Supporting information

Improvement of optoelectronic and photovoltaic properties through the insertion of a naphthalenediimide unit in donor-acceptor oligothiophenes

Sharad R. Bobe[a,1], Akhil Gupta[b,c,1,*], Ante Bilic[d], Sidhanath V. Bhosale[a,*], Sheshanath V. Bhosale[c,*]

[a] Polymers and Functional Material Division, CSIR-Indian Institute of Chemical Technology, Hyderabad 500 007, Telangana, India; bhosale@iict.res.in

[b] Medicinal Chemistry, Monash Institute of Pharmaceutical Sciences, Monash University, Parkville Victoria 3052, Australia; akhil.gupta@monash.edu

[c] School of Applied Sciences, RMIT University, GPO Box 2476, Melbourne Victoria 3001, Australia; Tel: +61 3 9925 2680; E-mail address: sheshanath.bhosale@rmit.edu.au

[d] CSIRO Manufacturing, Virtual Nanoscience Lab, Parkville Victoria 3052, Australia

[1] SRB and AG contributed equally to this work.

1. General Methods and Materials:

All the reagents and chemicals used, unless otherwise specified, were purchased from Sigma-Aldrich Company. The solvents used for reactions were obtained from Merck Speciality Chemicals and were used as such. Unless otherwise specified, all ^{1}H and ^{13}C NMR spectra were recorded using ADVANCE 300 MHz and 75 MHz spectrometer, respectively. Chemical shifts (δ) are measured in parts per million. Thin Layer Chromatography (TLC) was performed using 0.25 mm thick plates precoated with Merck Kieselgel 60 F_{254} silica gel, and visualised using ultraviolet light (254 nm and 365 nm). Mass spectrometric data were obtained by electron spray ionization (ESI-MS) technique on an Agilent Technologies 1100 Series (Agilent Chemistation Software) mass spectrometer. High-resolution mass spectra (HRMS) were obtained by using ESIQTOF mass spectrometry. FTIR spectra were obtained on a Perkin Elmer FT-IR 400 spectrometer. Melting points were measured using a Gallenkamp MPD350 digital melting point apparatus and are uncorrected. UV-vis absorption spectra were recorded using a Hewlett Packard HP 8453 diode array spectrometer. PESA

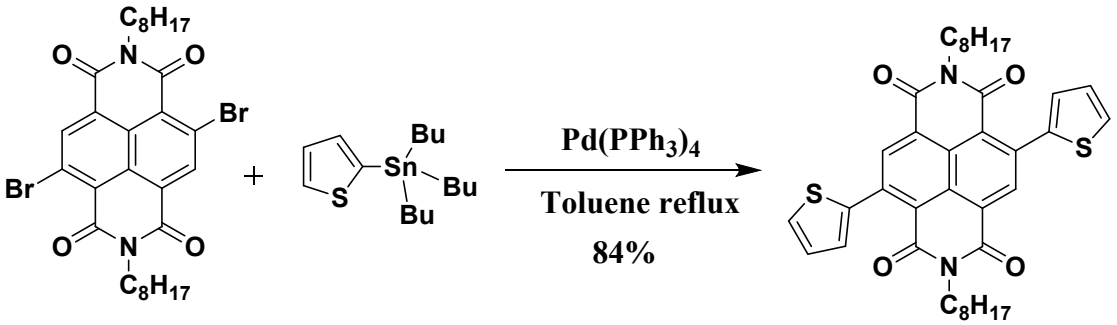
measurements were recorded using a Riken Keiki AC-2 PESA spectrometer with a power setting of 5 nW and a power number of 0.5. Samples for PESA were prepared on on cleaned glass substrates. The thermal stability of DPP1 was investigated by thermogravimetric analysis (TGA). TGA was run at a heating rate of 10 °C/min, from room temperature to 800 °C.

Device fabrication and characterization of photovoltaic devices was carried out in a similar fashion as reported previously.[S1]

2. Experimental procedures:

4,9-Dibromo-2,7-dioctylbenzo[3,8]phenanthroline-1,3,6,8(2H,7H)-tetraone (abbreviated to "dibromo-NDI" throughout this experimental procedure) was synthesized in accordance with a literature report.[S2]

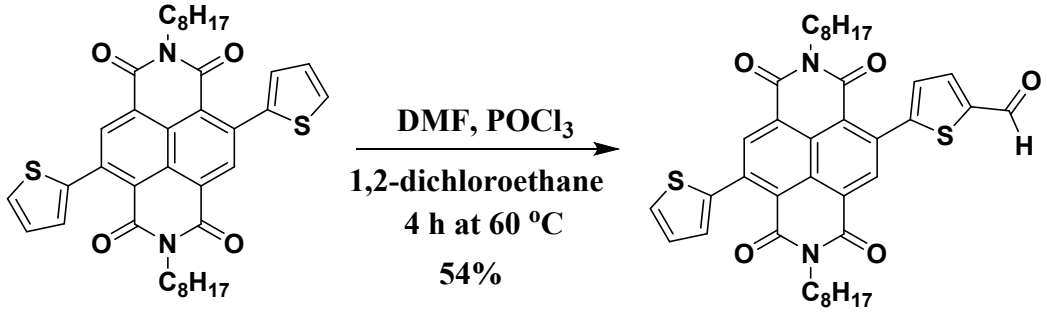
2.1 2,7-dioctyl-4,9-di(thiophen-2-yl)benzo[*lmn*][3,8]phenanthroline-1,3,6,8(2*H*,7*H*)-tetraone



1 **2**

To a degassed solution of dibromo-NDI (**1**) (0.65 gm, 1 mmol) and tributyl(thiophen-2-yl)stannane (0.75 gm, 2.0 mmol) in toluene (20 mL) was added tetrakisPd(0) (0.058g, 0.05 mmol) at room temperature under argon. The resulting reaction mixture was heated to reflux overnight. The orange coloured solution was worked up with ethyl acetate and water. The organic layer was separated, washed with water followed by brine, dried over anhydrous sodium sulphate and recovered to get crude orange oil, which was subjected to column chromatography on silica gel (dichloromethane:hexane 1:1) to yield 0.55 g (84%) of titled compound **2** as an orange solid. M. Pt.:164-166 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.77 (S, 2H), 7.57-7.58 (dd, *J*=1.22 Hz, 2H), 7.28-7.29 (dd, *J*=1.22 Hz, 2H), 7.20-7.21 (m, 2H), 4.08-4.11 (t, 4H), 1.64-1.68 (t, 4H), 1.33-1.24 (m, 20H), 0.84-0.87 (t, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.90, 161.69, 140.41, 136.37, 127.89, 127.65, 127.18, 127.13, 125.11, 123.21, 40.89, 31.50, 29.02, 28.92, 27.73, 26.79, 22.34, 13.81; (ESI) m/z: calculated for $C_{38}H_{43}N_2O_4S_2$ 655.82, found $[M+H]^+$ 655.78.

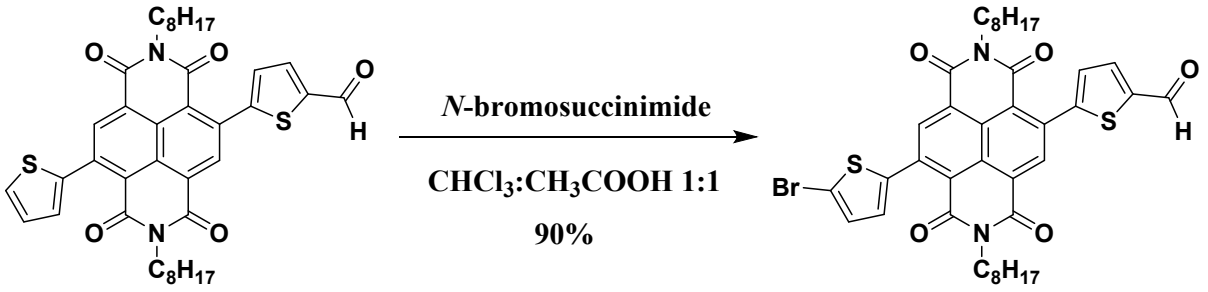
2.2 Synthesis of 5-(2,7-dioctyl-1,3,6,8-tetraoxo-9-(thiophen-2-yl)-1,2,3,6,7,8-hexahydrobenzo[*lmn*][3,8]phenanthrolin-4-yl)thiophene-2-carbaldehyde (3)



2 **3**

Dry DMF (0.065 mL, 0.7 mmol) was dissolved in dry 1,2-dichloroethane (20 mL). $POCl_3$ (0.072 mL, 0.78 mmol) was added drop wise to this solution at 0 °C. The reaction mixture was stirred at 0 °C for 30 min under nitrogen atmosphere. The reaction mixture was allowed to warm to room temperature and substrate **2** (510 mg, 0.78 mmol) was added. The reaction mixture was heated to 60 °C and stirred for 4 h. The reaction mixture was cooled and quenched using aq. $NaHCO_3$ solution (40 mL). Organic layer was separated, washed with water twice followed by brine, dried over anhydrous sodium sulphate and recovered to get crude dark yellowish-brown oil which was subjected to column chromatography on silica gel (dichloromethane:hexane 6:4)) to get 290 mg (54%) of **3** as a reddish-orange solid. M. Pt.: 148-150 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.01 (s, 1H), 8.79 (s, 1H), 8.69 (s, 1H), 7.87-7.85 (d, *J*=3.77 Hz,1H), 7.61-7.59 (d, *J*=3.77, 1H), 7.33-7.31 (d, *J*=3.58 Hz, 1H), 7.29-7.28 (d, *J*=3.77 Hz, 1H), 7.20-7.23 (m, *J*=3.58 Hz, 1H), 4.05-4.13 (m, 4H), 1.65-1.67 (m, 4H), 1.25-1.30 (m, 20H), 0.84-0.88 (t, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 182.82, 161.90, 161.69, 150.56, 144.87, 141.14, 140.38, 138.52, 137.10, 136.13, 135.27, 128.48, 128.27, 128.03, 127.49, 127.11, 125.75, 125.42, 124.22, 123.39, 41.39, 31.74, 29.68, 29.25, 29.15, 27.95, 27.02, 22.59, 14.05; FT-IR (KBr, cm^{-1}) υ 2953, 2922, 2852, 1708, 1669, 1579, 1525, 1436, 1419, 1375, 1312, 1252, 1218, 1182, 1078, 931, 795, 763, 696, 591, 482; (ESI) m/z: $C_{39}H_{42}N_2O_5S_2$ $[M+H]^+$ 683; HRMS (ESI) m/z: calculated for $C_{39}H_{43}N_2O_5S_2$:683.2597, found 683.2607.

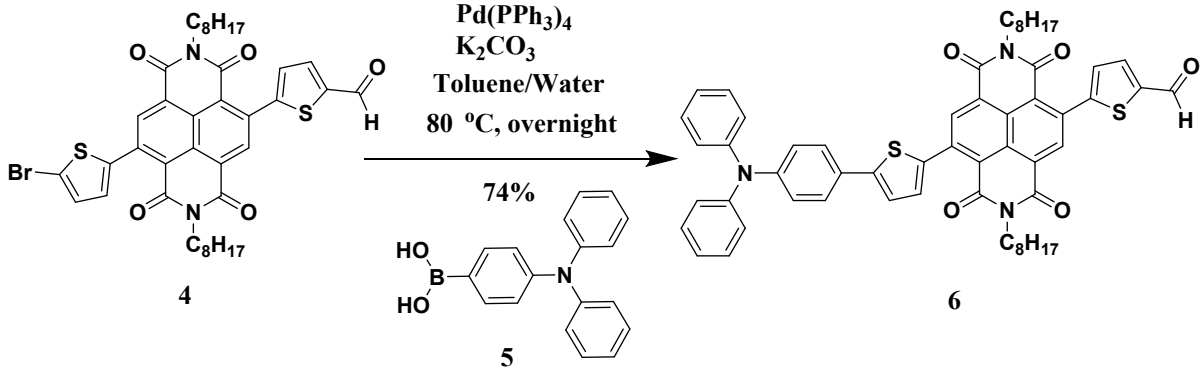
2.3 Synthesis of 5-(9-(5-bromothiophen-2-yl)-2,7-dioctyl-1,3,6,8-tetraoxo-1,2,3,6,7,8-hexahydrobenzo[*lmn*][3,8]phenanthrolin-4-yl)thiophene-2-carbaldehyde (4)



3 **4**

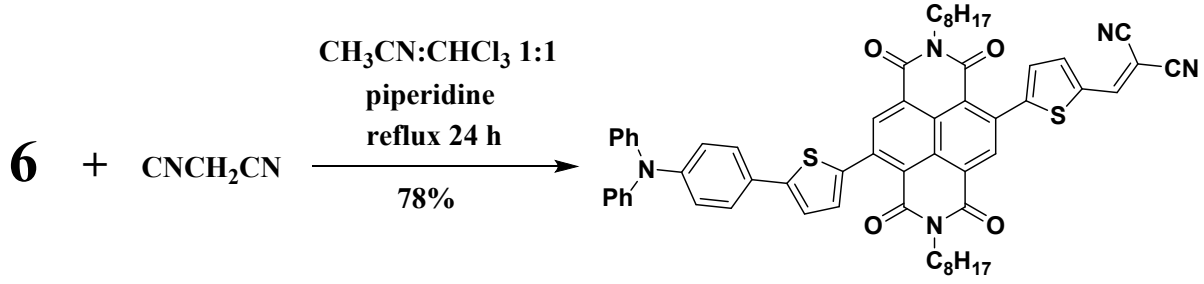
Compound **3** (286 mg, 0.42 mmol) was taken in a 100 mL RB flask in 1:1 solvent mixture of acetic acid:chloroform (v/v) (20.0 mL) and *N*-bromosuccinimide (90 mg, 0.52 mmol) was added at room temperature. The resulting solution was stirred at room temperature overnight in the absence of light. Solid appeared in the flask was filtered off, washed with methanol and dried under vacuum (@ 60 °C) to get 290 mg (90%) of **4** as a reddish-brown solid. M. Pt. 152-154 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.01 (S, 1H), 8.74 (S, 1H), 8.69 (S, 1H), 7.87-7.85 (d, *J*=3.77 Hz, 1H), 7.29-7.28 (d, *J*=3.77 Hz, 1H), 7.17-7.16 (d, *J*=3.77 Hz, 1H), 7.10-7.09 (d, 1H), 4.05-4.14 (m, 4H), 1.63-1.68 (m, 4H), 1.25-1.31 (m, 20H), 0.84-0.88 (t, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 182.86, 161.80, 150.42, 144.94, 141.84, 139.75, 138.50, 136.72, 135.47, 136.16, , 137.10, 136.13, 135.27, 130.23, 129.02, 128.55, 128.51, 128.03, 127.99, 125.70, 123.23, 41.27, 31.90, 31.76, 29.70, 29.26, 29.18, 27.97, 27.04, 22.61, 14.05; FT-IR (KBr, cm^{-1}) υ 2925, 2854, 1706, 1669, 1576, 1525, 1424, 1376, 1312, 1250, 1213, 1038, 797, 763, 674; (ESI) m/z: $C_{39}H_{41}BrN_2O_5S_2$ $[M+2H]^+$ 763; HRMS (ESI) m/z: calculated for $C_{39}H_{42}BrN_2O_5S_2$ 761.1702, found 761.1713.

2.4 Synthesis of 5-(9-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)-2,7-dioctyl-1,3,6,8-tetraoxo-1,2,3,6,7,8-hexahydrobenzo[*lmn*][3,8]phenanthrolin-4-yl)thiophene-2-carbaldehyde (6)



(4-(diphenylamino)phenyl)boronic acid (**5**) (58.0 mg, 0.20 mmol) was added to the solution of **4** (242 mg, 0.16 mmol) in 20 mL toluene: water (16:4) mixture in a 100 mL round bottom flask. The reaction mixture was degassed for 15 min using argon. TetrakisPd(0) (Pd $(PPh_3)_4$) (37.0 mg, 0.032 mmol) and potassium carbonate (96.0 mg, 0.70 mmol) were added to the reaction mixture. The resulting suspension was heated to 80 °C and stirred overnight. After cooling the reaction mixture to room temperature, the solvent was evaporated using rotary evaporator. The crude product was purified on silica gel column chromatography eluted with dichloromethane: hexane (6:4). The titled product **6** was obtained as a green solid (220 mg, 74%). M. Pt.: 120-122 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 10.01 (s, 1H), 8.86 (s, 1H), 8.67 (s, 1H), 7.85-7.86 (d, *J*=3.77 Hz, 1H), 7.51-7.54 (d, 2H), 7.39-7.40 (d, *J*=3.77 Hz, 1H), 7.32-7.26 (m, 6H), 7.04-7.31 (m, 8H), 4.05-4.16 (m, 4H), 1.63-1.68 (m, 4H), 1.25-1.31 (m, 20H), 0.84-0.88 (t, 6H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 182.86, 161.80, 150.42, 144.94, 141.84, 139.75, 138.50, 136.72, 135.47, 136.16, , 137.10, 136.13, 135.27, 130.23, 129.02, 128.55, 128.51, 128.03, 127.99, 125.70, 123.23, 41.27, 31.90, 31.76, 29.70, 29.26, 29.18, 27.97, 27.04, 22.61, 14.05; FTIR (KBr, cm^{-1}) υ 3062, 2921, 2850, 1705, 1664, 1582, 1503, 1488, 1440, 1374, 1310, 1181, 1038, 927, 792, 751, 722, 694, 615, 587, 515; (ESI) m/z: $C_{57}H_{55}N_3O_5S_2$ $[M]^+$ 926, HRMS (ESI) m/z: calculated for $C_{57}H_{55}N_3O_5S_2$ 926.3617, found 926.3618.

2.5 Synthesis of 2-((5-(9-(5-(4-(diphenylamino)phenyl)thiophen-2-yl)-2,7-dioctyl-1,3,6,8-tetraoxo-1,2,3,6,7,8-hexahydrobenzo[lmn][3,8]phenanthrolin-4-yl)thiophen-2-yl)methylene) malononitrile (S1)



S1

Compound **6** (92.6 mg, 0.10 mmol) and malononitrile (26.5 mg, 0.40 mmol) were dissolved in 1:1 solvent mixture of aceonitrile:chloroform (15 mL) in a 50 mL round bottom flask at room temperature followed by the addition of piperidine (2 μL, 0.02 mmol). The resulting reaction mixture was heated at reflux overnight and the solvent was evaporated under reduced pressure. The crude material was purified through column chromatography on silica gel (1% methanol in dichloromethane.) to give 105 mg (78%) of compound **S1** as a bluish-black solid. M. Pt. 124-126 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.84 (s, 1H), 8.75 (s, 1H), 7.82 (s, 1H), 7.52-7.54 (d, 2H), 7.33 (d, 1H), 7.27-7.32 (m, 6H), 7.13-7.15 (d, 4H), 7.05-7.10 (m, 4H), 6.93 (s,1H), 4.10-4.15 (m, 4H), 1.65-1.71 (m, 4H), 1.25-1.38 (m, 20H), 0.83-0.86 (t, 6H); FTIR (KBr, cm^{-1}) υ 2922, 2852, 2213, 1705, 1665, 1577, 1489, 1444, 1377, 1313, 1286, 1255, 1181, 794, 754, 722, 696, 516; HRMS (ESI) m/z: calculated for $C_{60}H_{57}N_5O_4S_2$ 975.3839, found 975.3846.

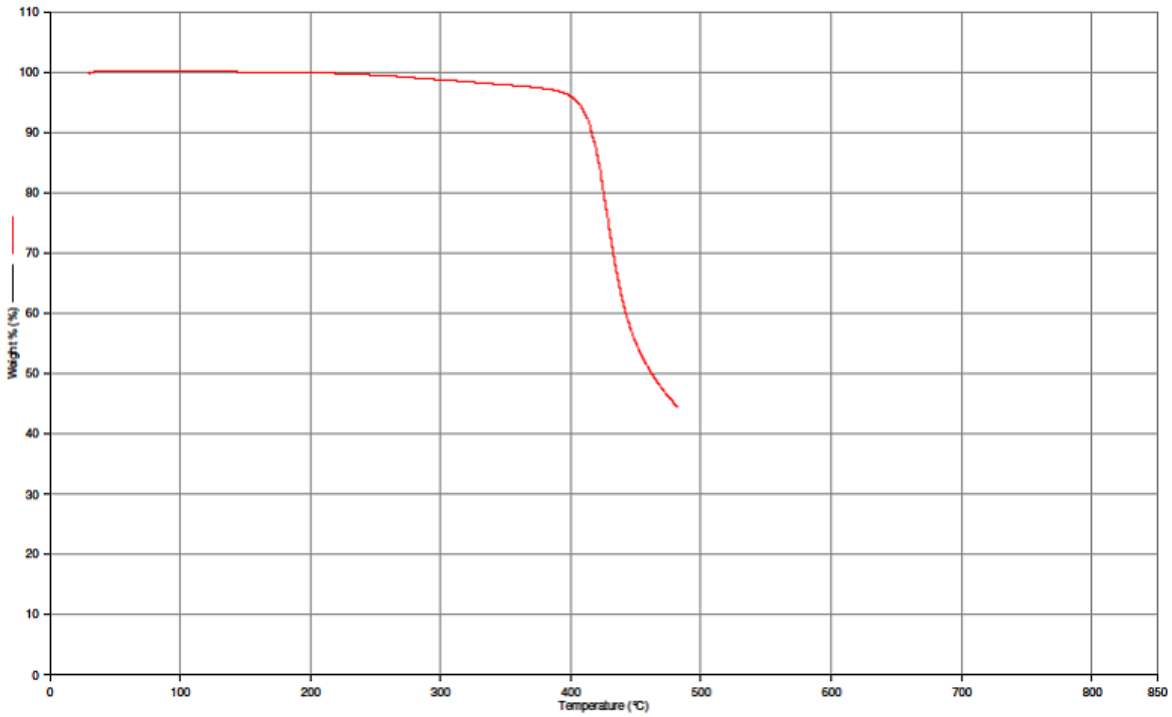


Fig. S1. TGA trace of **S1** under nitrogen atmosphere. Heating rate: 10 °C/min from room temperature to 500 °C

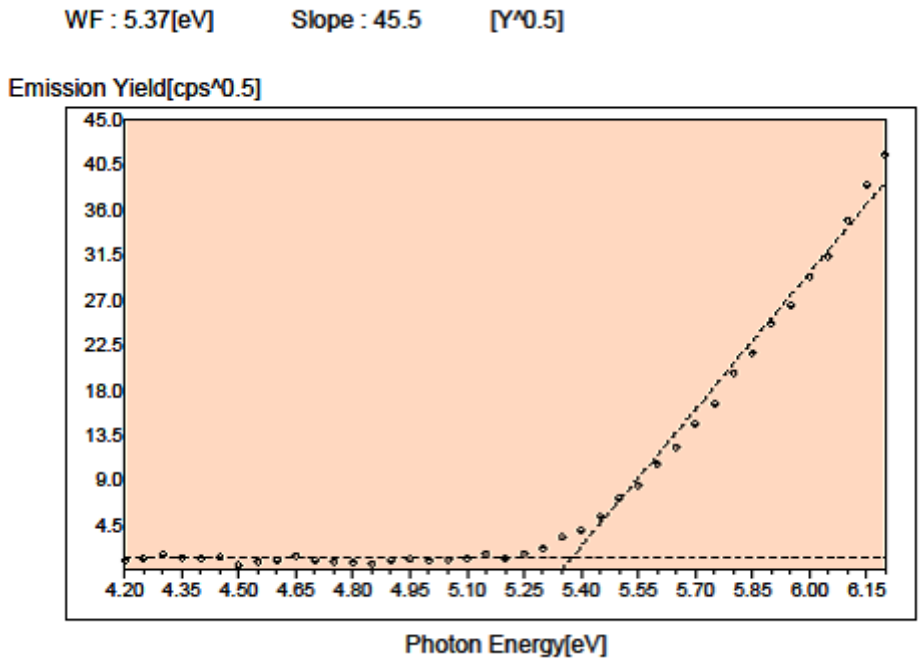


Fig. S2 PESA spectrum of **S1** film. The dashed-lines show the fits to extract ionisation potentials which correspond to the HOMO energy levels.

Table S1

Comparative optical and electronic properties

Material	Absorption (solution) λ_{max}[a]/nm [ε/($M^{-1}cm^{-1}$)]	Absorption (film) λ_{max}[b]/onset/nm	E_{HOMO} eV[c]	$E_{bandgap}$ eV[d]	E_{LUMO} eV[e]
S1	632 [54,820]	650/880	-5.37	1.41	-3.96
R1	514 [41, 250]	540/730	-5.60	1.70	-3.90

[a] Absorption spectra were measured in chloroform solution.

[b] Absorption spectra of thin solid films spin-cast (equimolar solutions of **S1** and **R1** spun at 3000 rpm for 1 min) from chloroform solutions.

[c] HOMO levels of the dyes were measured using PESA on thin solid films on glass.

[d] Energy band gaps were estimated from the tangent of the edge of longest wavelength in film spectrum

[e] LUMO levels were calculated from the optical band gaps (film) and HOMO levels (E_{LUMO}= $E_{bandgap}$+ E_{HOMO})

3. Supporting figures

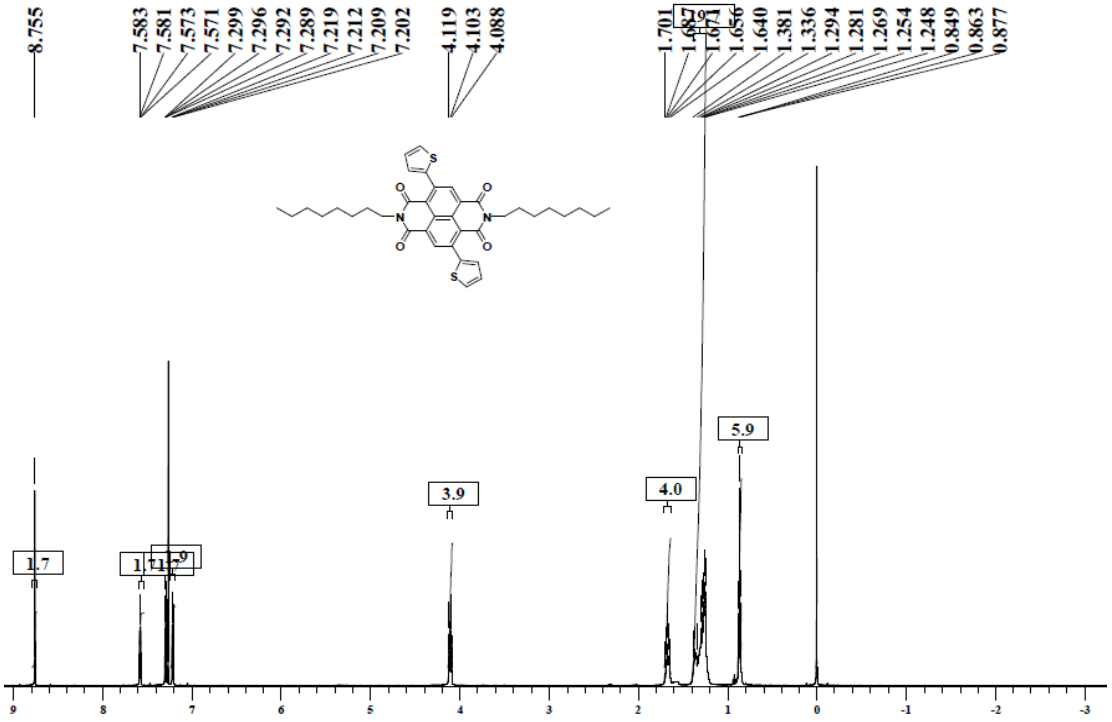


Fig. S3 [1]H NMR of compound **2**

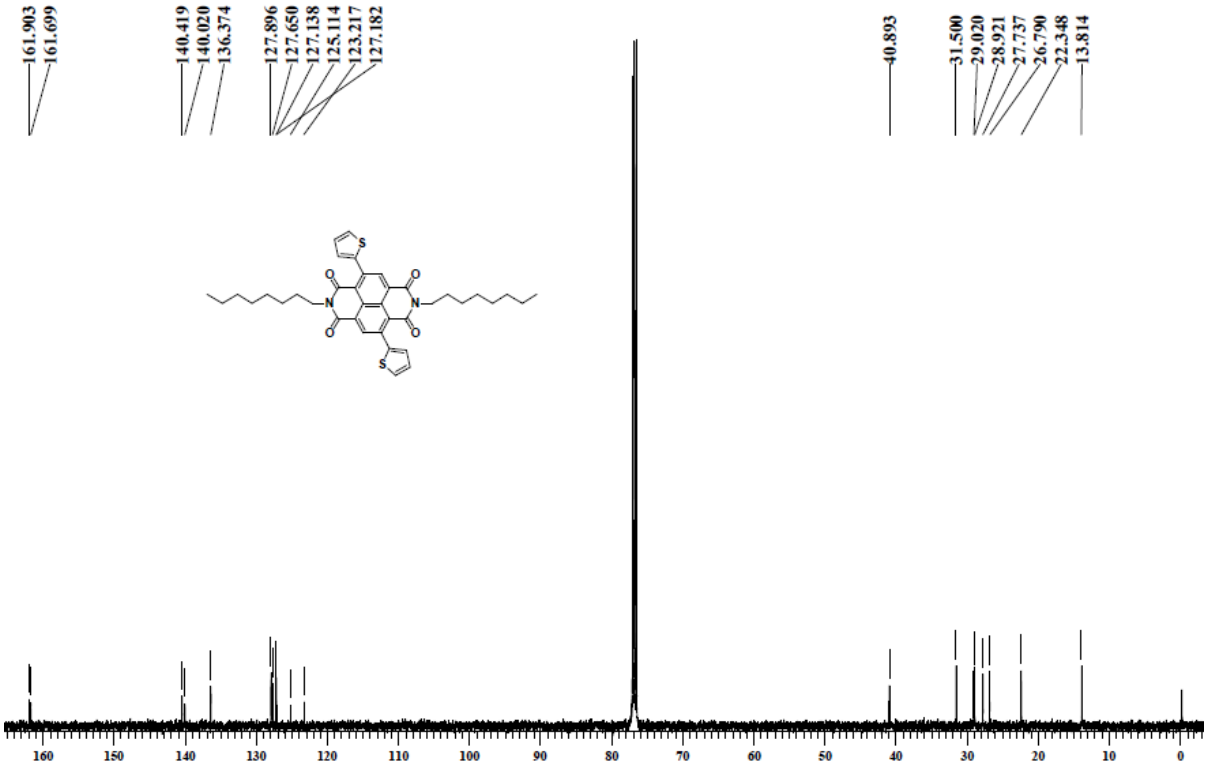


Fig. S4 [13] C NMR of compound **2**.

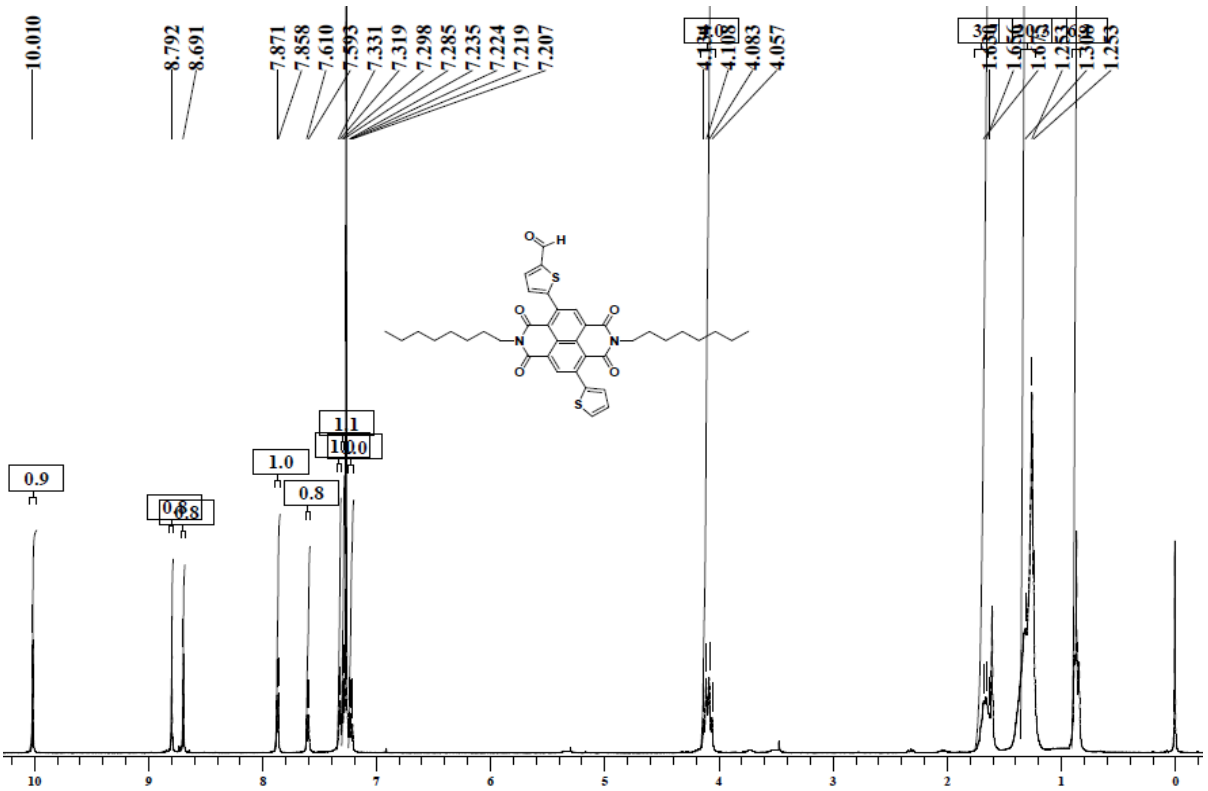


Fig. S5 ^{1}H NMR of **3**

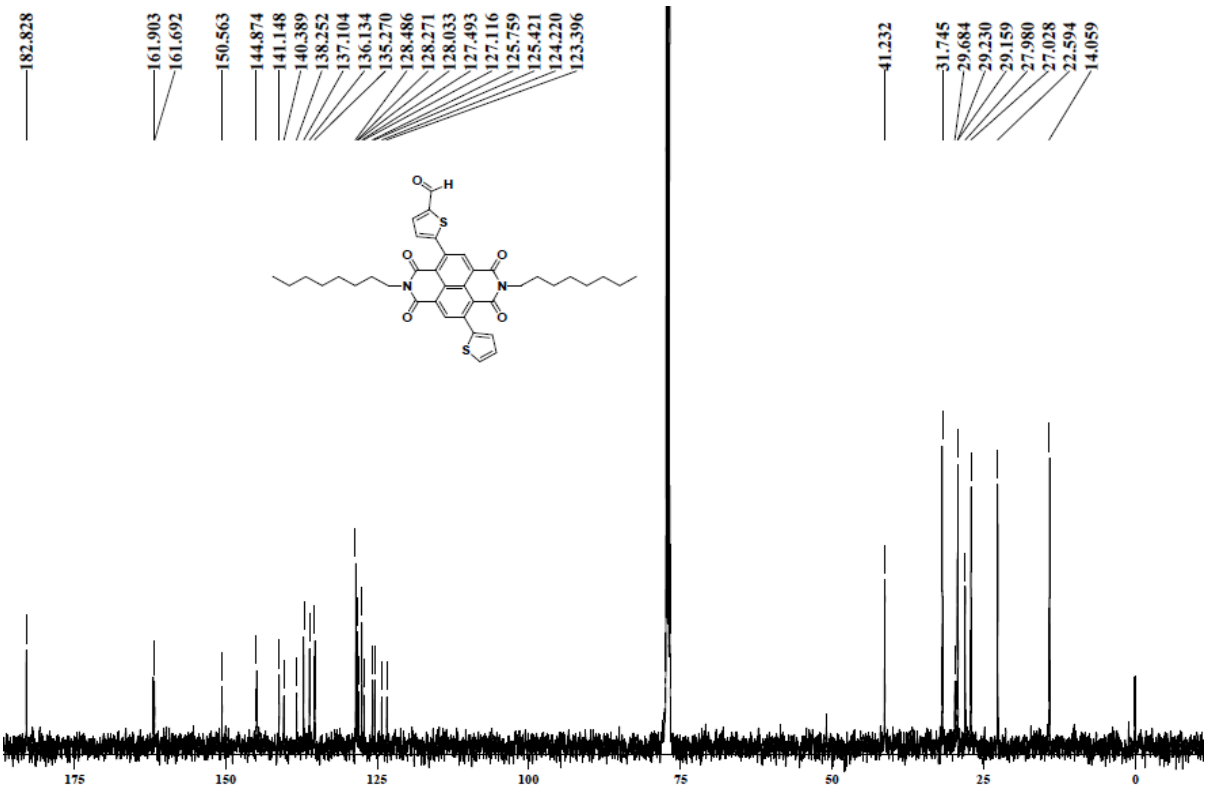


Fig. S6 ^{13}C NMR of compound **3**

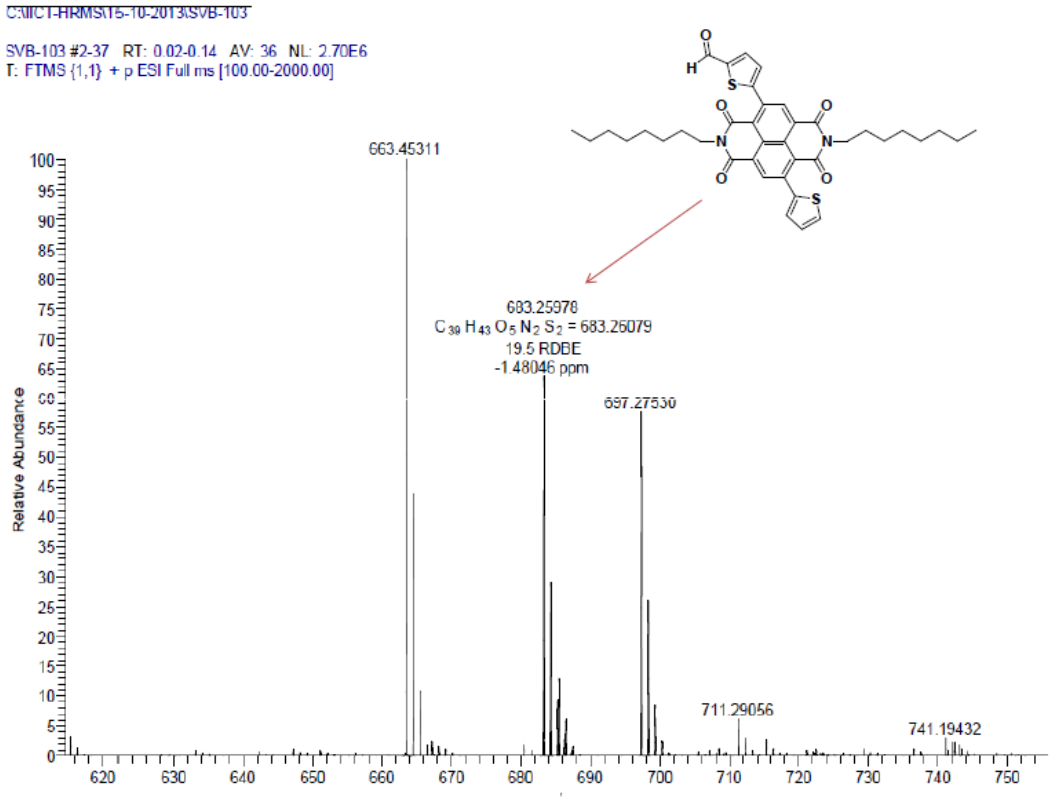


Fig. S7 HRMS of Compound **3**

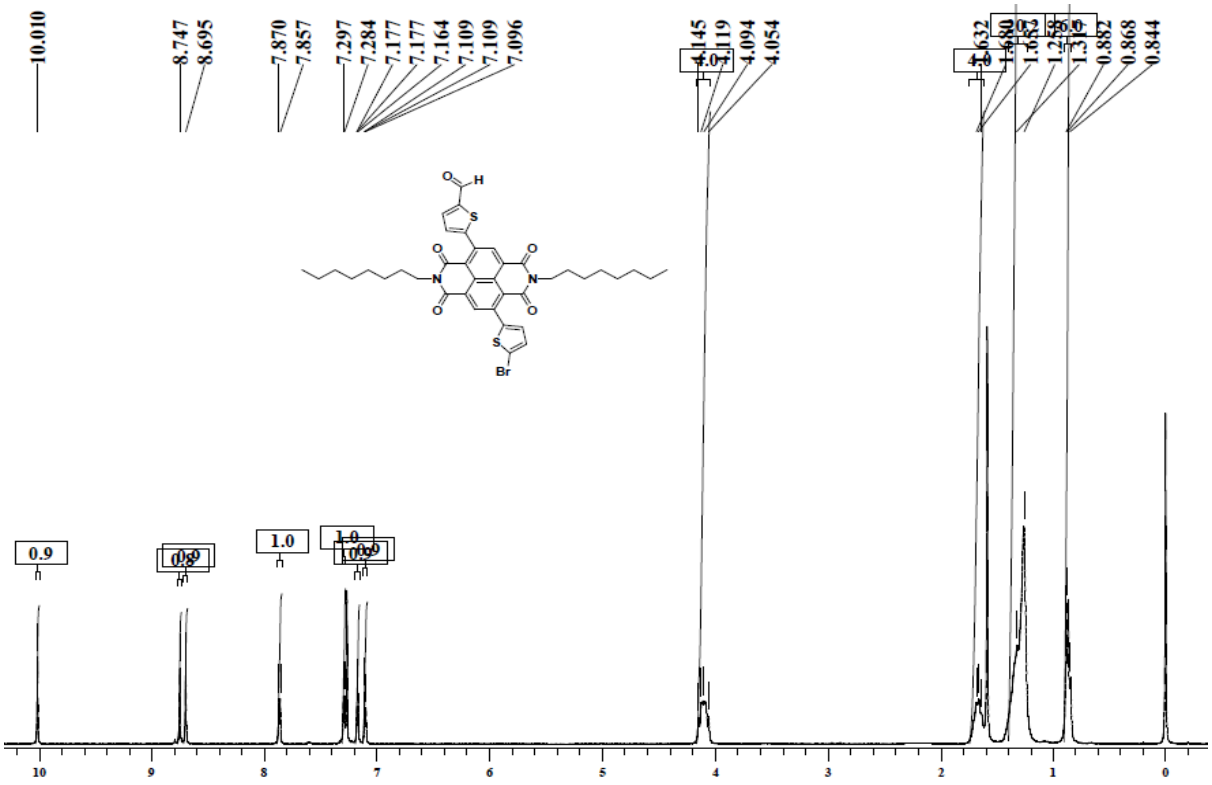


Fig. S8 ^{1}H NMR of compound **4**

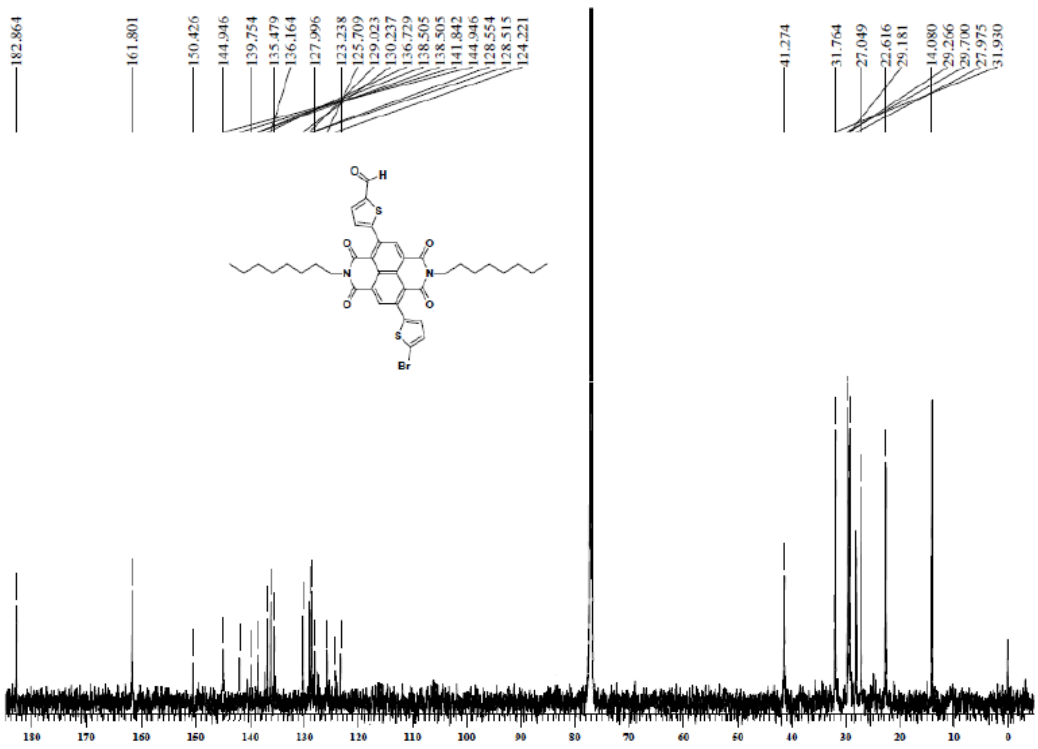


Fig. S9 ^{13}C NMR of compound **4**

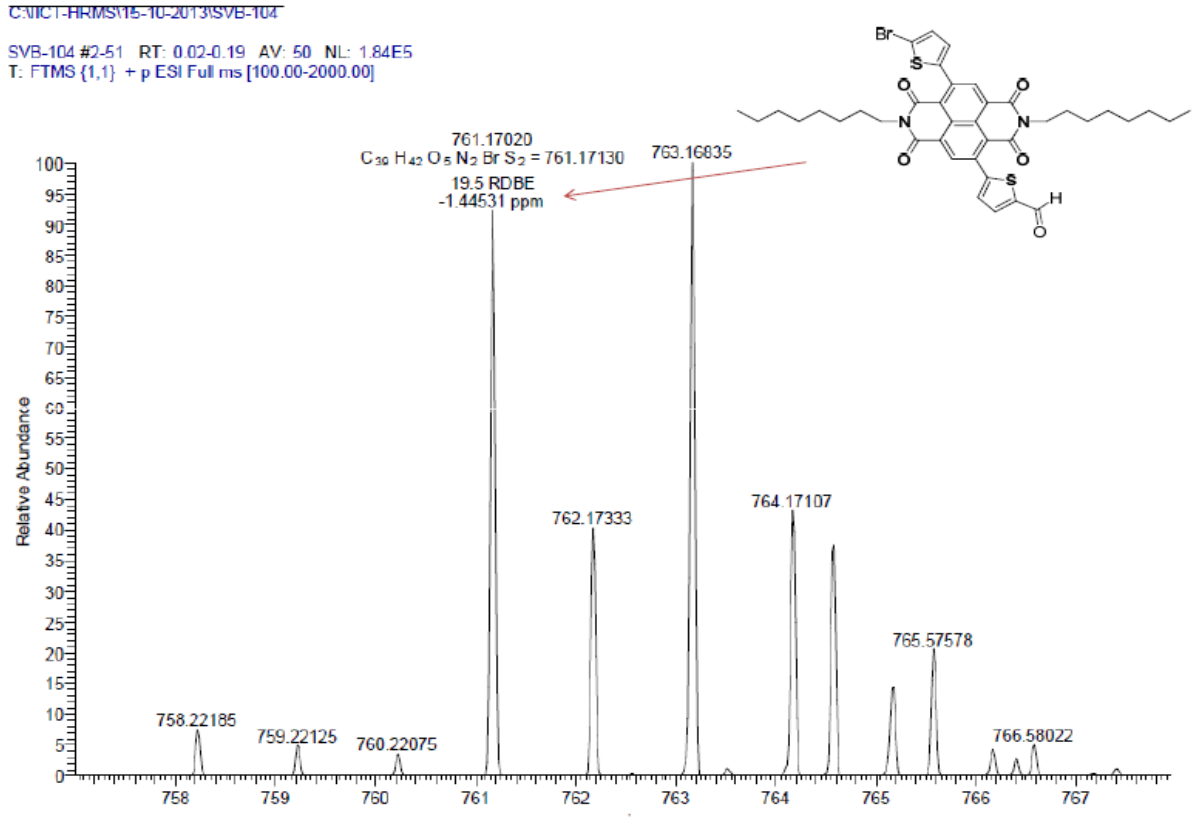


Fig. S10 HRMS of compound **4**

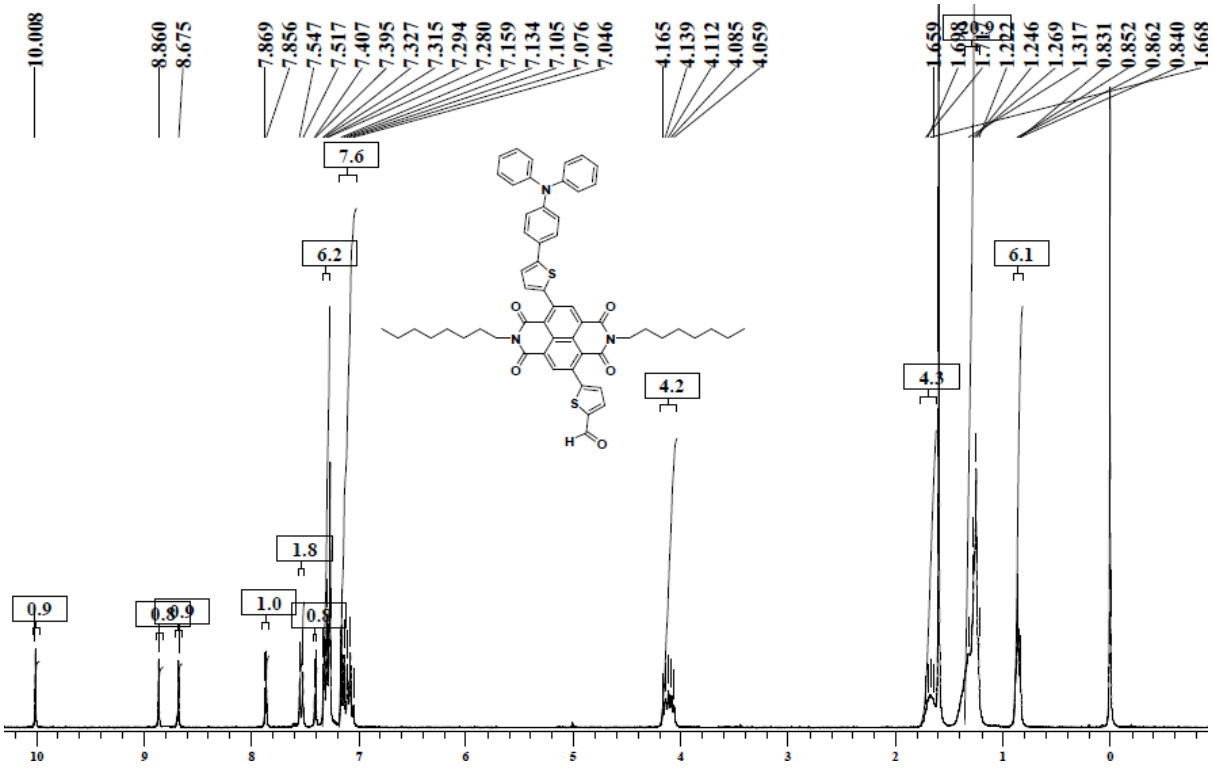


Fig. S11 [1] H NMR of **6**

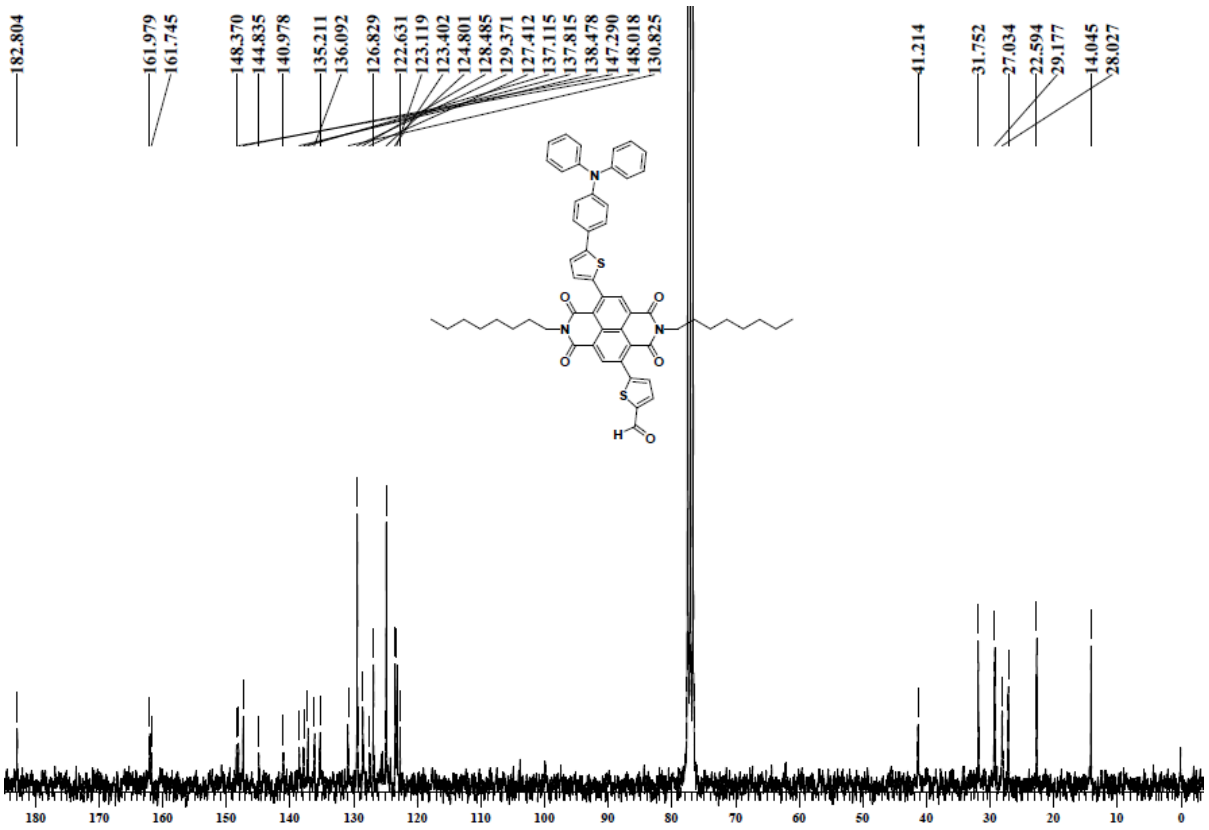


Fig. S12 [13]C NMR of compound **6**

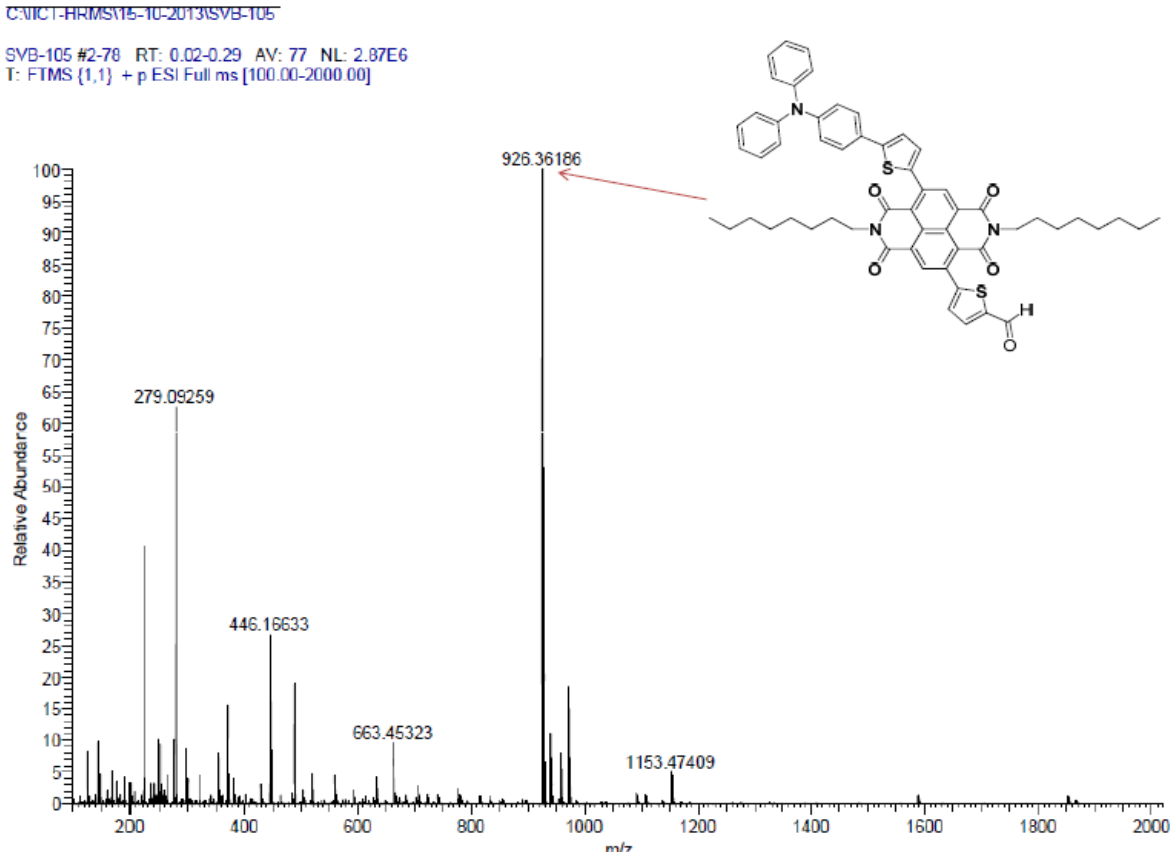


Fig. S13 HRMS of compound of **6**

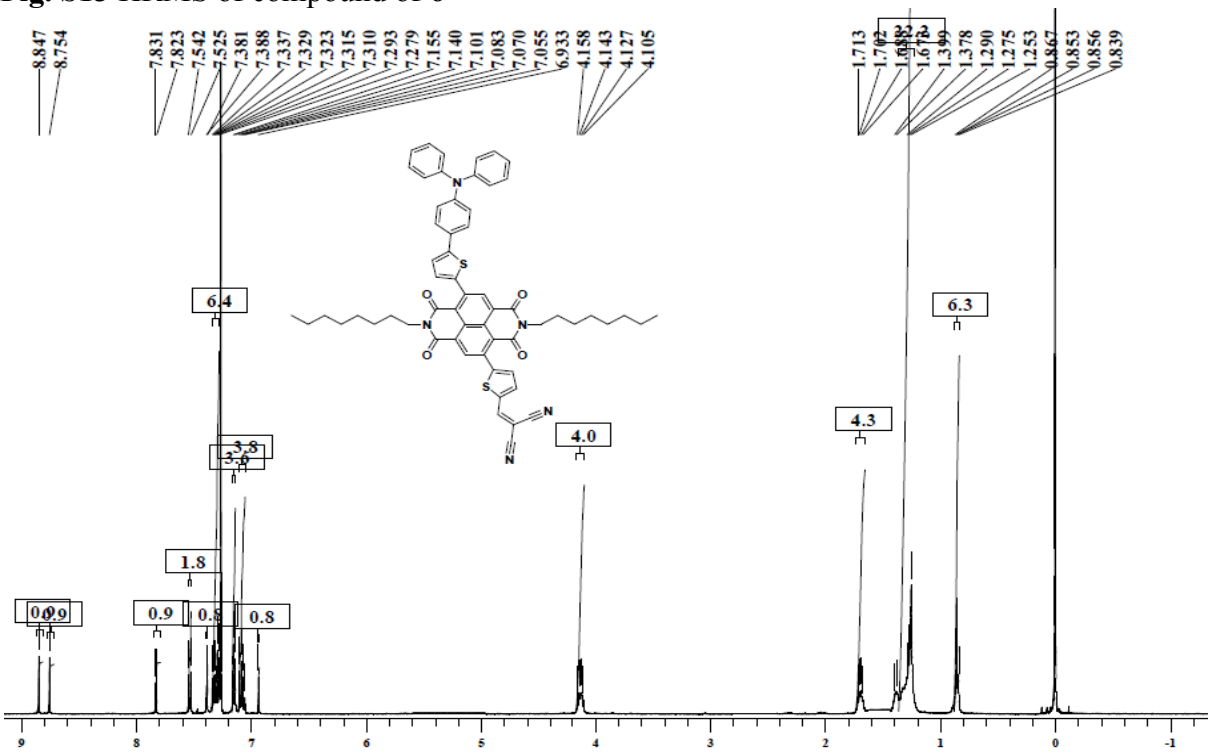


Fig. S14 ^{1}H NMR of **S1**

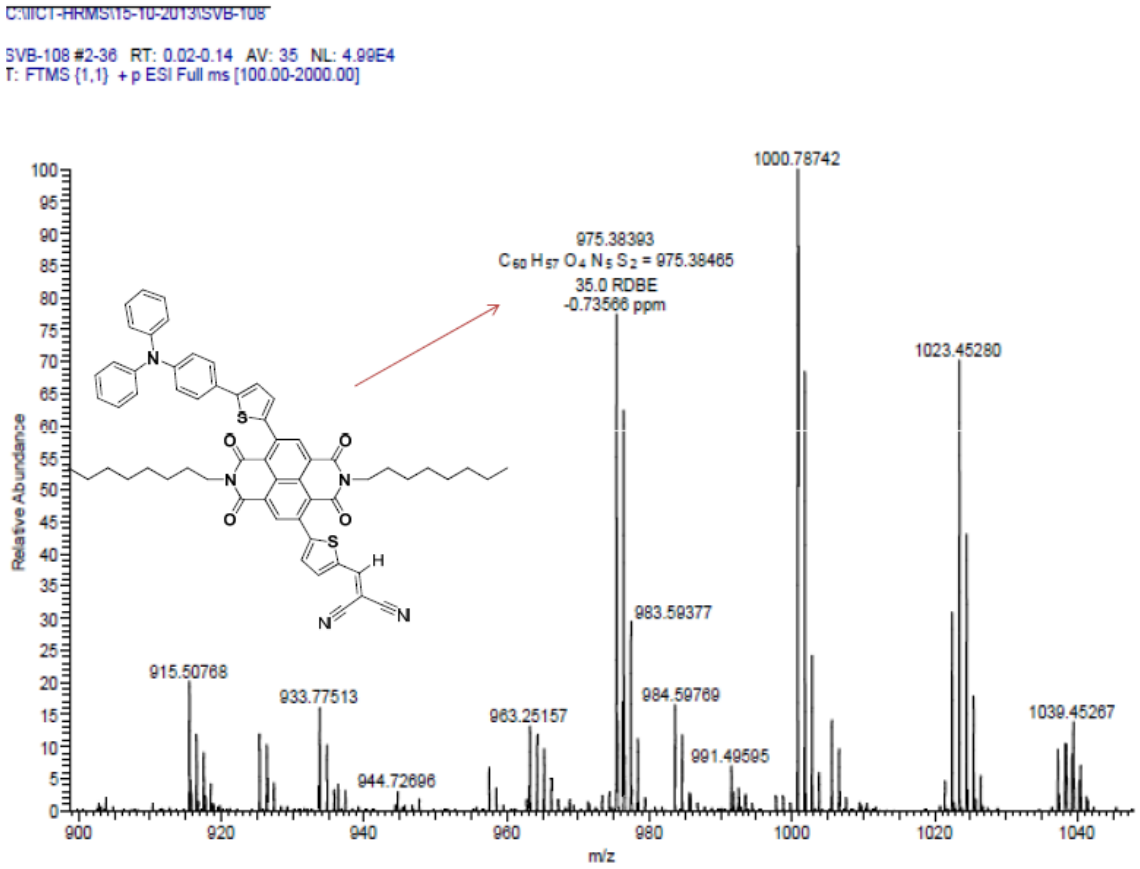


Fig. S15 HRMS of compound **S1**

References

S1 A. Gupta, V. Armel, W. Xiang, G. Fanchini, S. E. Watkins, D. R. MacFarlane, Udo Bach and R. A. Evans, *Tetrahedron*, 2013, **69**, 3584.

S2 H. Patil, A. Gupta, A. Bilic, S. L. Jackson, K. Latham and S. V. Bhosale, *J. Elect. Mater.*, 2014, **43**, 3243.