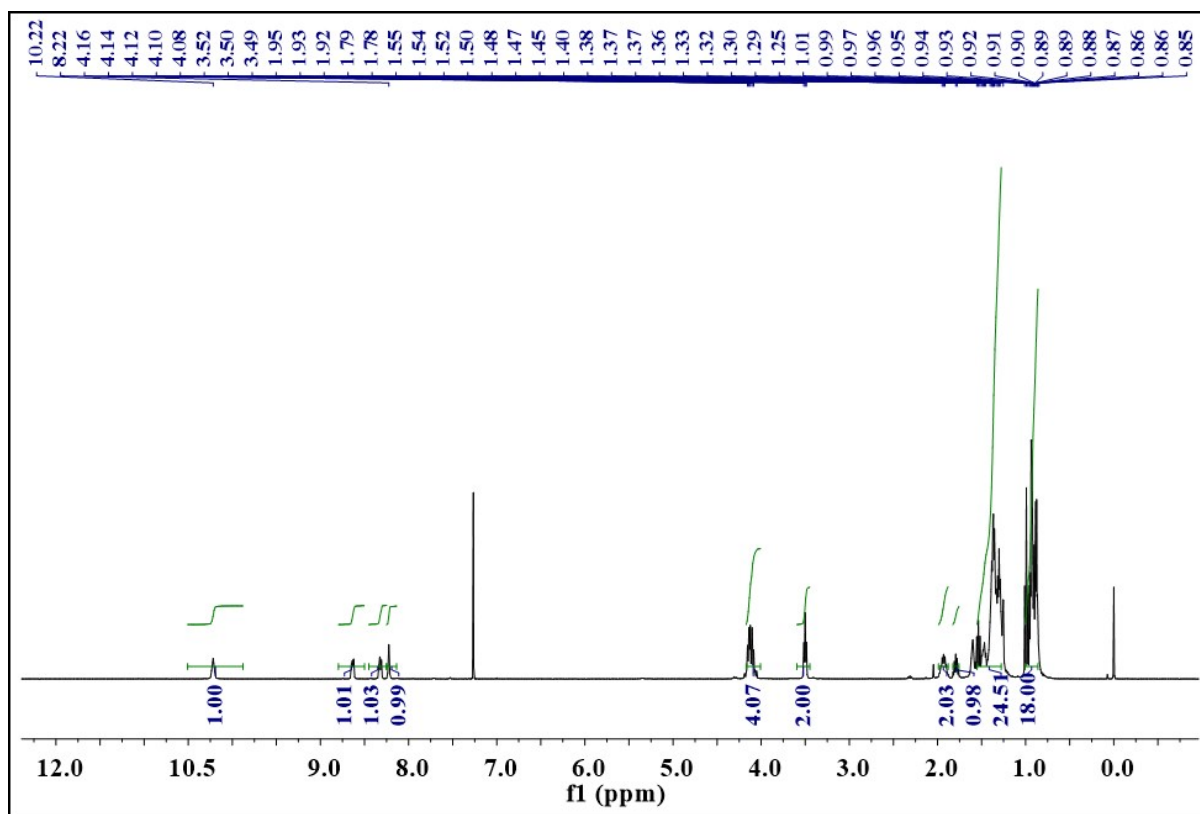


Fig. S7  $^1\text{H}$  NMR spectra of cNDI-1EHA

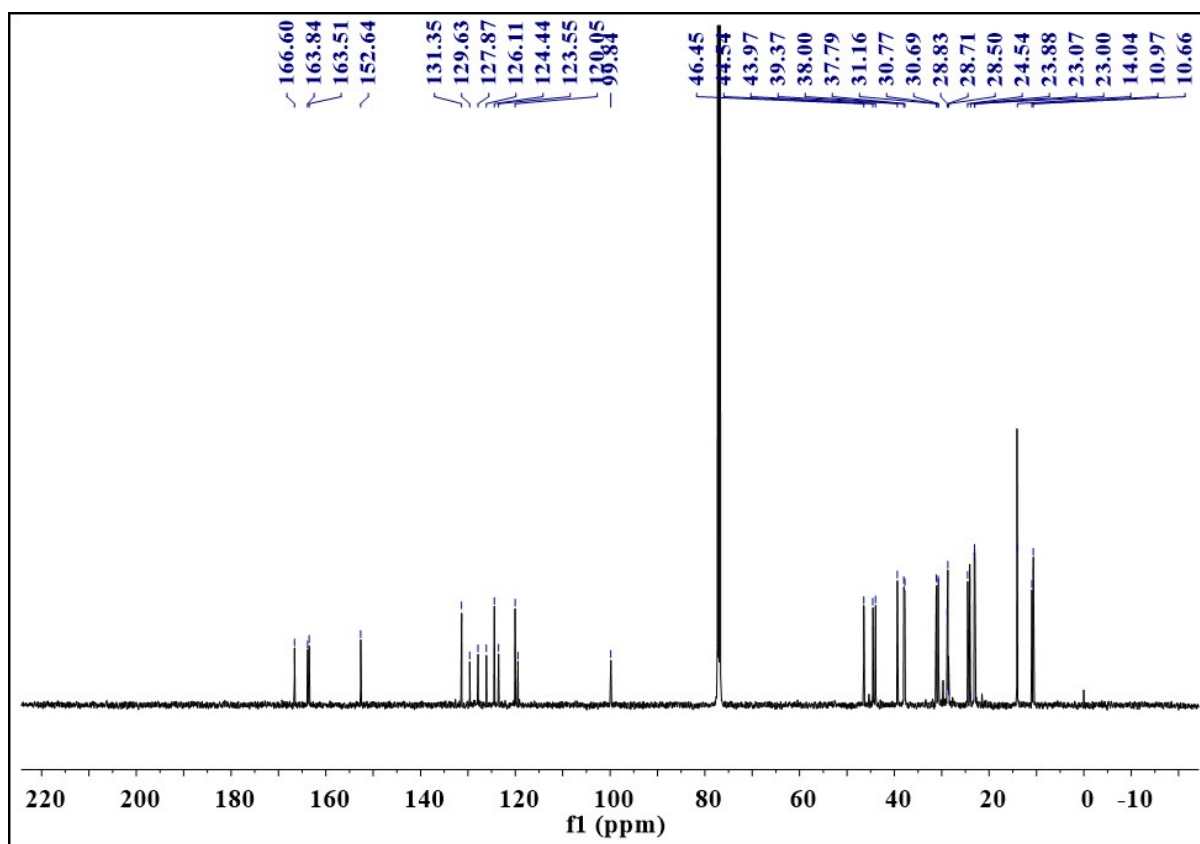
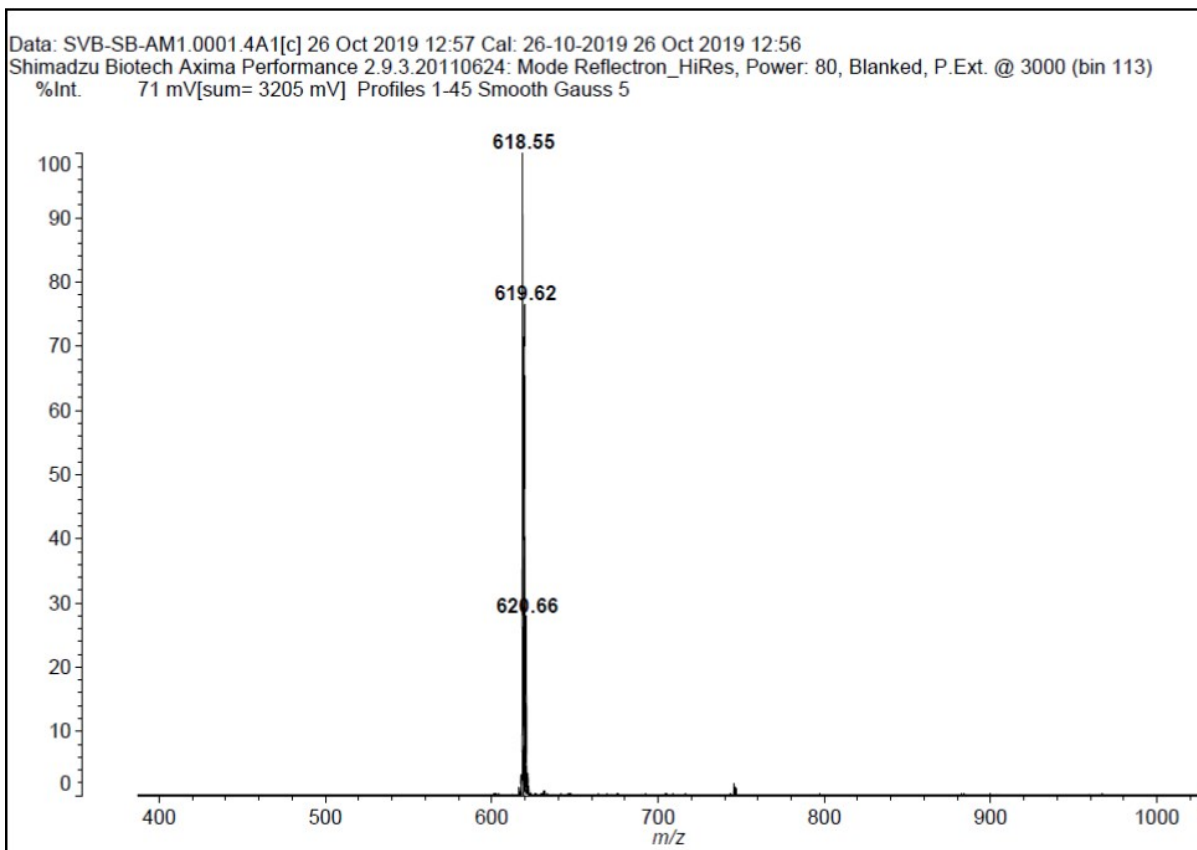
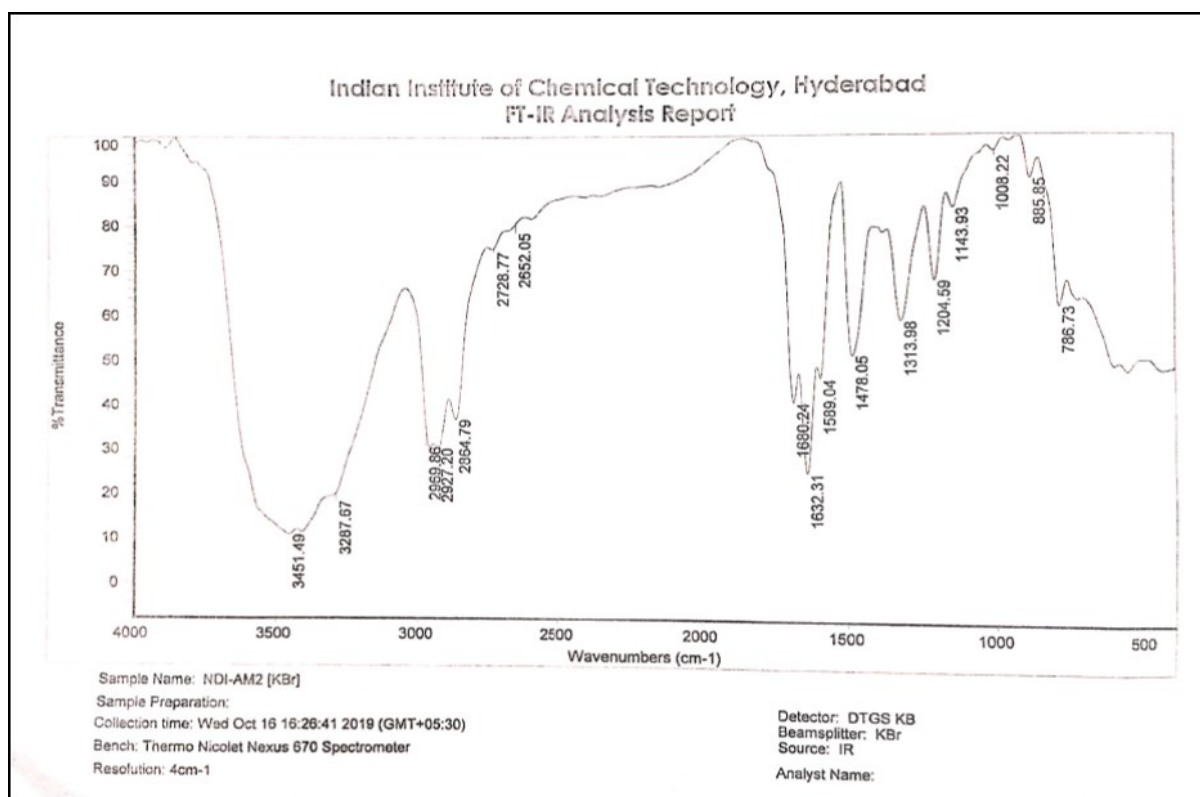


Fig. S8  $^{13}\text{C}$  NMR spectra of cNDI-1EHA



**Fig. S9** MALDI-TOF spectrum of cNDI-1EHA



**Fig. S10** FT-IR spectra of cNDI-2EHA

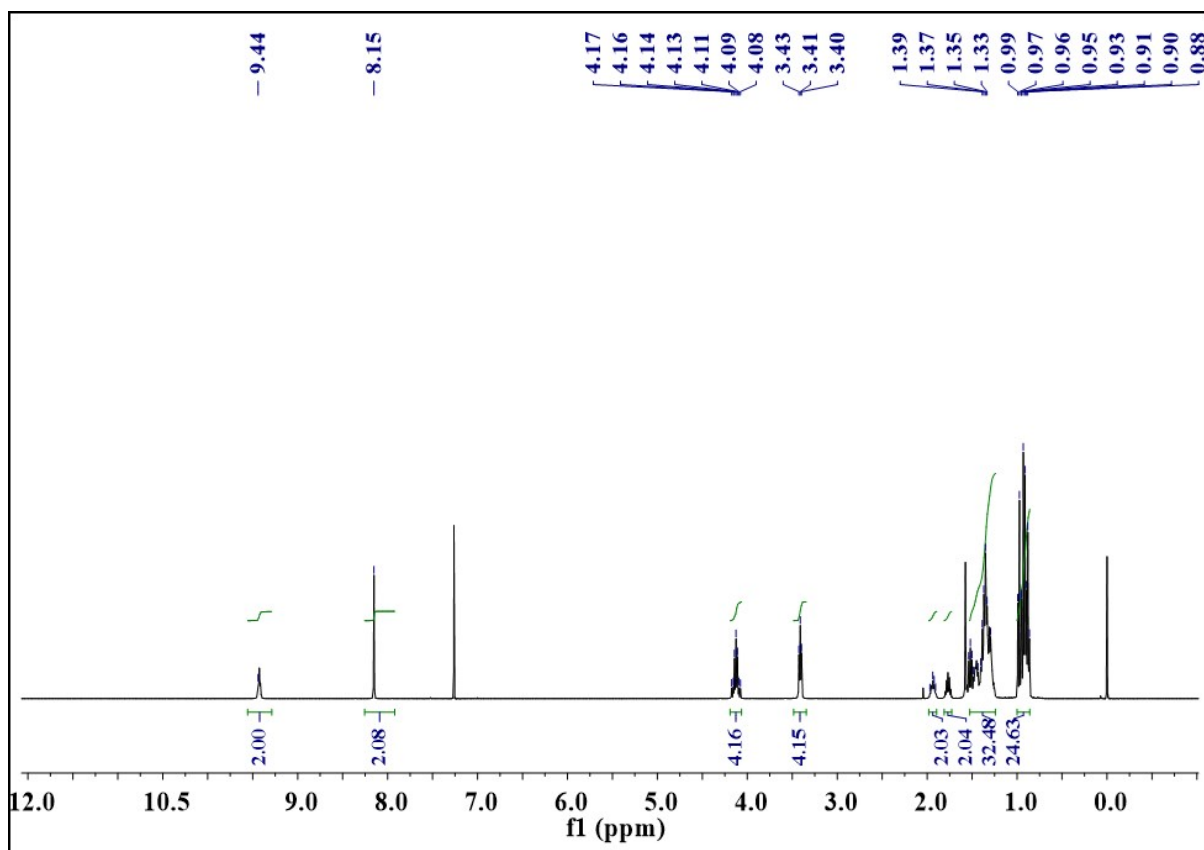


Fig. S11  $^1\text{H}$  NMR spectra of cNDI-2EHA

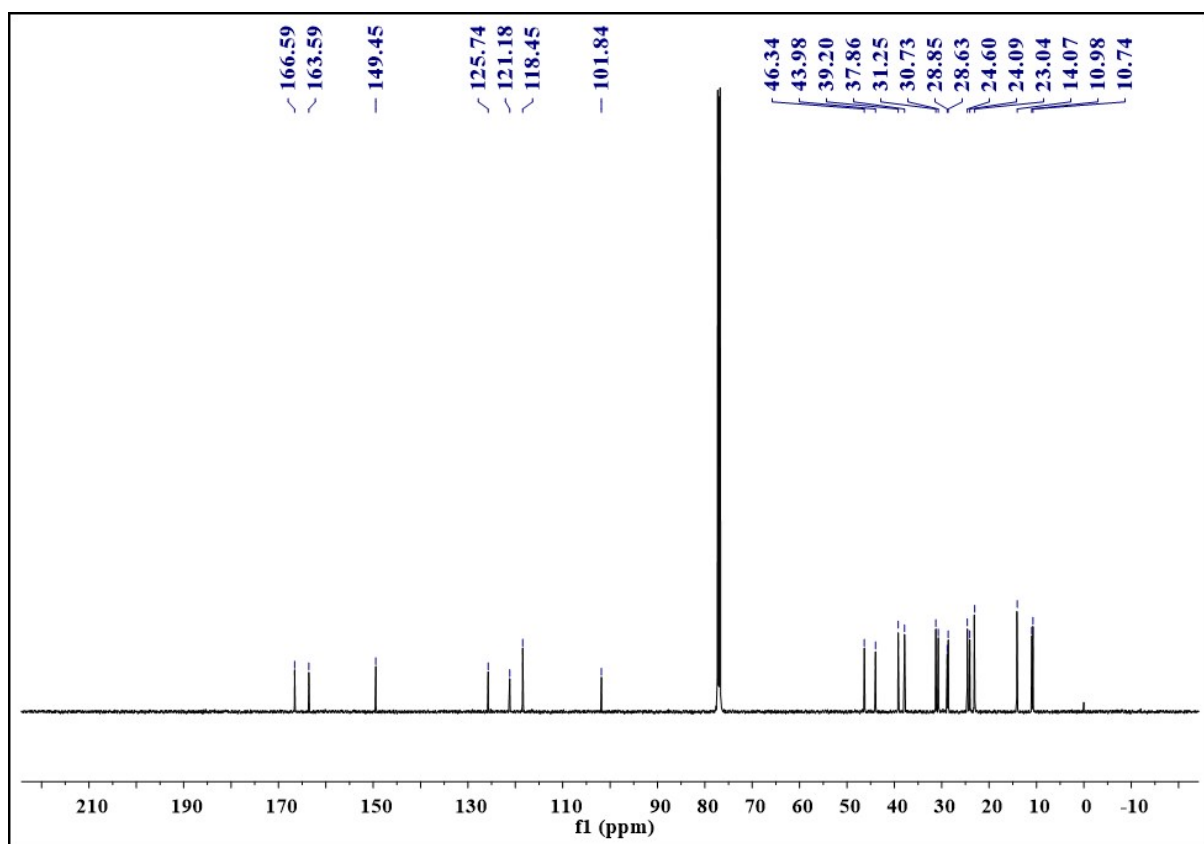
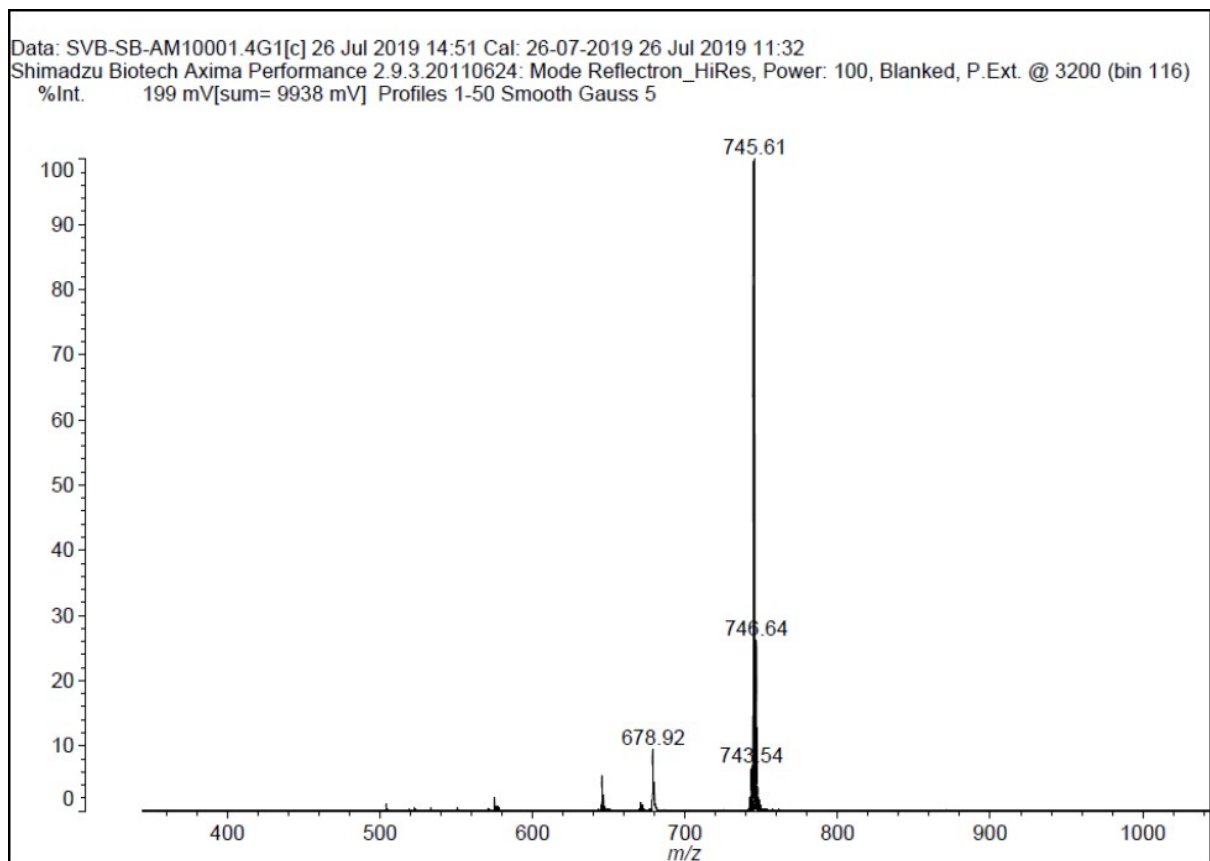
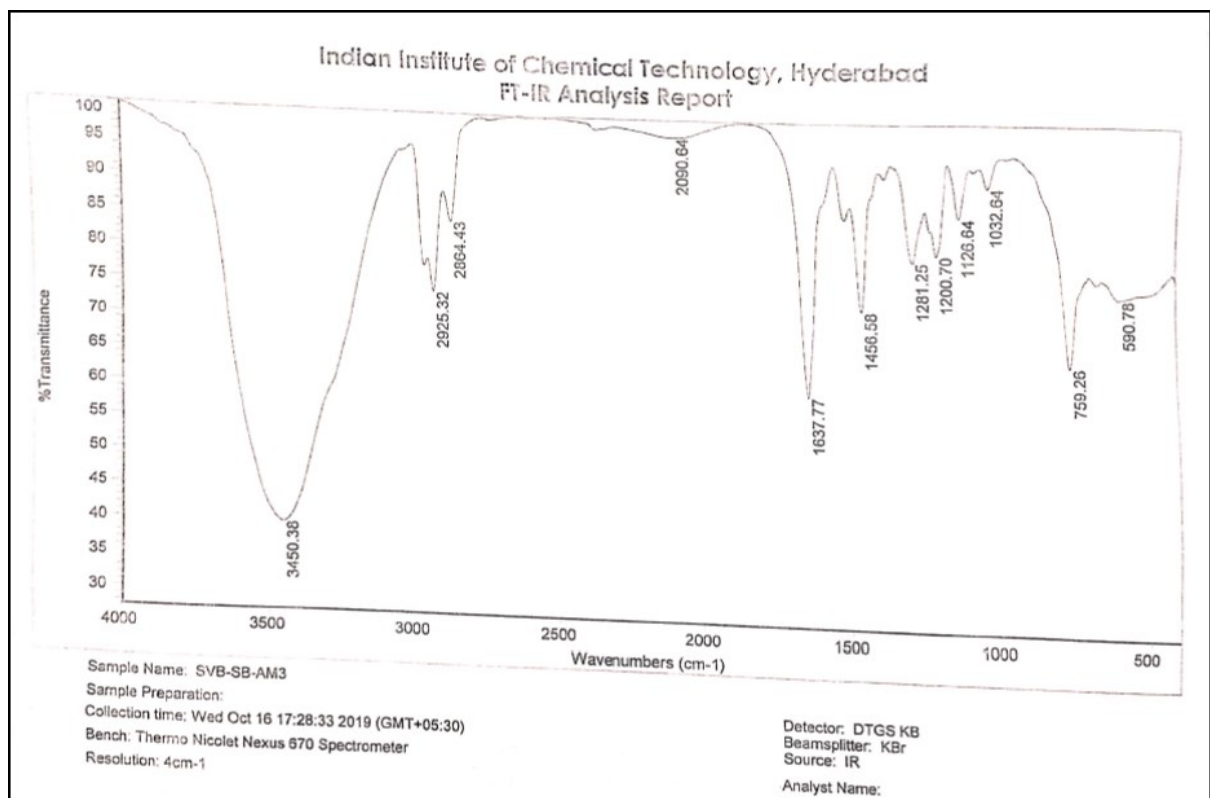


Fig. S12  $^{13}\text{C}$  NMR spectra of cNDI-2EHA



**Fig. S13** MALDI-TOF spectrum of cNDI-2EHA



**Fig. S14** FT-IR spectra of cNDI-3EHA

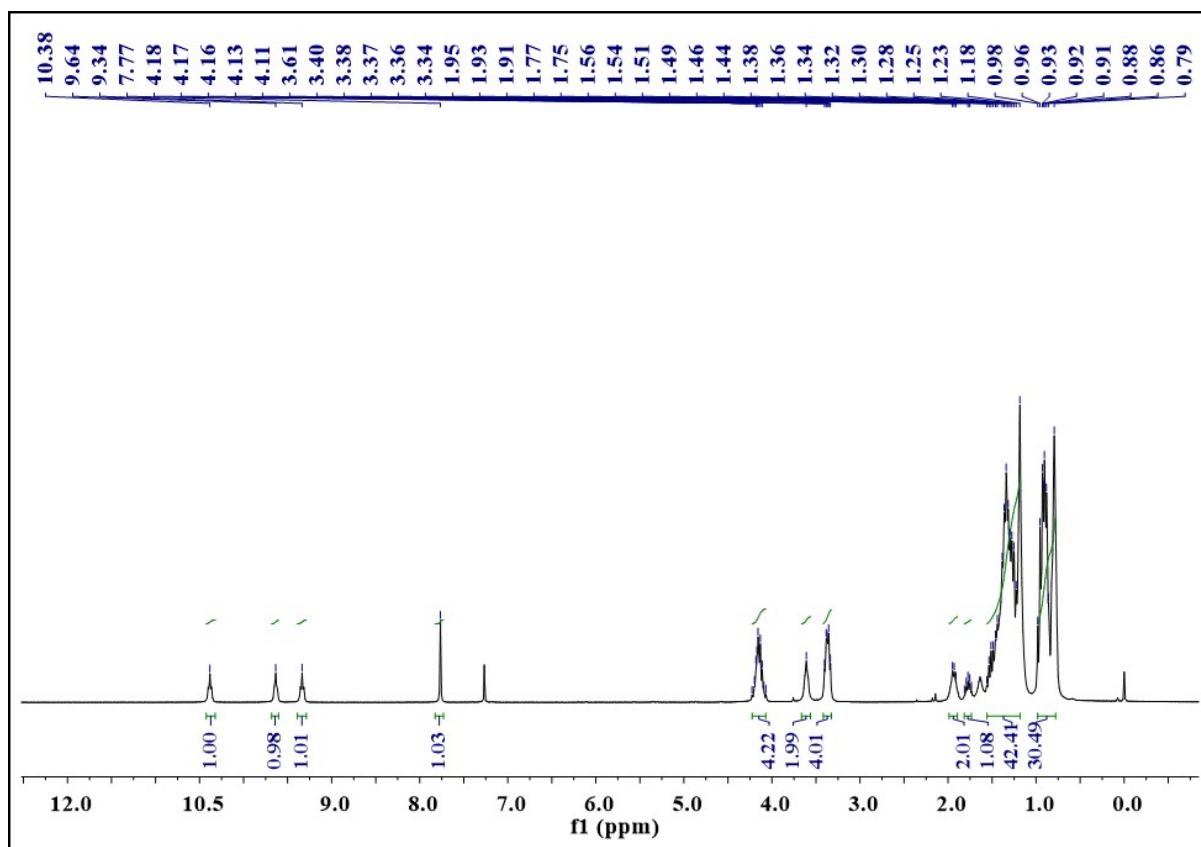


Fig. S15  $^1\text{H}$  NMR spectra of cNDI-3EHA

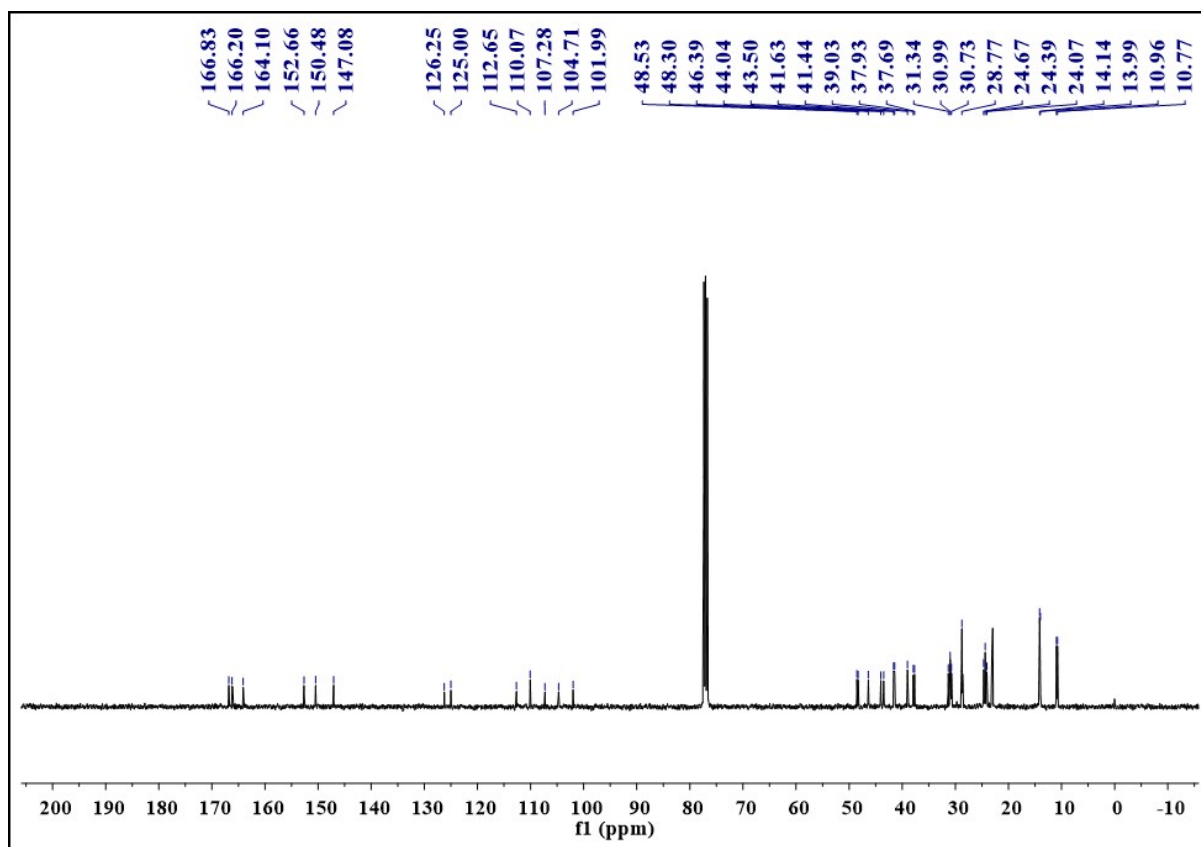


Fig. S16  $^{13}\text{C}$  NMR spectra of cNDI-3EHA



Data: SBP-SB-AM3.0001.3C1[c] 26 Sep 2019 15:48 Cal: 26-09-2019 26 Sep 2019 15:25  
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron\_HiRes, Power: 90, Blanked, P.Ext. @ 3000 (bin 113)  
%Int. 22 mV[sum= 559 mV] Profiles 1-25 Smooth Gauss 1

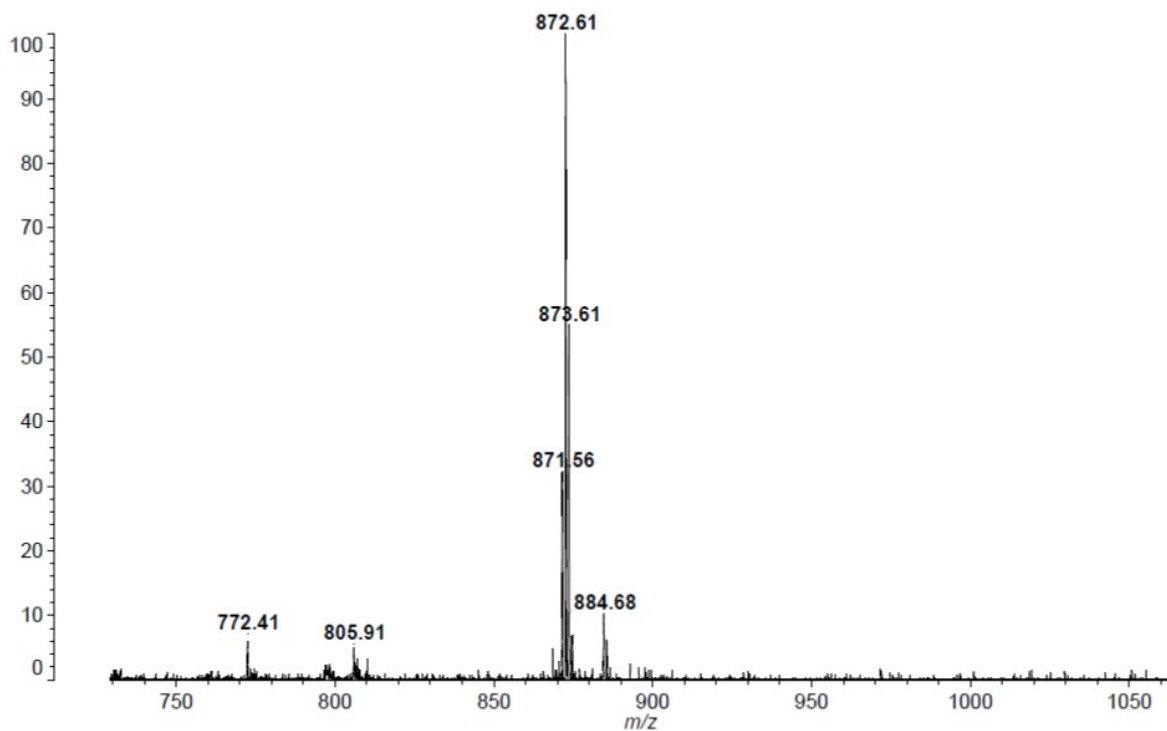


Fig. S17 MALDI-TOF spectrum of cNDI-3EHA

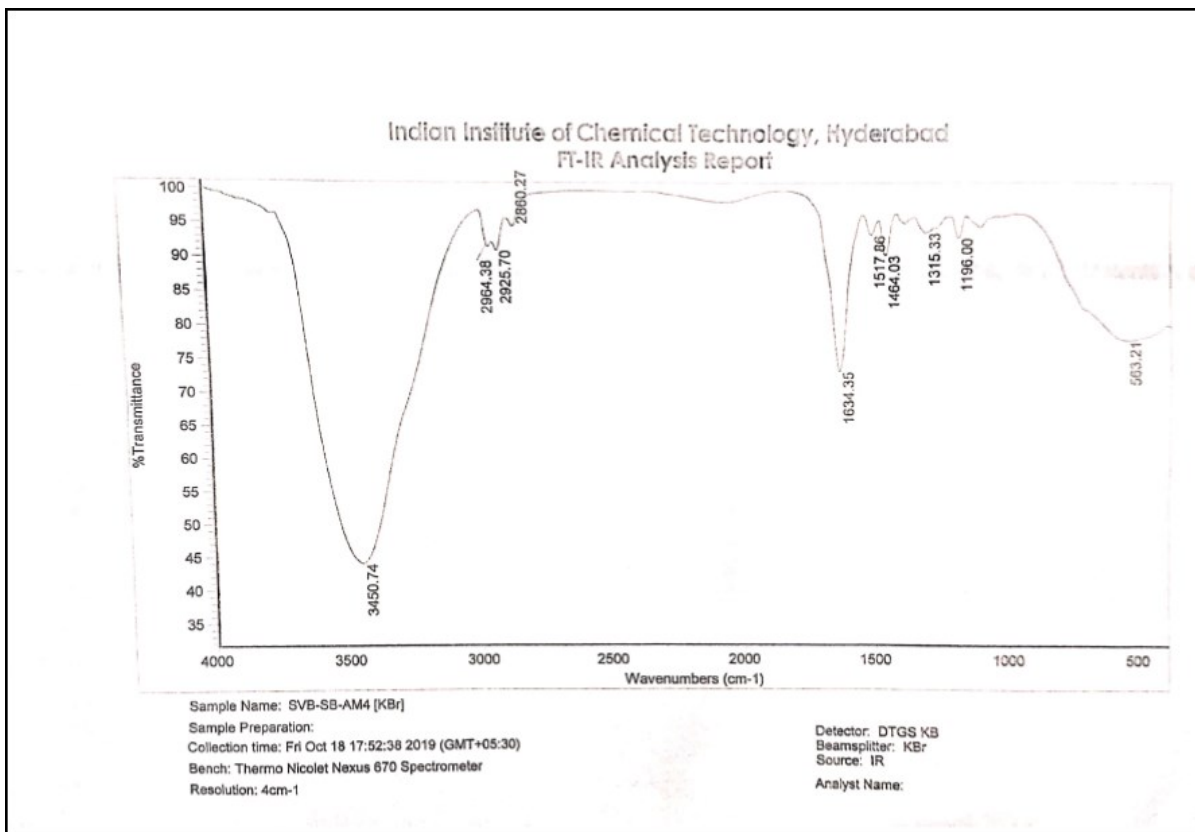


Fig. S18 FT-IR spectra of cNDI-4EHA

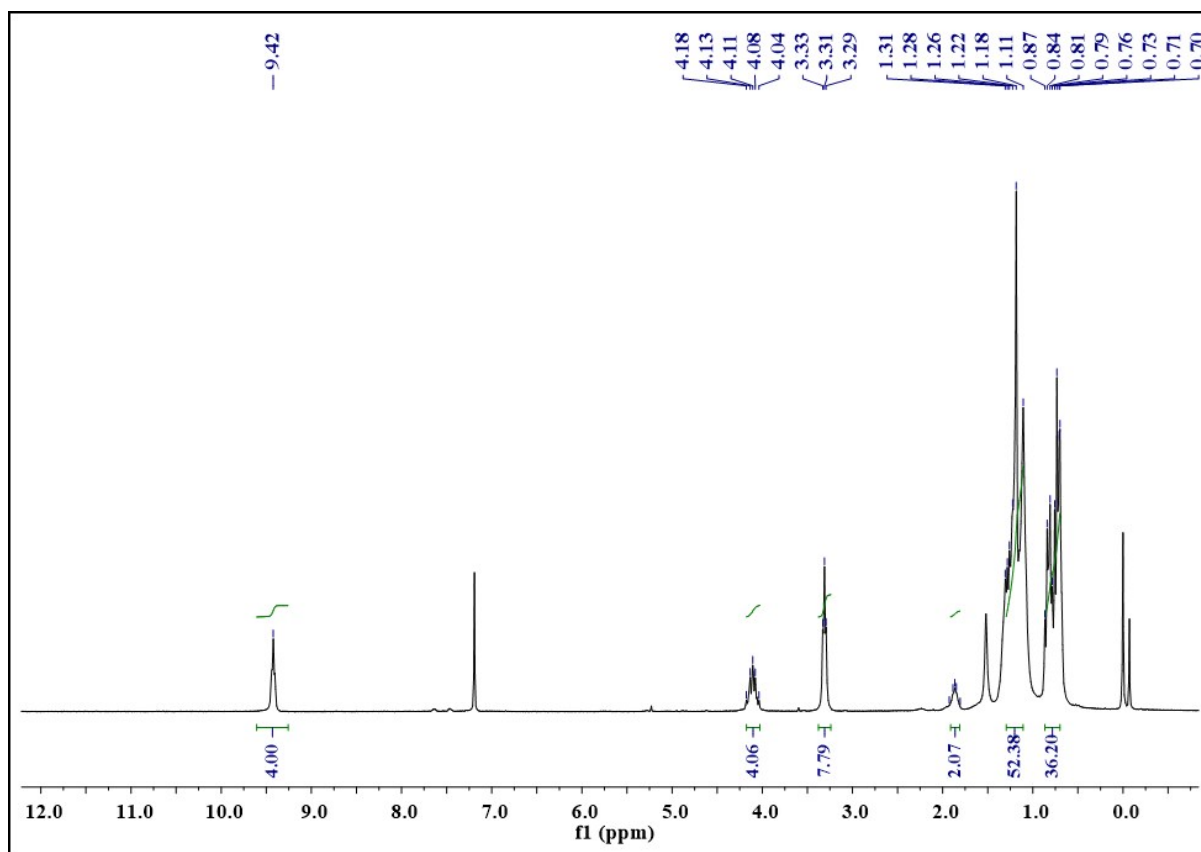


Fig. S19  $^1\text{H}$  NMR spectra of cNDI-4EHA

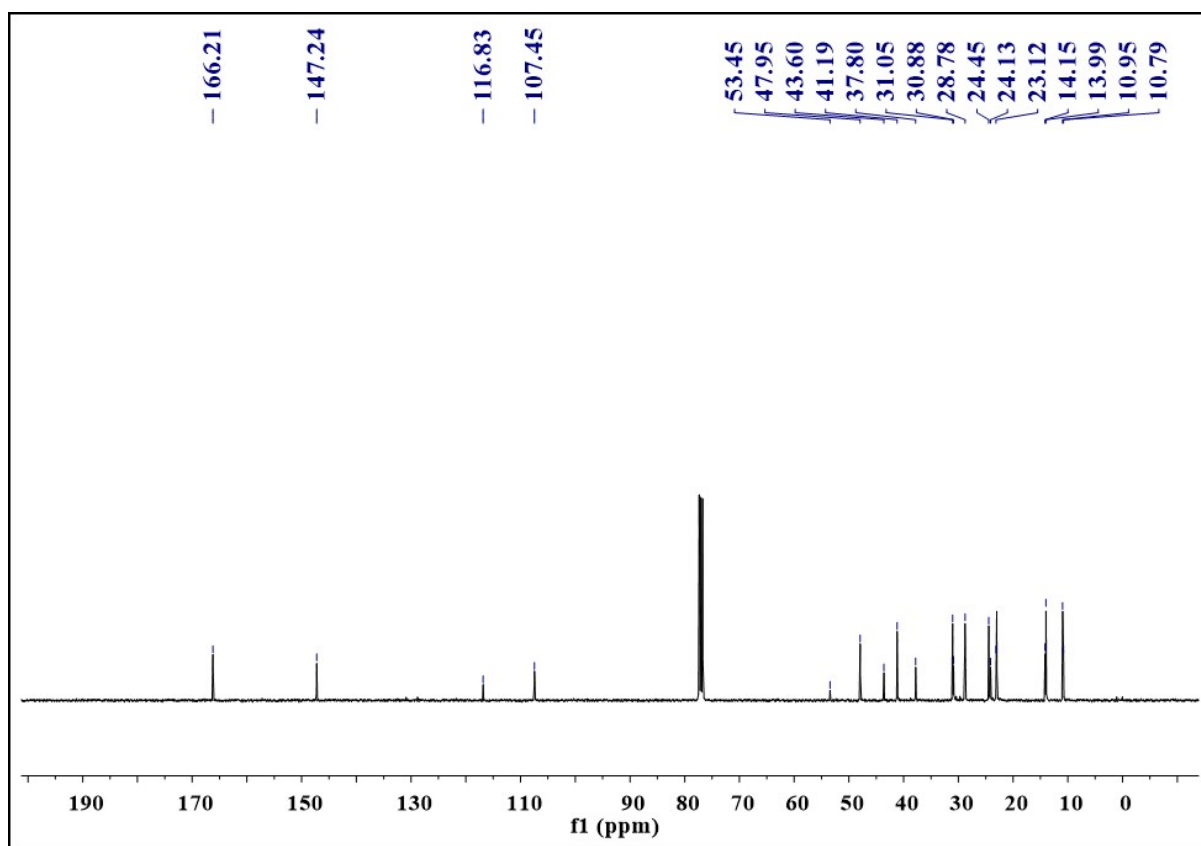
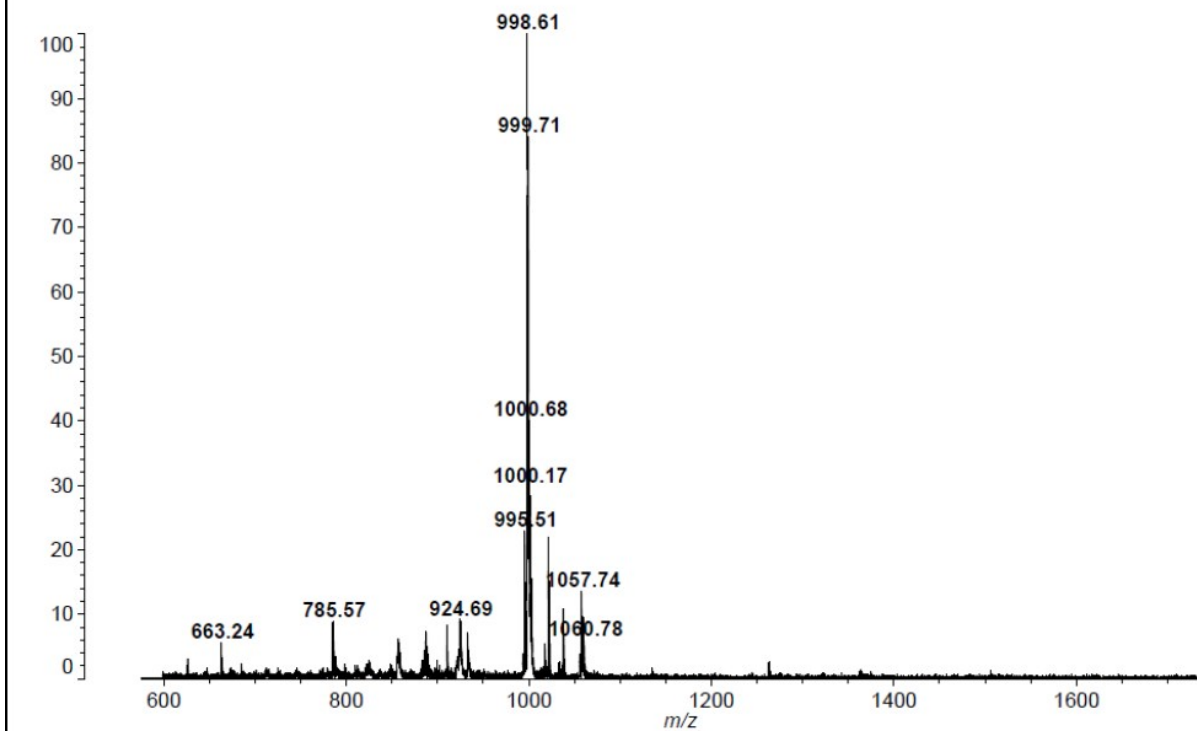


Fig. S20  $^{13}\text{C}$  NMR spectra of cNDI-4EHA

Data: SVB-SB-AM4,0001.4G4[c] 7 Sep 2019 10:47 Cal: 7-09-2019 7 Sep 2019 10:45  
Shimadzu Biotech Axima Performance 2.9.3.20110624: Mode Reflectron\_HiRes, Power: 98, Blanked, P.Ext. @ 3000 (bin 113)  
%Int. 214 mV[sum= 10702 mV] Profiles 1-50 Unsmoothed



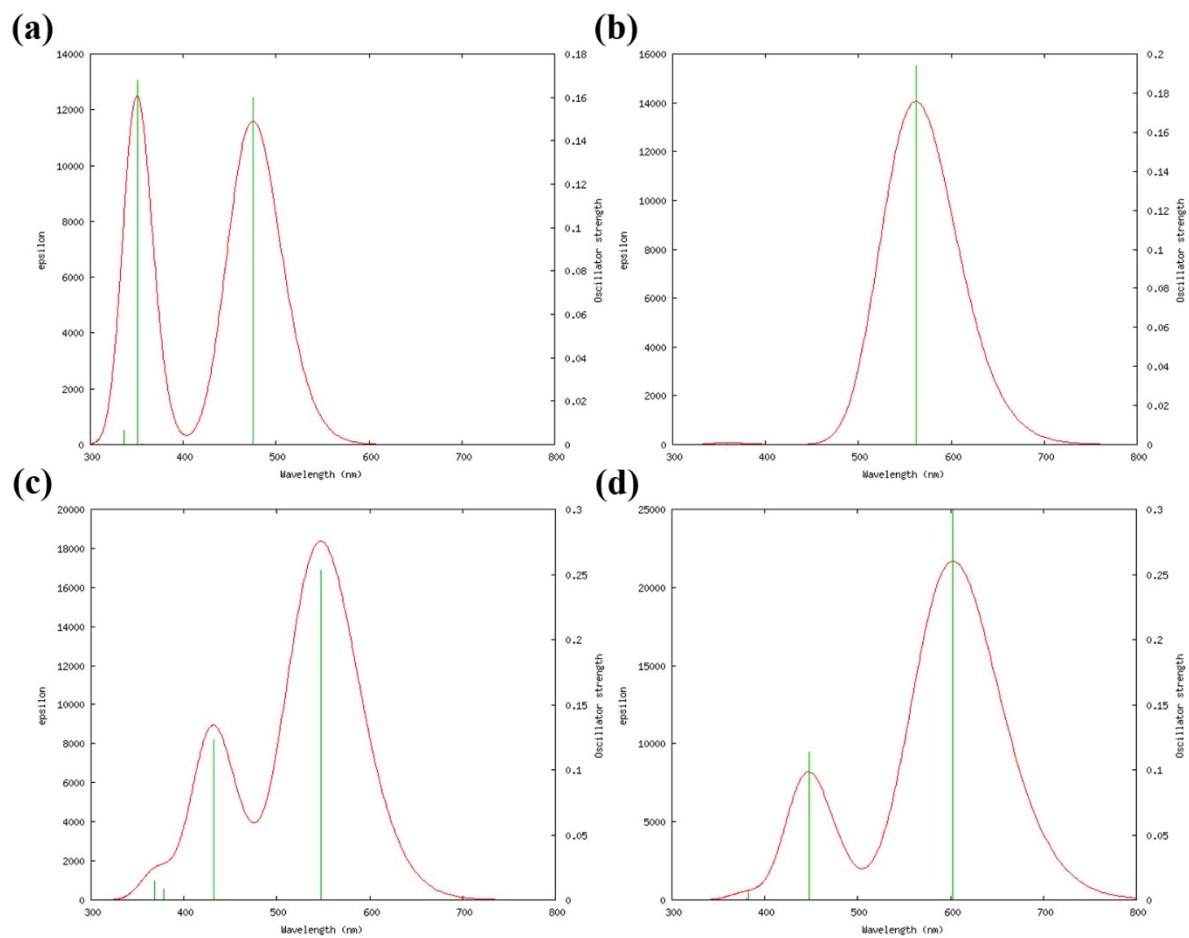
**Fig. S21** MALDI-TOF spectrum of cNDI-4EHA

**Table S1.** Experimental conditions and device architecture with electron mobility properties.

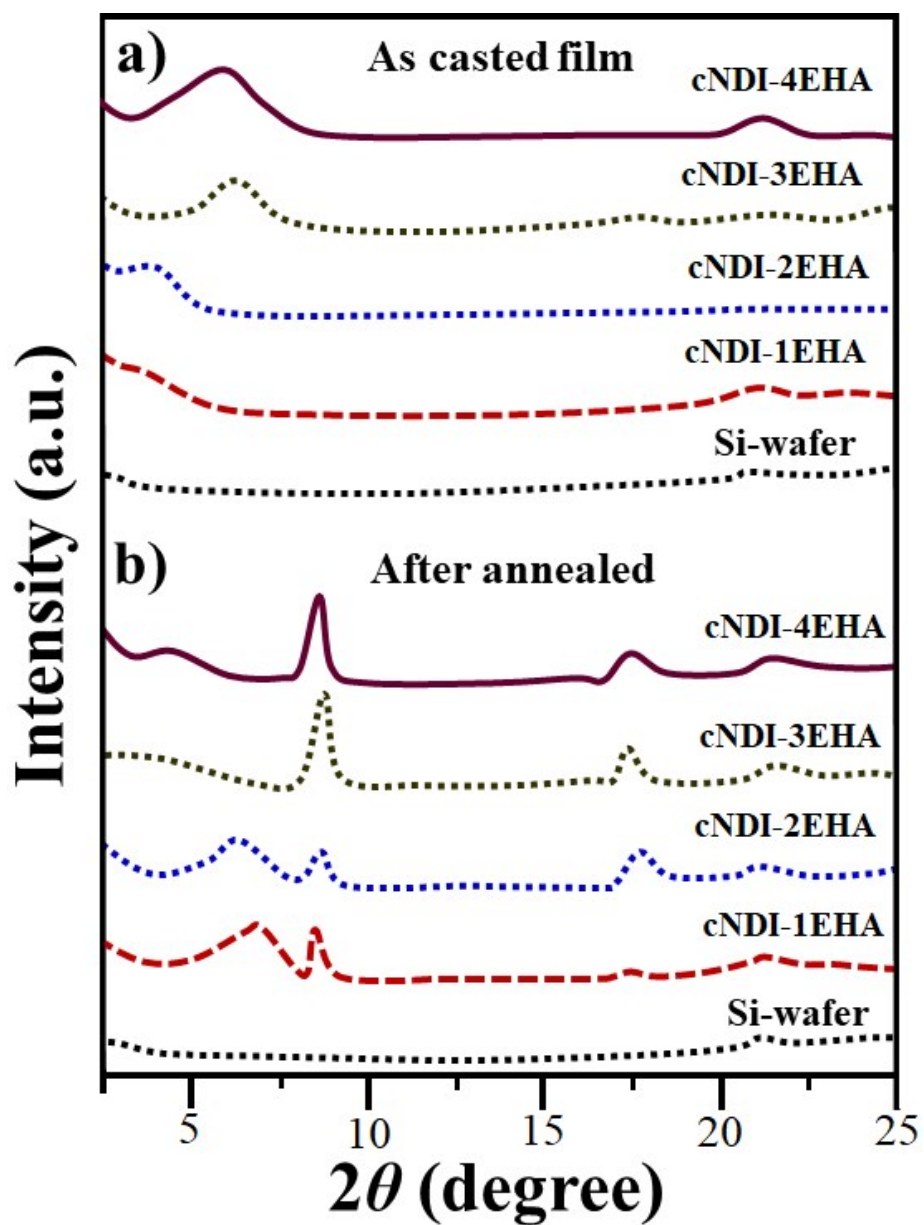
Sample Code	Concentration (Chlorobenzene)	RP M	Annealing Temperature	Device Structure	I/V response	e-mobility (cm <sup>2</sup> /Vs)	
cNDI-1EHA	60 mg/mL	1000	170°C	ITO/ZnO/NDI-AM1/Ag	✓	3.7x10 <sup>-8</sup>	
	60 mg/mL	2000					4.7x10 <sup>-11</sup>
	40 mg/mL	1000					-----
	30 mg/mL	1000		ITO/ ZnO/NDI-AM1/LiF/Ag			-----
	40mg/mL			ITO/ZnO/NDI-AM1/Al			1.14x10 <sup>-6</sup>
cNDI-2EHA	20 mg/mL	1000	170°C	ITO/ZnO/NDI-AM2/Ag	✓	0.6x10 <sup>-7</sup>	
	30 mg/mL					3.7x10 <sup>-8</sup>	
	40mg/mL					0.8x10 <sup>-7</sup>	
	40mg/mL			ITO/ ZnO/NDI-AM2/LiF/Ag			-----
	40mg/mL		ITO/ZnO/NDI-AM2/Al		1.25x10 <sup>-4</sup>		
cNDI-3EHA	40mg/mL	000	170°C	ITO/ZnO/NDI-AM3/Al	✓	2.56x10 <sup>-4</sup> 2.69x10 <sup>-4</sup>	
cNDI-4EHA	40 mg/mL	1000	170°C	ITO/ZnO/NDI-AM4/Ag	✗		
		1500		ITO/ ZnO/NDI-AM4/LiF/Ag	✗		
		1000		ITO/ZnO/NDI-AM4/Al	✓	1.4x10 <sup>-6</sup>	

**Table S2.** Calculated TD-DFT excitation properties of cNDI-1EHA, cNDI-2EHA, cNDI-3EHA and cNDI-4EHA

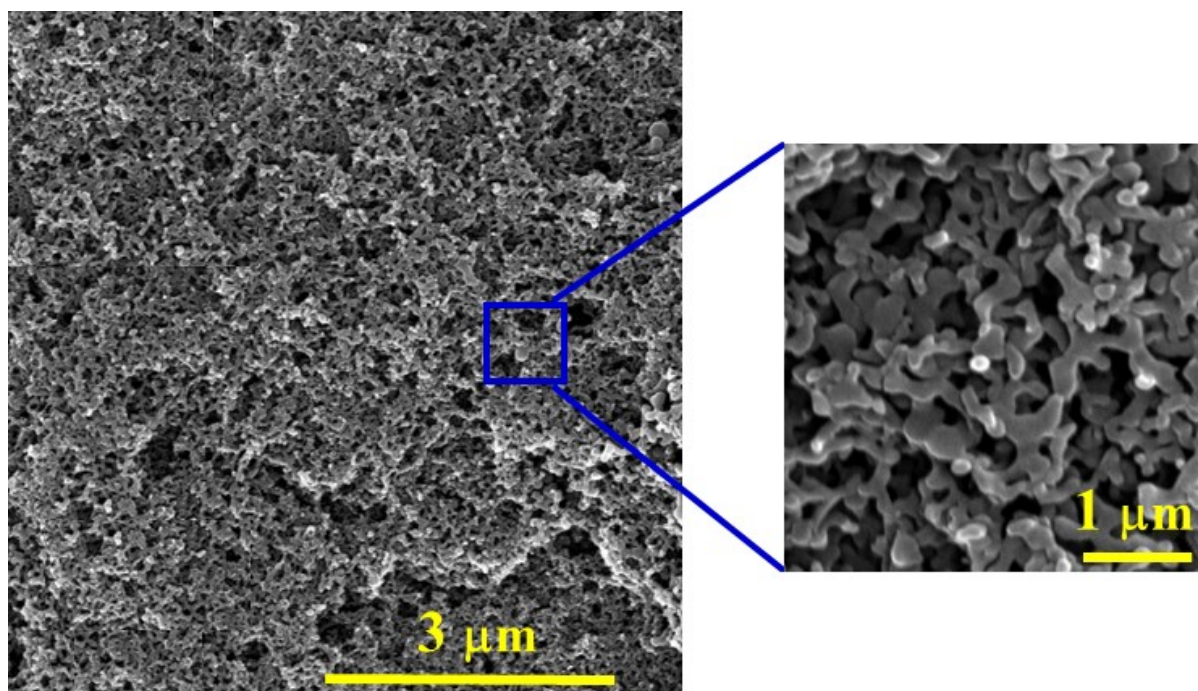
<b>Molecules</b>	<b>Excitation Energy (eV)</b>	<b>Excitation Wavelength (nm)</b>	<b>Oscillator Strength (f)</b>	<b>Excitations</b>	<b>Percentage contribution for transition</b>
cNDI-1EHA	2.6111	474.8	0.1598	168 ->169	HOMO->LUMO (98%)
	3.5351	350.7	0.1678	167 ->169	H-1->LUMO (89%)
				163 ->169	H-5->LUMO (4%)
cNDI-2EHA	2.2064	561.9	0.1939	204 ->205	HOMO->LUMO (100%)
cNDI-3EHA	2.2650	547.3	0.2534	240 -> 241	HOMO->LUMO (99%)
	2.8715	431.7	0.1230	239 -> 241	H-1->LUMO (97%)
cNDI-4EHA	2.0574	602.6	0.2991	276 -> 277	HOMO->LUMO (100%)
	2.7720	447.2	0.1131	275 -> 277	H-1->LUMO (99%)



**Fig. S22** The computed absorption spectra of cNDI-1EHA, cNDI-2EHA, cNDI-3EHA and cNDI-4EHA



**Fig. S23** XRD spectra of cNDI-1EHA, cNDI-2EHA, cNDI-3EHA and cNDI-4EHA before and after annealing, respectively.



**Fig. S24** SEM images of cNDI-3EHA after annealing (performed at 170 °C for 30 min), showing good crystalline self-assembled supramolecular crystalline structures.

**References:**

- <sup>S1</sup> Sasikumar, M.; Suseela, Y.V. and Govindaraju, T. *Asian J. Org. Chem.* **2013**, *2*, 779-785