

## Modulation of Power Conversion Efficiency of Organic Solar Cells *via* Architectural Variation of a Promising Non-fullerene Acceptor

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**Materials and Reagents:** All reactions were carried out either under argon or nitrogen atmosphere. Solvents were dried according to routine procedures. Spectroscopic grade solvents were used for measuring electrochemical and optical properties. Unless otherwise noted, the chemicals received from Sigma Aldrich and Alfa Aesar were used without further purification. Samples synthesized were purified by column chromatography followed by recrystallization.

**NMR and Mass Spectra measurements:**  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on Bruker Avance 500 MHz in  $\text{CDCl}_3$ . The chemical shift values have been referenced to the residual solvent signals. HRMS measurements were recorded on a microTOF-QII high resolution mass spectrometer from Bruker Daltonics coupled to a Waters Acquity UPLC system.

**Electrochemical Measurements:** Cyclic voltammetric measurements were carried out using CH potentiostat from CHI Instruments. CV experiments were done under continuous argon flow and a conventional three-electrode electrochemical cell was used. A glassy carbon working, a platinum counter and SCE reference electrodes were used. All the measurements were done in dichloromethane solution with 0.1 M TBAP as supporting electrolyte. All the spectra were recorded at a scan rate of 0.1 V/s.

**Steady State Absorption and Emission Measurements:** Steady state absorption measurements were done on carry 100 UV/VIS spectrophotometer. Quartz cell with optical path length of 10 mm was used for all steady-state measurements. Fluorescence emission measurements were done on a Horiba Jobin Yvon fluorolog 3-111.

Quantum yield was calculated according to the following formula and PBI 1 as a reference.

$$\text{QY} = [\text{QY}_{\text{ref}} \times I \times A_{\text{ref}} \times \eta^2] / [A \times I_{\text{ref}} \times \eta_{\text{ref}}^2];$$

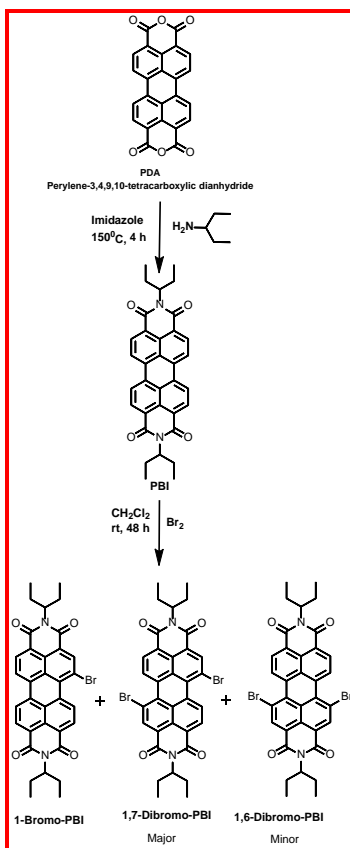
where QY = quantum yield; ref = reference (PBI); A = Absorbance; I = integrated

fluorescence intensity;  $\eta$  = refractive index of the solvent.

**Single Crystal XRD Measurement:** Single crystal X-ray diffraction measurements were done on a Bruker Apex diffractometer with a CCD detector with Mo- $K\alpha$  radiation.

**Quantum chemical calculations** were performed using Gaussian 09 software suite.

## Complete Synthetic and Analytical Details of all the Synthesized Molecules



Scheme S1. Synthesis of Perylenebisimide (PBI) , Mono-bromoperylenebisimide and dibromoperylenebisimide

Compound **1-2** and **3-4** were synthesized from the precursor mono bromo PBI and dibromo PBI respectively.

**1) Synthesis of Perylenebisimide(PBI) :** A solution of pent-3-ylamine (1.5 ml, 17 mmol), Perylene-3,4,9,10-tetracarboxylic dianhydride (PDA) (2.8g, 7 mmol) in imidazole (40 g) was stirred at 150 °C for 4 h, and then the mixture was diluted with ethanol. This was followed by the addition of 2M HCl. The reaction mixture was allowed to settle down. The precipitates formed were collected by vacuum filtration, oven dried and purified by repetitive silica gel column chromatography (chloroform) to desired product of yield 80 %. <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>) δ (ppm) 8.59 (d, *J* = 7.9 Hz, 4H), 8.53 (d, *J* = 8.0 Hz, 4H), 5.00 (m, 2H),

2.25 – 2.14 (m, 4H), 1.94 – 1.83 (m, 4H), 0.86 (t,  $J = 7.5$  Hz, 12H).  $m/z$  calc.  $C_{34}H_{30}N_2O_4 = 530.2206$ ; found  $[M+nH] = 531.2247$ .

**2) Synthesis of 1-Bromoperylenebisimide(1-Bromo-PBI):** Excess bromine (4ml, 86 mmol) was added to a solution of PBI (0.7, 1.3 mmol) in  $CH_2Cl_2$  and the reaction mixture was stirred at room temperature for 48 h. The progress of the reaction was monitored by TLC. After the removal of excess bromine, compound was purified by repetitive silica gel column chromatography with hexane/chloroform as eluents. First band obtained was a mixture of 1,7 -and 1,6-di-bromoperylenebisimide. Second band was identified as 1-bromo perylenebisimide. Further purification of second band by recrystallization yielded mono-bromo PBI as red solid. yield 57%.:  $^1H$  NMR spectrum (500 MHz,  $CDCl_3$ )  $\delta$  (ppm) = 9.72 (d,  $J = 8.2$  Hz, 1H), 8.85 (s, 1H), 8.63 (dd,  $J = 7.6$  Hz, 3H), 8.55 (dd,  $J = 8.1$ , 2H), 4.99 (m, 2H), 2.19 (m, 4H), 1.93 – 1.82 (m, 4H), 0.86 (m, 12H).  $m/z$  calc.  $C_{34}H_{29}N_2O_4Br = 608.1311$ ; found  $[M+nH] = 609.1358$ .

**3) Synthesis of 1,7-dibromoperylenebisimide:** This compound was obtained from the mixture of dibromoperylenebisimide by rigorous purification as per literature procedure.<sup>ref-s1</sup> Repetitive recrystallization as per reported procedure yielded pure 1,7-dibromoperylenebisimide in moderate yields.  $^1H$  NMR spectrum (500 MHz,  $CDCl_3$ )  $\delta$  (ppm) = 9.44 (d,  $J = 8.1$  Hz, 2H), 8.86 (s, 2H), 8.63 (d,  $J = 8.0$  Hz, 2H), 4.98 (m, 2H), 2.20 (m, 4H), 1.87 (m, 4H), 0.85 (m, 12H).

**4) Synthesis of Compound 1:** A dry Schlenk tube was charged with  $[PdCl_2(PPh_3)_2]$  (0.005g), CuI (Catalytic), dry THF (5 ml) and  $N,N$ -diisopropylamine (3 ml). The resulting solution was degassed vigorously under argon. This was followed by the addition of corresponding 1-Bromo PBI (1 eq.) and 2-[(Trimethylsilyl)ethynyl]thiophene (25  $\mu$ L) and 3 eq. of  $K_2CO_3$  (for in situ deprotection). The reaction mixture was refluxed at 70-80  $^{\circ}C$ . After the completion

of reaction, the solvent was evaporated under vacuum. The reaction mixture was mounted on a column with silica gel (230-400 mesh size) and was eluted with hexane:chloroform (20:80). Further purification was done by recrystallization in hexane/CHCl<sub>3</sub> to get a red solid. Yield: 84%. <sup>1</sup>H NMR spectrum (500 MHz, CDCl<sub>3</sub>): δ (ppm) 10.06 (d, *J* = 8.2 Hz, 1H), 8.74 (s, 1H), 8.61 (m, 5H), 7.43 (m, 2H), 7.09 (two merged doublets, 1H), 5.00 (m, 2H), 2.20 (m, 4H), 1.88 (m, 4H), 0.86 (m, 12H). <sup>13</sup>C NMR spectrum (125 MHz, CDCl<sub>3</sub>): δ (ppm) 10.35, 10.37, 23.98, 24.04, 56.69, 56.81, 92.26, 94.07, 118.90, 118.91, 121.14, 121.97, 122.56, 125.71, 125.72, 125.79, 126.27, 126.28, 126.86, 127.49, 128.18, 128.77, 130.12, 130.17, 130.26, 130.30, 132.58, 132.77, 132.92, 132.94, 133.36, 133.38, 136.85, 136.93, 137.10, 162.56, 163.14, 163.61, 163.68. HRMS: *m/z* calc: 637.2156 [M+H]<sup>+</sup>; found: 637.2174. Anal. Calc. C, 75.45; H, 5.07; N, 4.40; Found C, 74.61; H, 5.18; N, 4.10.

**Compound 2:** Compound 2 was synthesized by the same procedure as employed for 1 using 3-Ethynylthiophene (10 μL). Yield: 90%. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ (ppm) 10.20 (d, *J* = 8.2 Hz, 1H), 8.80 (s, 1H), 8.63 (m, 5H), 7.70 (two merged doublets, 1H), 7.40 (two merged doublets, 3.7 Hz, 1H), 7.30 (two merged doublets, 1H), 5.02 (m, 2H), 2.21 (m, 4H), 1.89 (m, 4H), 0.87 (m, 12H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ (ppm) 10.34, 10.36, 23.98, 24.03, 28.71, 56.68, 56.72, 89.77, 93.98, 119.32, 120.39, 121.99, 122.57, 125.45, 125.79, 125.81, 125.82, 126.32, 127.50, 128.20, 128.51, 129.72, 133.02, 133.41, 133.52. HRMS: *m/z* calc: 637.2156 [M+H]<sup>+</sup>; found: 637.2168. Anal. Calc. C, 75.45; H, 5.07; N, 4.40; Found C, 74.91; H, 5.06; N, 4.32.

**5) Synthesis of Compound 3:** A dry Schlenk tube was charged with [PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>] (0.010 g), CuI (catalytic), dry THF (5 ml) and N,N-diisopropylamine (5 ml). The resulting solution was degassed vigorously under

argon. This was followed by the addition of corresponding 1,7-DibromoPBI (0.050g) and 2- [(Trimethylsilyl)ethynyl]thiophene (35  $\mu$ L) and  $K_2CO_3$  (for in situ deprotection). The reaction mixture was refluxed at 70-80  $^{\circ}C$ . After the completion of reaction, the solvent was evaporated under vacuum. The reaction mixture was mounted on a column with silica gel (230-400 mesh size) and was eluted with hexane:chloroform (10:90). Further purification was done by recrystallization in hexane/ $CHCl_3$  to get a red solid. Yield: 82%.  $^1H$  NMR spectrum (500 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 9.93 (d,  $J = 8.25$  Hz, 1H), 8.80 (s, 1H), 8.65 (d,  $J = 8.21$  Hz 1H), 7.42 (m, 2H), 7.08 (two merged doublets, 1H), 5.02 (m, 1H), 2.23 (m, 2H), 1.88 (m, 2H), 0.87 (m, 6H).  $^{13}C$  NMR spectrum (125 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 10.29, 10.32, 10.35, 24.02, 56.80, 90.99, 93.80, 118.85, 119.55, 121.17, 121.20, 125.94, 126.36, 126.72, 126.80, 126.90, 128.64, 132.53, 132.62, 132.65, 133.08. HRMS: m/z calc: 743.2033  $[M+H]^+$ ; found: 743.2042. Anal. Calc. C, 74.37; H, 4.61; N, 3.77; Found C, 74.11; H, 4.30; N, 3.44.

**6) Synthesis of Compound 4:** Compound **4** was synthesized by the same procedure as employed for **3** using 3-Ethynylthiophene (20  $\mu$ L). Yield: 89%.  $^1H$  NMR spectrum (500 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 10.00 (d,  $J = 8.27$  Hz, 1H), 8.78 (s, 1H), 8.67 (d,  $J = 8.21$  Hz, 1H), 7.66 (two merged doublets, 1H), 7.38 (two merged doublets, 1H), 7.27 (m, 1H), 5.02 (m, 1H), 2.23 (m, 2H), 1.88 (m, 2H), 0.87 (m, 6H).  $^{13}C$  NMR spectrum (125 MHz,  $CDCl_3$ ):  $\delta$  (ppm) 10.30, 10.32, 24.01, 56.77, 89.46, 89.50, 92.71, 119.20, 119.89, 120.36, 120.40, 125.39, 125.43, 125.93, 126.08, 126.33, 126.34, 126.43, 126.74, 126.84, 127.14, 127.34, 127.56, 128.55, 128.56, 129.69, 129.76, 129.78, 129.90, 132.85, 133.15, 133.93. HRMS: m/z calc: 743.2033  $[M+H]^+$ ; found: 743.2052. Anal. Calc. C, 74.37; H, 4.61; N, 3.77; Found C, 73.86; H, 4.22; N, 3.43.

# NMR Spectra of Synthesized Molecules

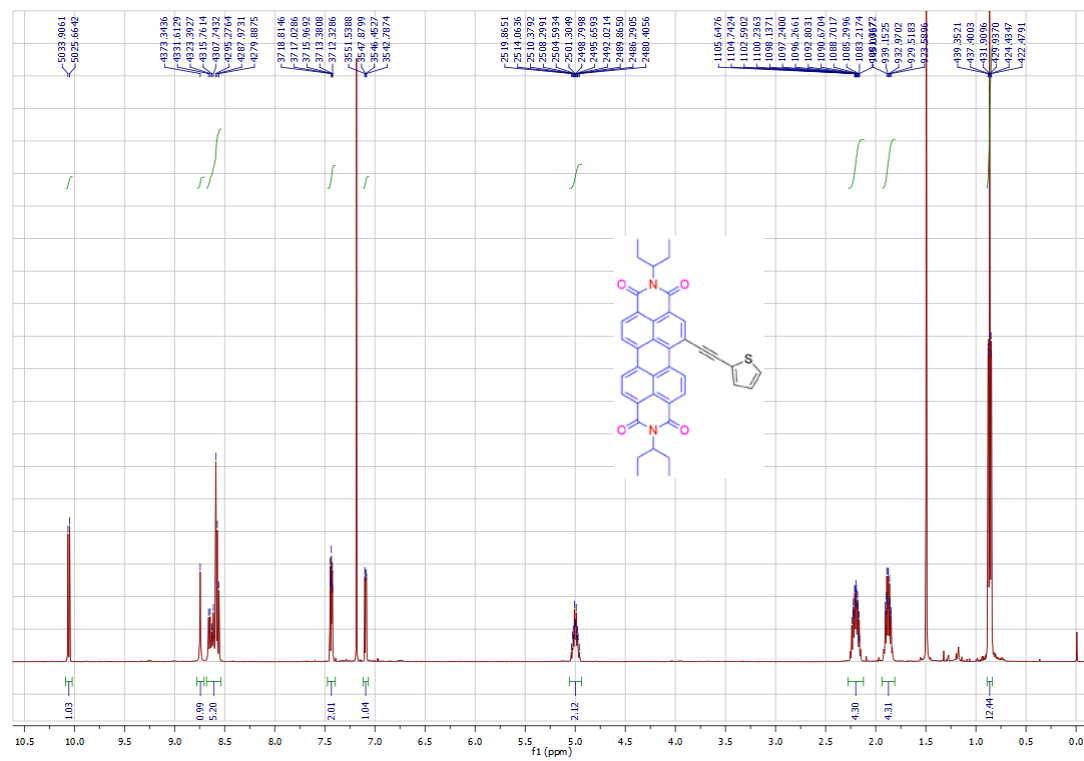


Figure S1. <sup>1</sup>H NMR spectrum of compound 1 in CDCl<sub>3</sub>.

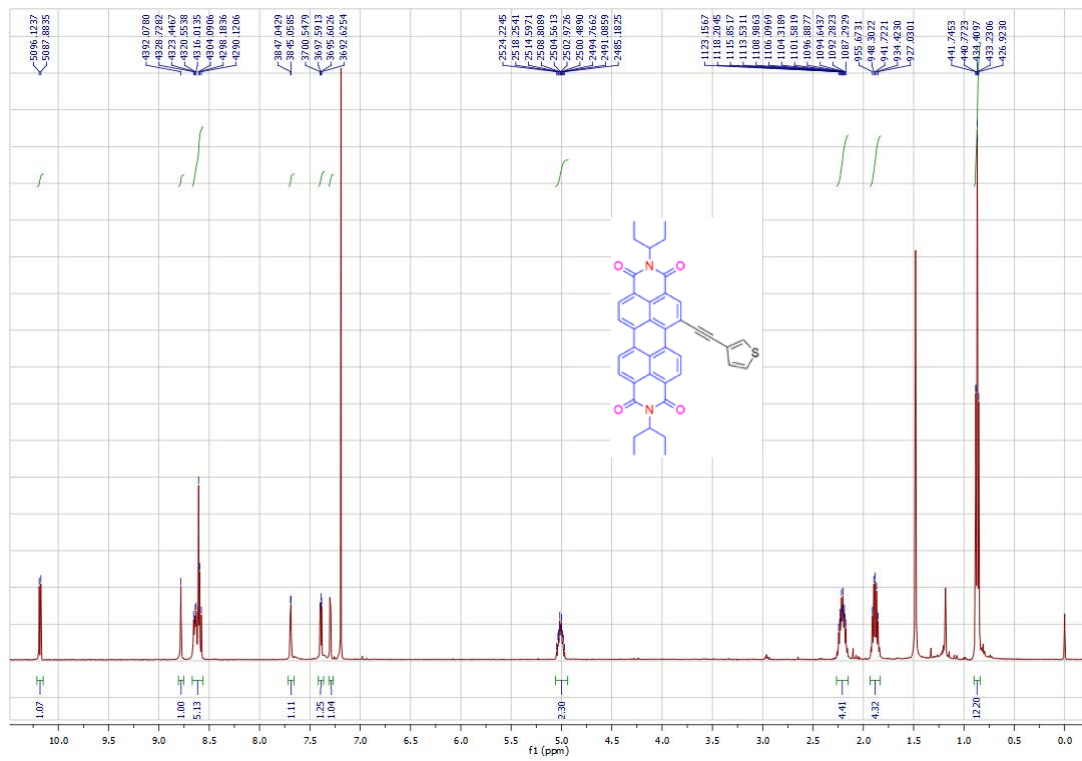


Figure S2. <sup>1</sup>H NMR spectrum of compound 2 in CDCl<sub>3</sub>.



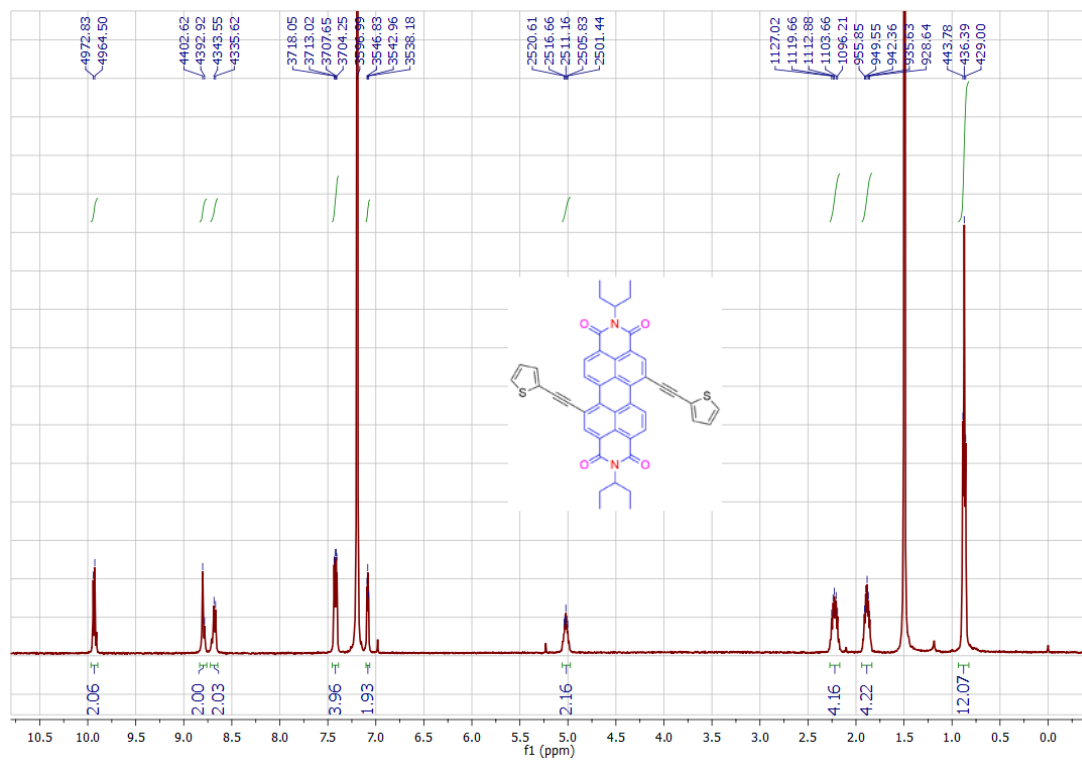


Figure S3. <sup>1</sup>H NMR spectrum of compound 3 in CDCl<sub>3</sub>.

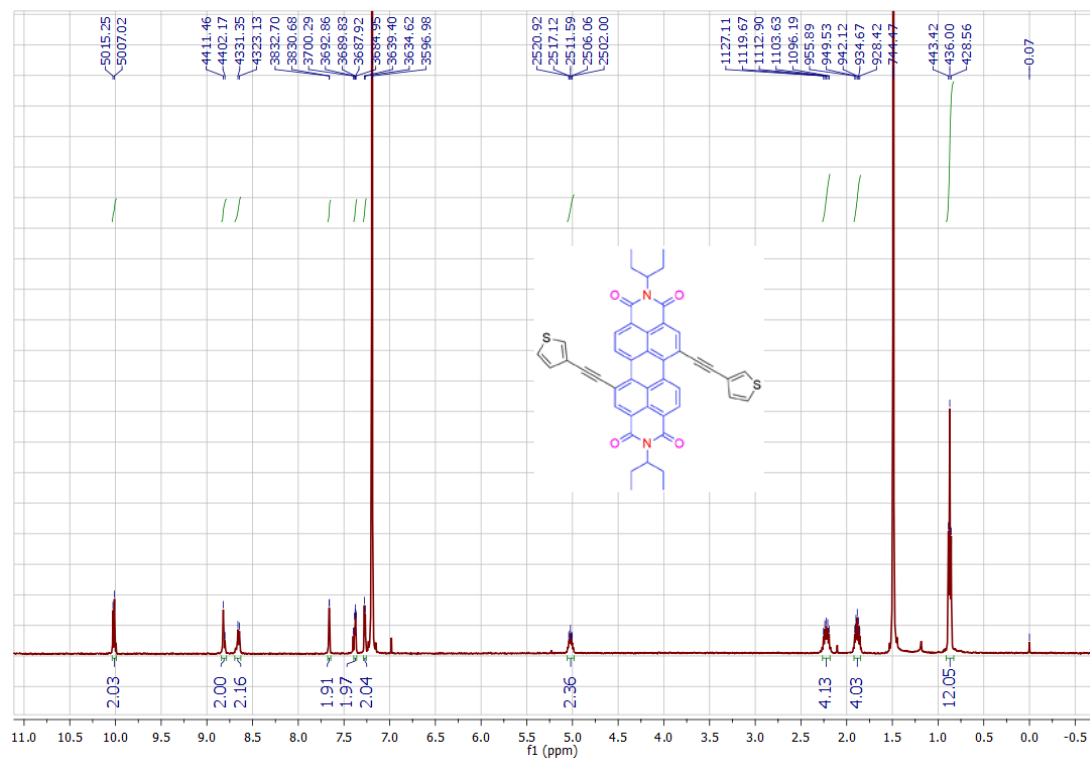


Figure S4.  $^1\text{H}$ NMR spectrum of compound 4 in  $\text{CDCl}_3$ .

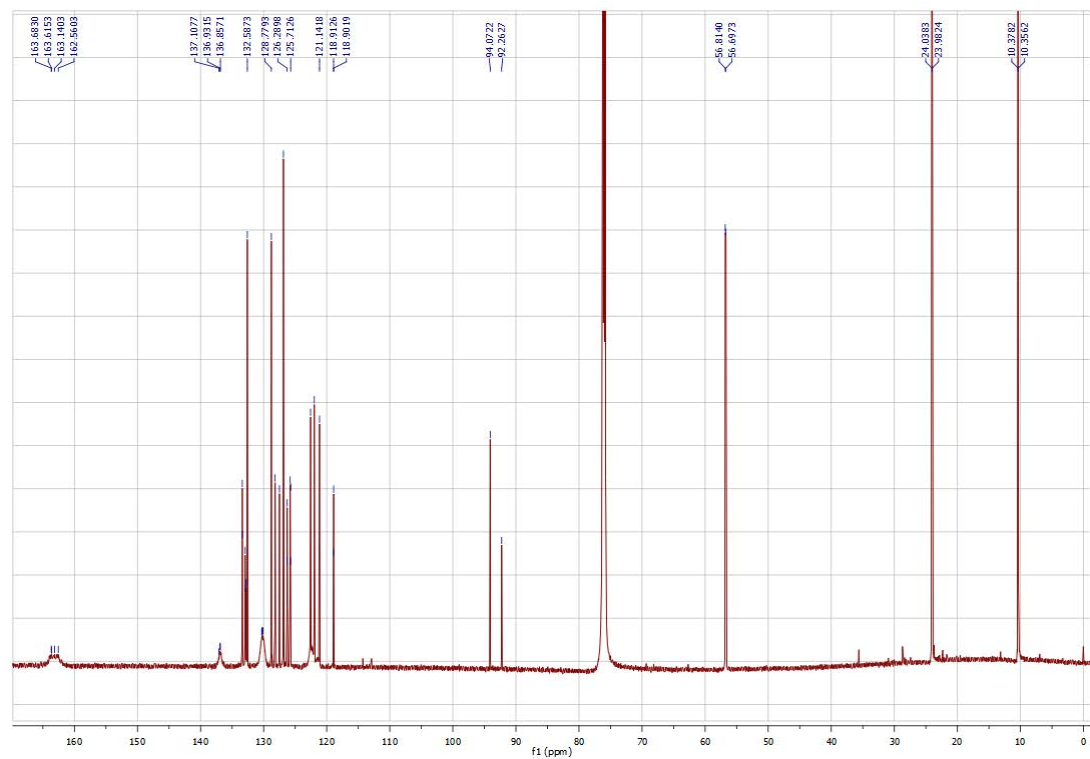


Figure S5.  $^{13}\text{C}$ NMR spectrum of compound 1 in  $\text{CDCl}_3$ .

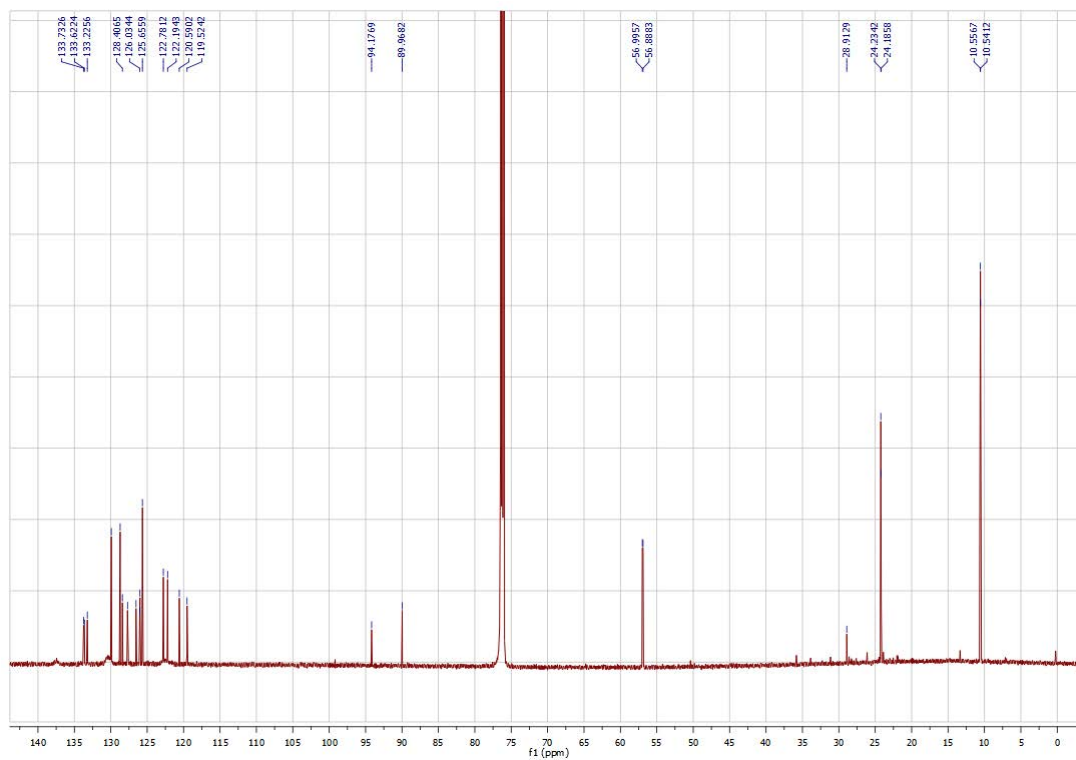


Figure S6.  $^{13}\text{C}$ NMR spectrum of compound 2 in  $\text{CDCl}_3$ .

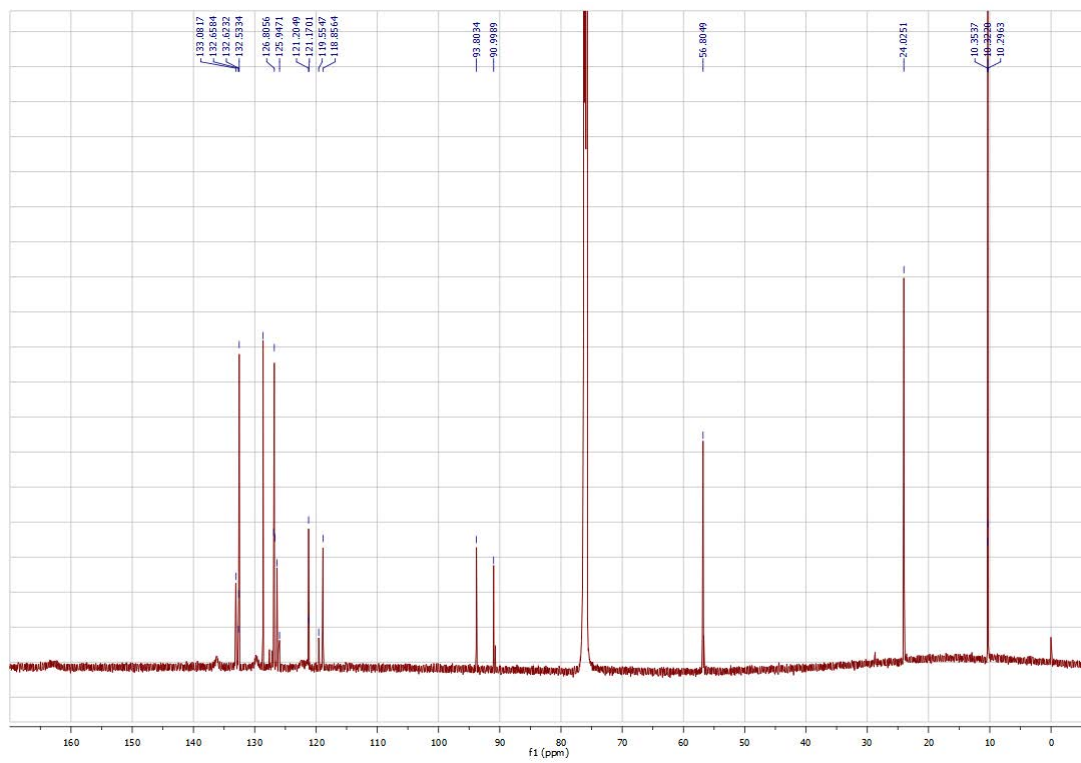


Figure S7.  $^{13}\text{C}$  NMR spectrum of compound 3 in  $\text{CDCl}_3$ .

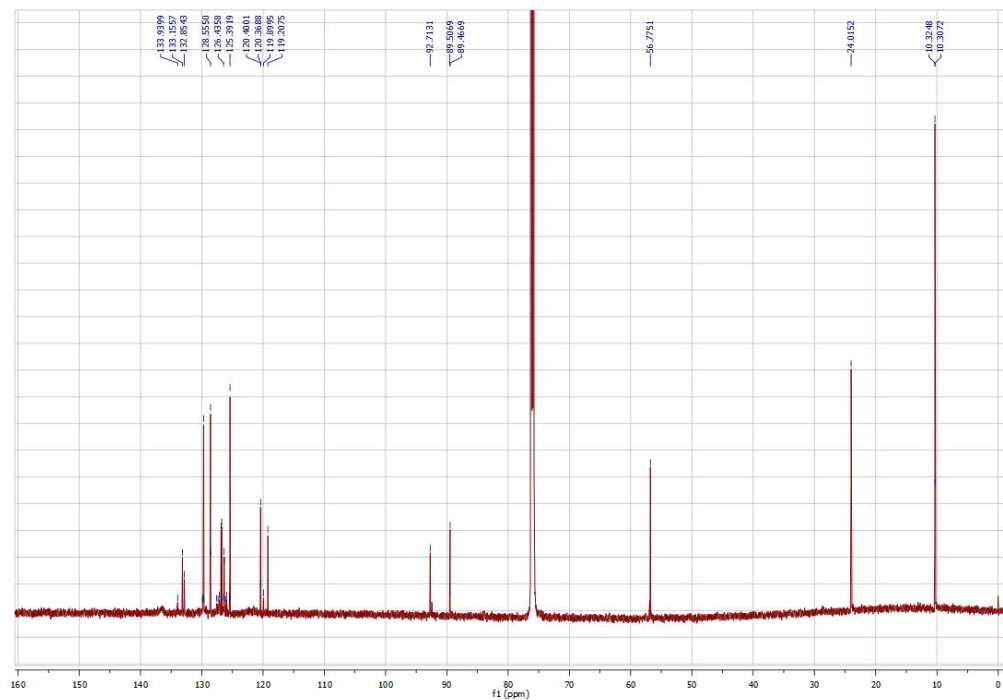


Figure S8.  $^{13}\text{C}$ NMR spectrum of compound 4 in  $\text{CDCl}_3$ .

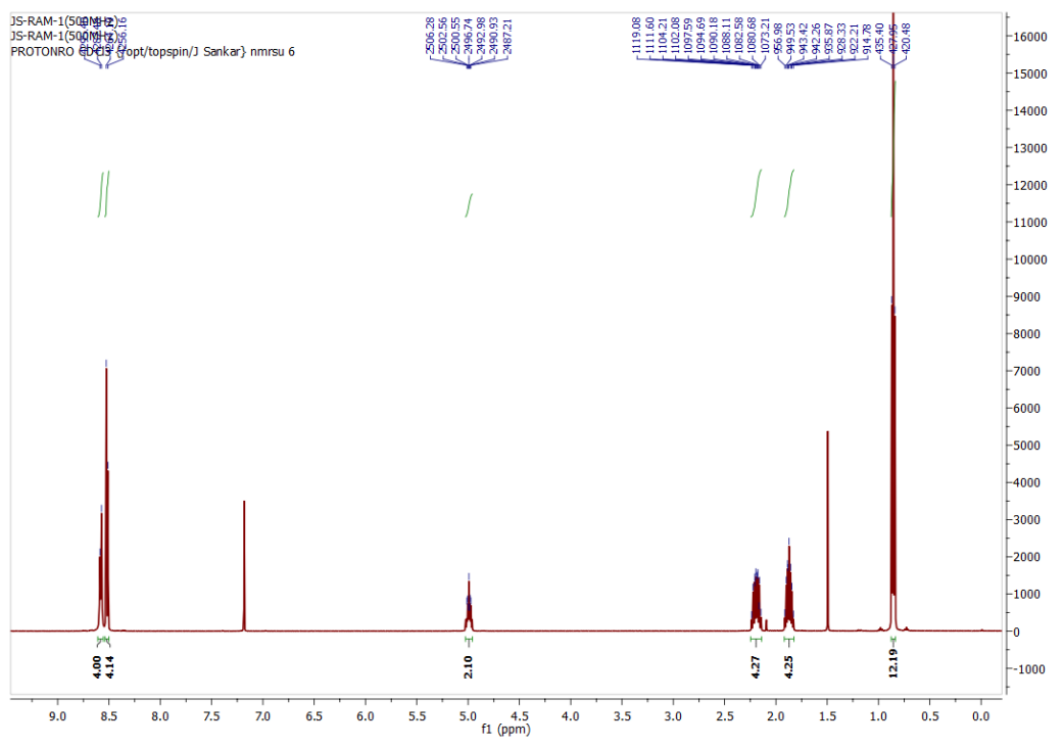


Figure S9.  $^1\text{H}$ NMR spectrum of PBI in  $\text{CDCl}_3$ .

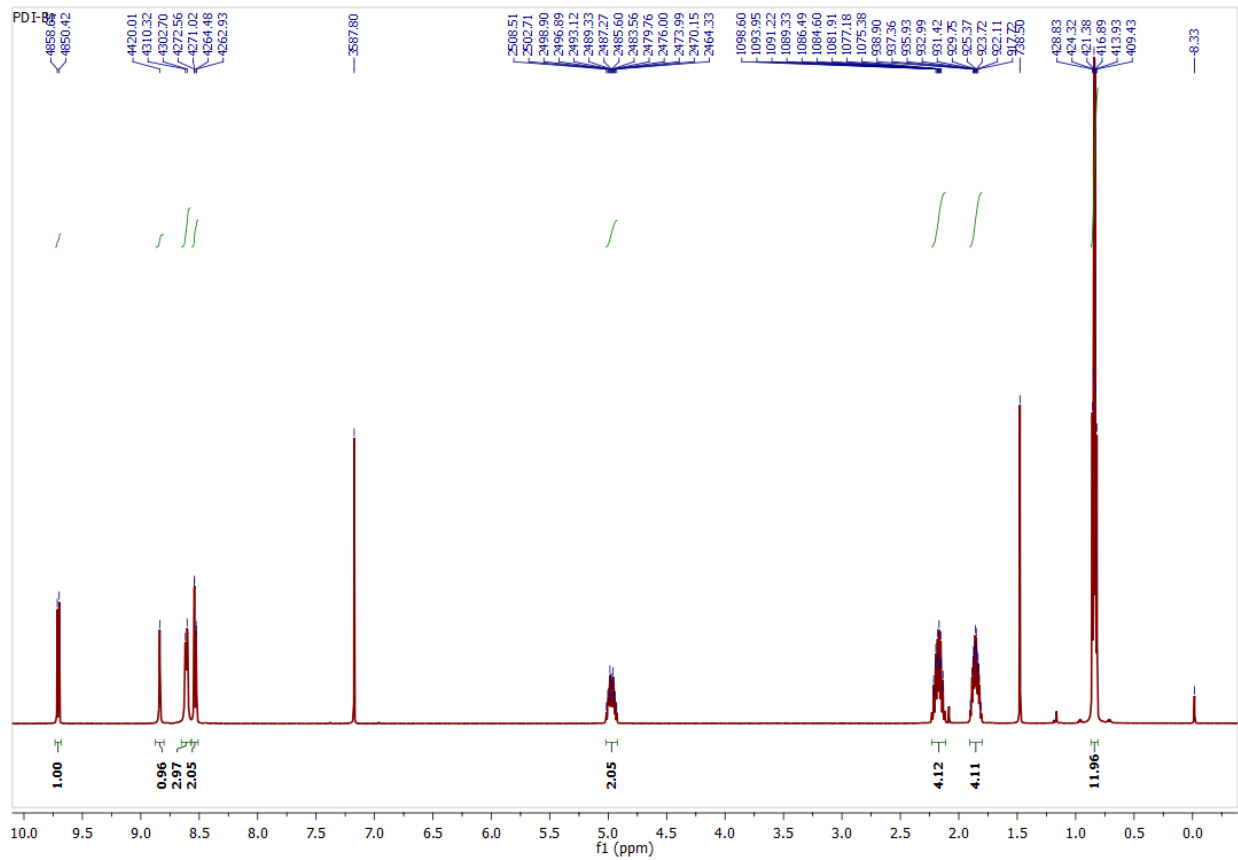


Figure S10. <sup>1</sup>H NMR spectrum of 1-Bromo-PBI in CDCl<sub>3</sub>.

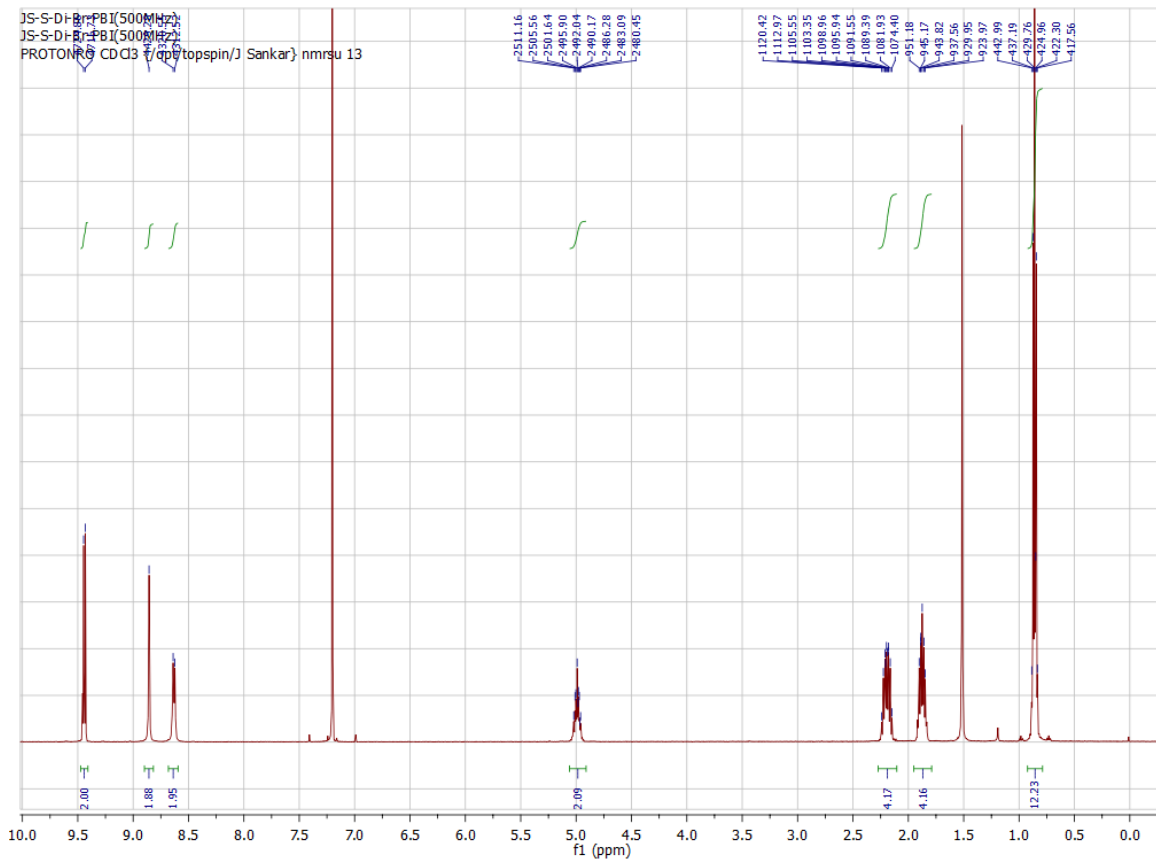


Figure S11. <sup>1</sup>H NMR spectrum of 1,7- Dibromo-PBI in CDCl<sub>3</sub>

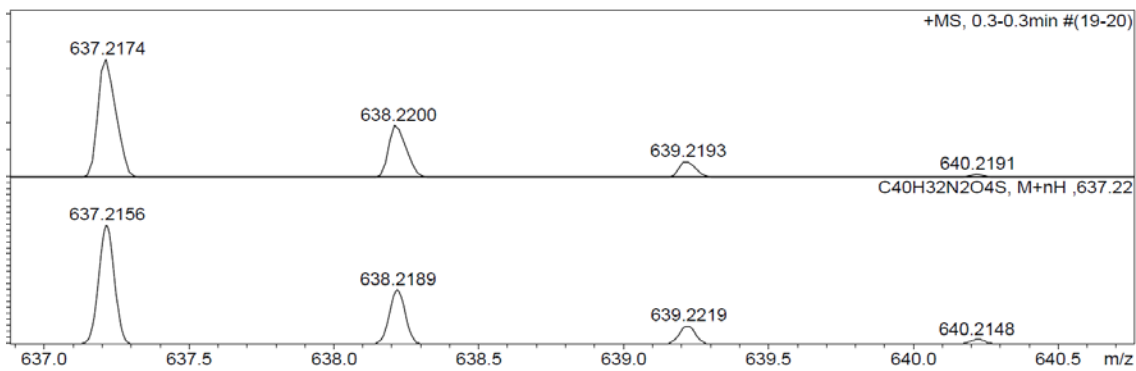


Figure S12. HRMS mass spectrum of compound 1.

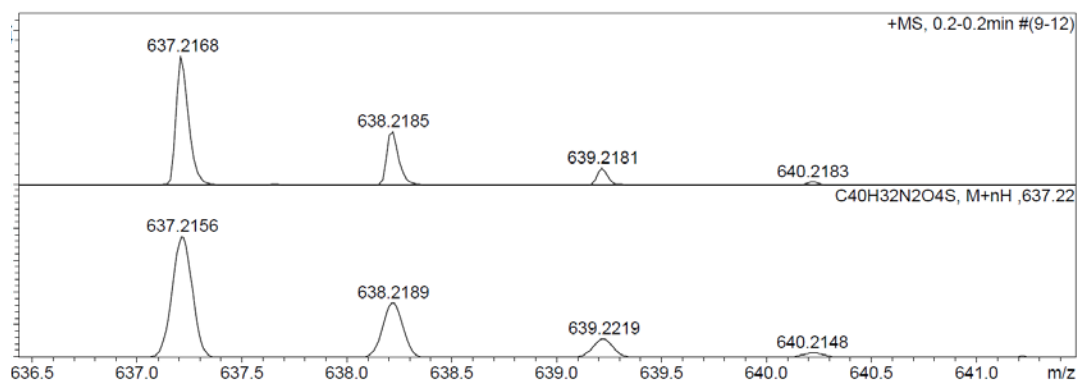


Figure S13. HRMS mass spectrum of compound 2.

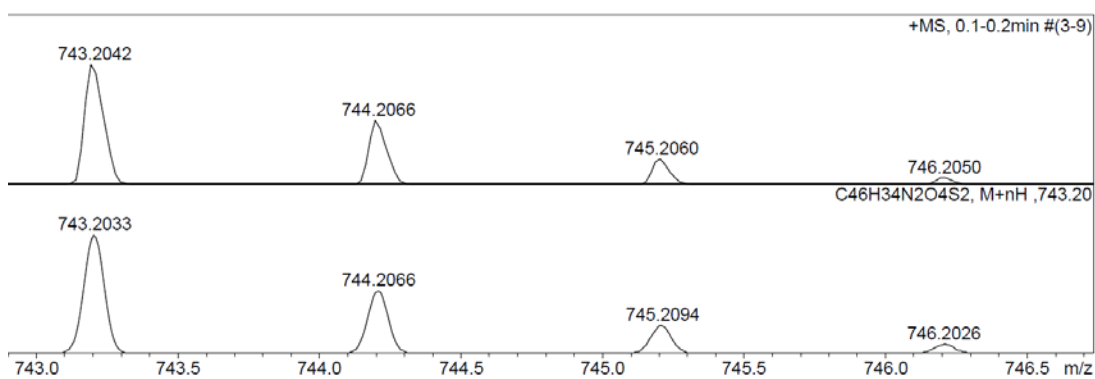


Figure S14. HRMS mass spectrum of compound 3.



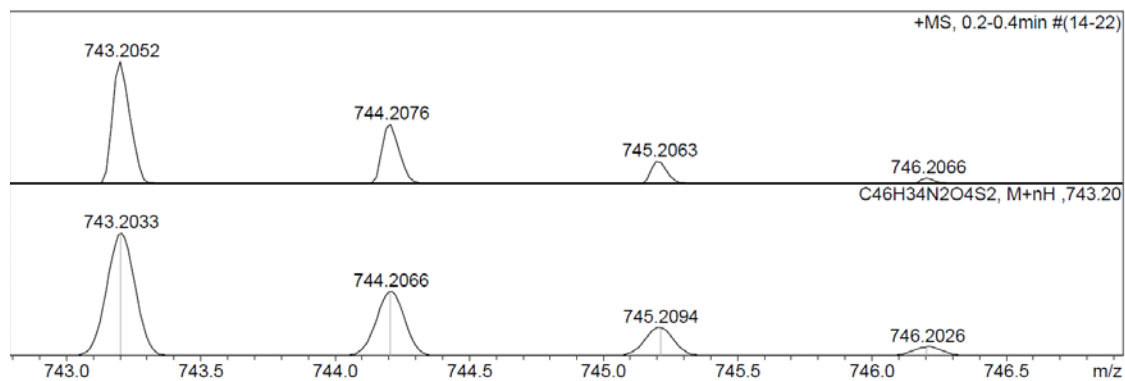


Figure S15. HRMS mass spectrum of compound 4.

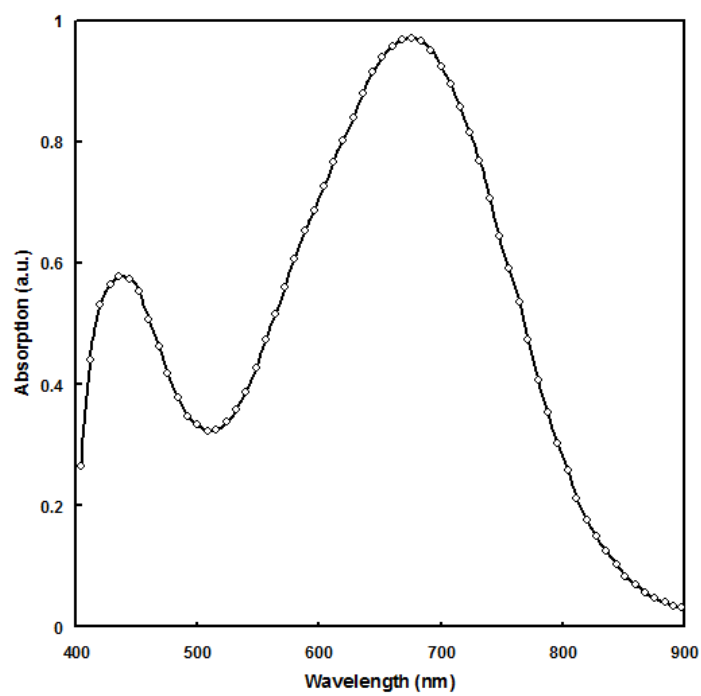


Figure S16. Absorption spectra of conjugated polymer P in thin film.

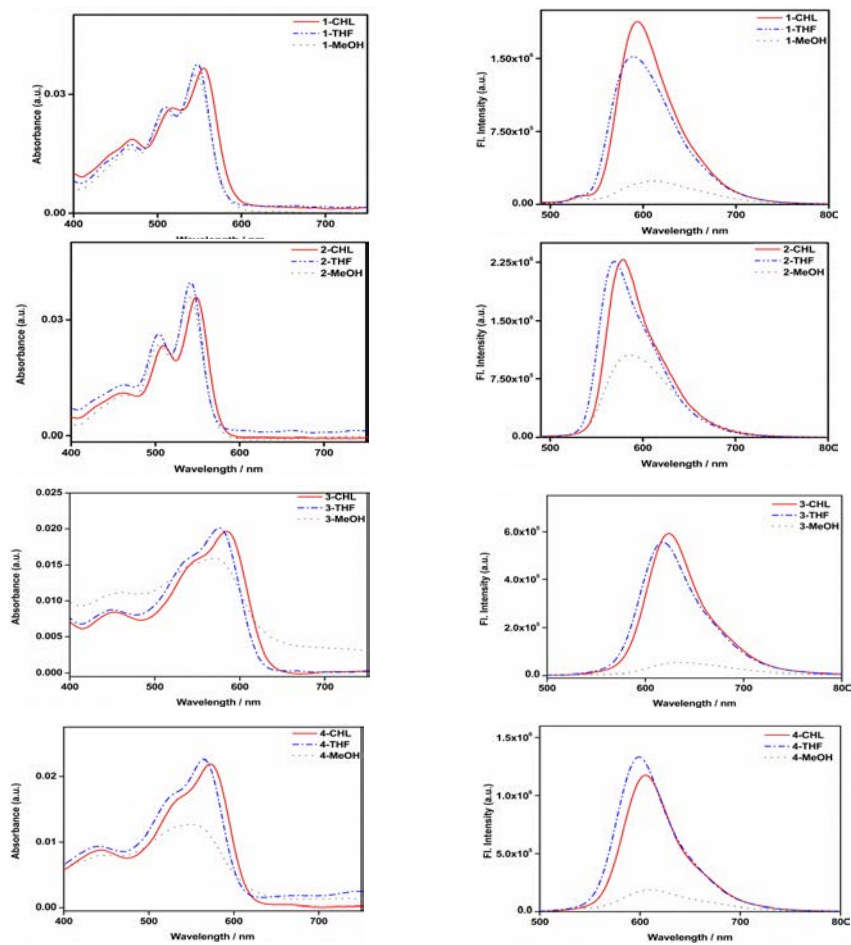


Figure S17.. Solvent dependences of the absorption and emission spectra of molecules 1-4

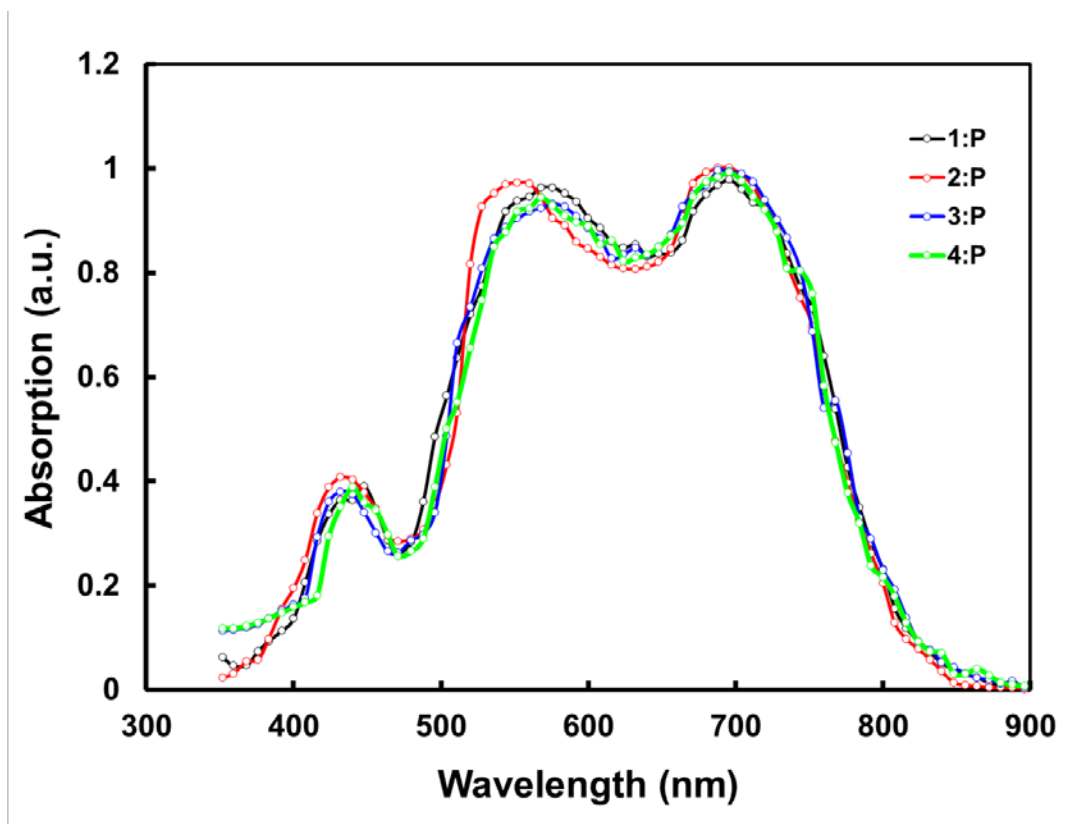


Figure S18 Optical absorption spectra of blend thin films

Table S1: Photovoltaic parameters of the organic cell fabricated using 1-4 without SVA treatment

Compound	$J_{sc}$ (mA/cm <sup>2</sup> )	$V_{oc}$ (V)	FF	PCE
1	7.44	1.04	0.42	3.25 %
2	6.76	1.04	0.40	2.81 %
3	7.98	0.98	0.43	3.36 %
4	7.45	0.98	0.43	3.14 %

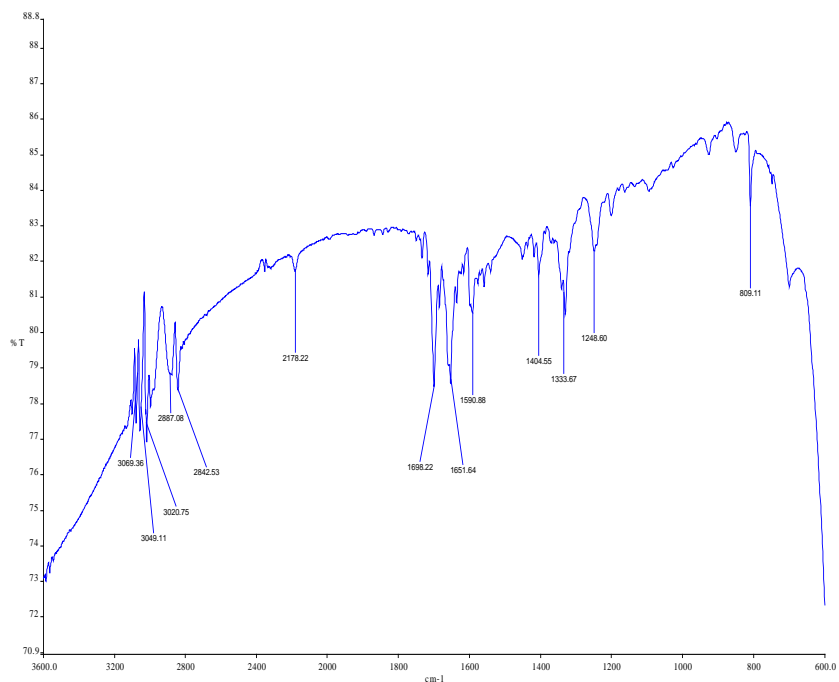


Figure S19. IR spectra of the molecule 1

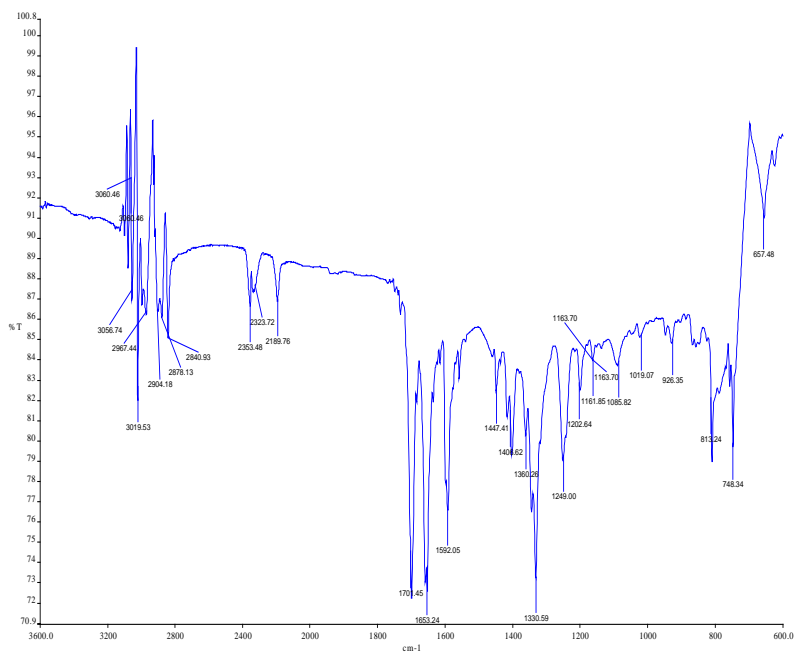


Figure S20. IR spectra of the molecule 2

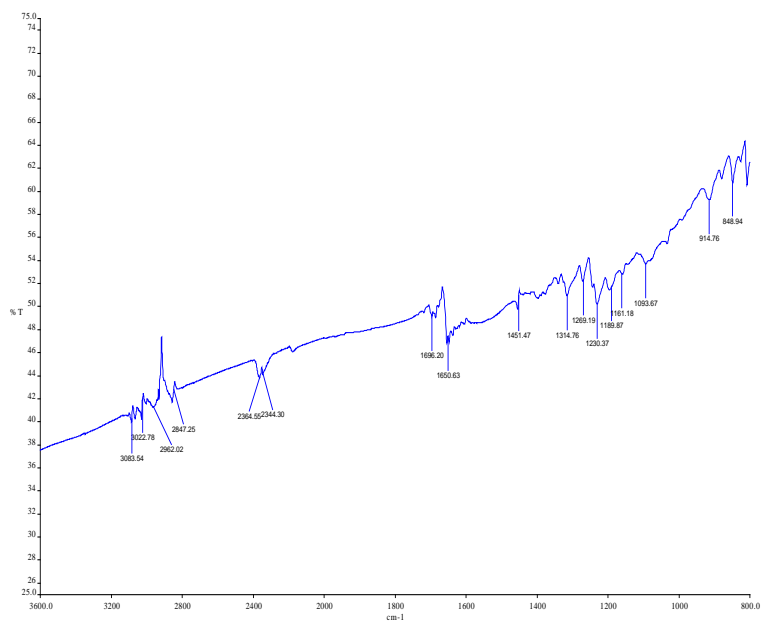


Figure S21. IR spectra of the molecule 3.

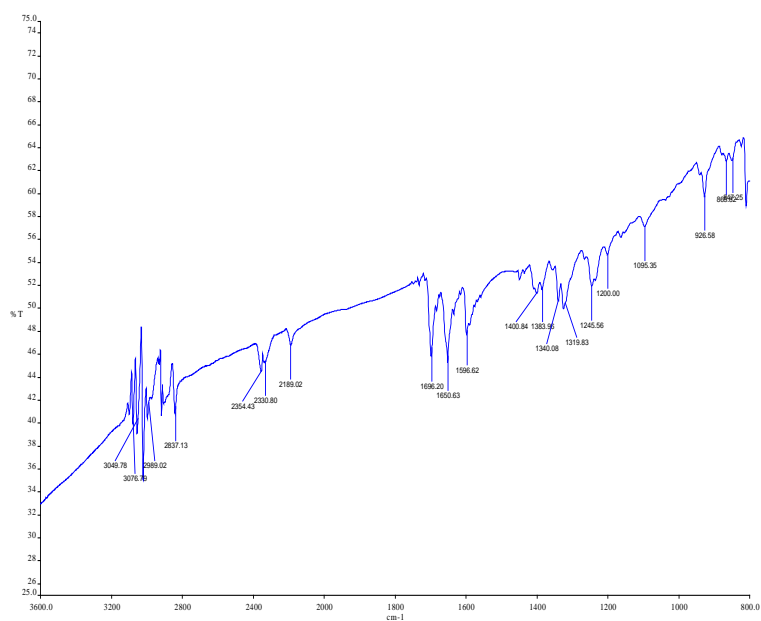


Figure S22. IR spectra of the molecule 4

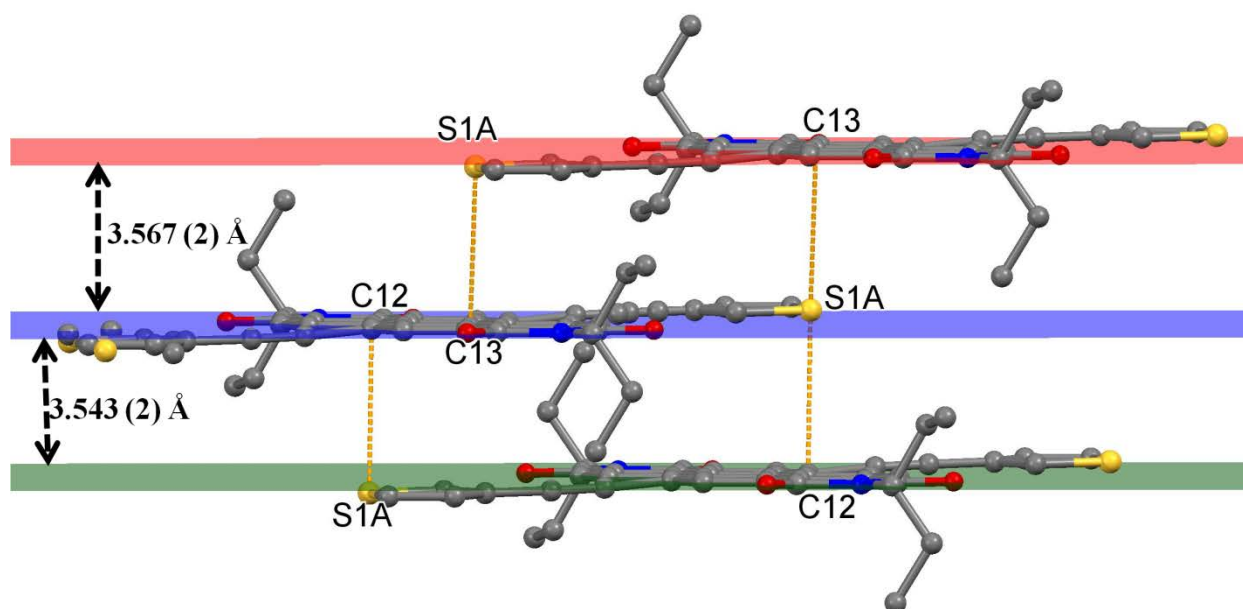
## X-diffraction data

**Table S2:** Crystallographic and refinement data of compounds **1** and **4**

DATA	<b>1</b>	<b>4</b>
<b>Formula</b>	C <sub>41</sub> H <sub>34</sub> C <sub>12</sub> N <sub>2</sub> O <sub>4</sub> S	C <sub>46</sub> H <sub>34</sub> N <sub>2</sub> O <sub>4</sub> S <sub>2</sub>
<b>Formula Weight</b>	721.66	742.87
<b>CCDC No.</b>	1569915	1042505
<b>Crystal System; Space group</b>	Monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>	Triclinic; <i>P</i> -1
<i>a</i> (Å)	17.987(7)	7.2661(9)
<i>b</i> (Å)	7.440(2)	7.4190(9)
<i>c</i> (Å)	27.623(10)	16.444(2)
$\alpha$ (°)/ $\beta$ (°)/ $\gamma$ (°)	90/ 105.357(13)/ 90	91.005(3), 102.408(4), 98.557(2)
<b>Volume /Density (g/cm<sup>3</sup>)</b>	3564(2)/ 1.345	854.99(18)/ 1.443
<i>Z</i> / <i>Z'</i>	4/ 1	1/ 1
<i>F</i> (000)/ $\mu$ (mm <sup>-1</sup> )	1504/ 0.286	388/ 0.209
$\theta$ (min, max)	2.283, 21.533	2.540, 24.99
<i>h</i> <sub>min,max</sub> , <i>k</i> <sub>min,max</sub> , <i>l</i> <sub>min,max</sub>	-17, 17; -6, 7; -28, 28	-8, 8; -8, 8; -19, 19
<b>No. of ref.</b>	59312	14690
<b>No. unique ref./ obs. ref.</b>	3567, 2761	3020, 2047
<b>No. of parameters</b>	460	262
<b>R<sub>all</sub>, R<sub>obs</sub></b>	0.2004, 0.1670	0.0997, 0.0603
<b>wR<sub>2 all</sub>, wR<sub>2 obs</sub></b>	0.4976, 0.4684	0.1535, 0.1373
$\Delta\rho_{\text{min,max}}$ (eÅ <sup>-3</sup> )	-0.884, 1.131	-0.371, 0.476
<b>G. o. F</b>	2.313	1.021

**Table S3:** List of selected torsion angle in **4** (°)

C6 -N1 -C3 -C4	65.8(3)
C10 -N1 -C3 -C2	118.6(3)
N1 -C3 -C4 -C5	166.2(2)
C1 -C2 -C3 -N1	-55.5(3)
C1 -C2 -C3 -C4	177.6(2)
C2 -C3 -C4 -C5	-66.3(3)
C3 -N1 -C6 -O1	0.2(4)
C3 -N1 -C10 -O2	-0.4(4)
C9 -C11 -C12 -C18A	173.5(3)
C19A -C20A -C21A -C22A	178.3(6)



**Fig S23:** Interlayer packing in **4**.

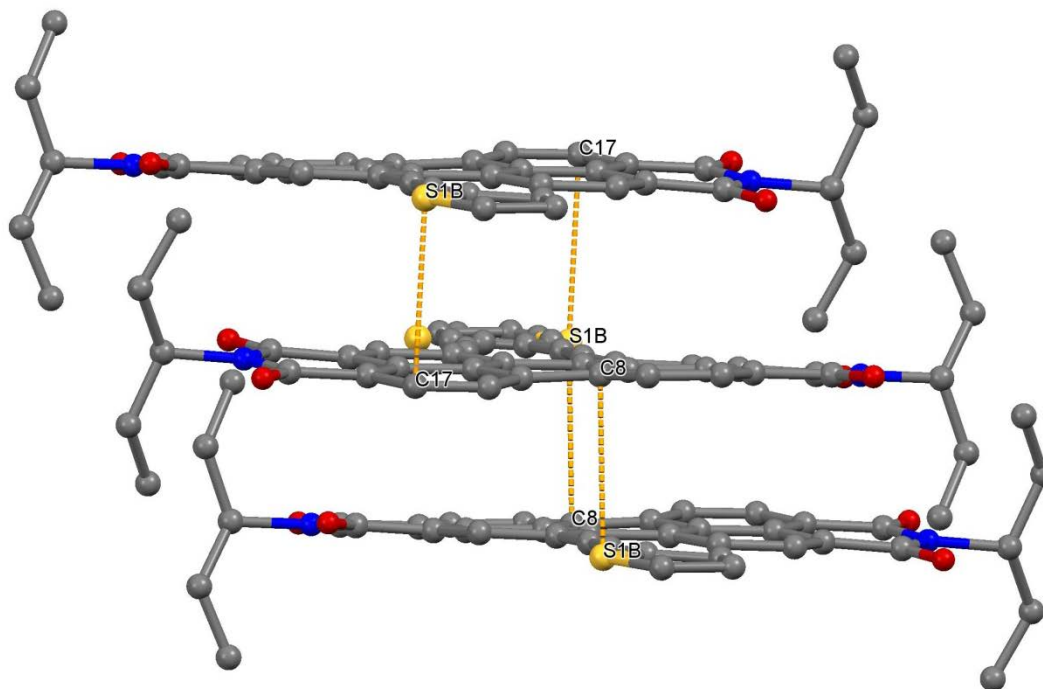
**Table S4:** List of  $\pi \dots \pi$  stacking in **4** (**Fig. S23**)

	$D(\text{\AA})$	symmetry
S1A...C13 ( $\pi_1 \dots \pi_1$ )	3.567 (2)	$x+1, y+1, z$
C12...S1A ( $\pi_2 \dots \pi_2$ )	3.543 (2)	$x+1, y, z$

**Table S5:** List of selected torsion angle ( $^\circ$ ) in Compound **1**

C25 -N1 -C2 -C3	-178.3(8)
C2- N1 -C25 -C26	69.4(14)
C1 -N1 -C25 -C28	96.9(15)
C28 -C25- C26 -C27	175.5(18)
N1 -C25 -C26 -C27	29(2)
C26 -C25 -C28 -C29	174.5(17)
N1 -C25 -C28 -C29	-38(3)
C24 -N2 -C30 -C33	-80.6(15)
C23 -N2 -C30 -C33	99.0(14)
C24 -N2 -C30 -C31	65.9(14)
C33 -C30 -C31 -C32	175.2(16)
N2 -C30 -C31 -C32	34(2)
C31 C30 C33 C34	175.4(18)
N2 -C30 -C33 -C34	-42(2)
C11 -C10 -C13 -C14	176.9(7)
<b>C9 -C10 -C13 -C14</b>	<b>-1.2(12)</b>
<b>C11 -C10 -C13 -C22</b>	<b>-5.9(13)</b>
<b>C7 -C8 -C15 -C16</b>	<b>-3.8(13)</b>
C9 -C8 -C15 -C16	176.0(8)

C7 -C8 -C15 -C14	173.8(8)
<b>C9 -C8 -C15 -C14</b>	<b>-6.5(12)</b>
C35B -C36B -C37B -C38B	2(11)
C35B -C36B -C37B -S1B	-177(8)



**Figure S24:** Intermolecular stacking in compound **1**

**Table S6:** List of  $\pi \dots \pi$  stacking in Compound **1**(Fig. S24)

	$D(\text{\AA})$	symmetry
S1B...C17 ( $\pi 1 \dots \pi 1$ )	3.468 (2)	-x+1, -y+1, -z+1
C8...S1B ( $\pi 2 \dots \pi 2$ )	3.463 (2)	-x+1, -y+2, -z+1

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