

# Supporting information

## Synthesis of a pentalene centered polycyclic fused system

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## §1. Measurements and Materials

The  $^1\text{H}$ -NMR,  $^{13}\text{C}$ -NMR spectra were recorded on a BRUCK 400MHz instrument and the TOF-MS spectra were determined using a BEFLEX III. Elemental analyses were performed on a Carlo-Erba-1106 instrument. The ESR was measured with Bruker ESP-300 instrument. The UV-Visible absorption spectra were measured with a Shimadzu UV-1601PC double-beam spectrophotometer.

Cyclic voltammograms (CVs) were recorded on a CHI660D electrochemical workstation (CH Instruments, Austin, TX). The working electrode consisted of a glassy carbon disk (3.0 mm in diameter) that was polished on a felt pad with 0.05 $\mu\text{m}$  alumina (Buehler, Ltd., Lake Bluff, IL), sonicated in water and absolute ethanol for 3 min, and then dried in an oven at 100 $^{\circ}\text{C}$  before being transferred into the inert atmosphere dry box. A platinum wire served as a counter electrode, and a silver wire was utilized as a quasi-reference electrode which was referenced after each series of experiments against the ferrocene/ferrocenium couple to obtain the potentials vs SCE,<sup>1</sup> taking  $E^{\circ}(\text{Fc}/\text{Fc}^+)=0.424\text{ V}$ , vs SCE.<sup>2</sup> The concentrations used to obtain each voltammogram are given in the corresponding figure captions.

Tetra-n-butylammounium hexfluorophostphate ( $\text{TBAPF}_6$ ) used as the supporting electrolyte for the electrochemical measurement was obtained from Alfa-Aesar Co. Ltd., recrystalized and dried in vacuo prior to use. All other reagents were obtained commercially and used as supplied. All the solvents used in electrochemical measurements and photophysical measurements were of HPLC grade quality, purchased and used without further purification unless otherwise noted.

## §2. Experimental Section

### 3-bromo-1-(phenylsulfonyl)-1H-indole (**3**)<sup>3</sup>

Phenylsulfonyl-1H-indole **2** (5.00 g 19.4 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (150 mL). To the result solution, Br<sub>2</sub> (1.32 mL) was added drop wise. The red reaction mixture was then stirred at r.t. for 4.5 h, and then poured into a saturated solution of aq. NaHCO<sub>3</sub> the resulting two layers were separated, and the organic layer successively washed with aq. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (5%), H<sub>2</sub>O, and brine, and then dried with MgSO<sub>4</sub>. Then, the solvent was removed under reduced pressure and the crude residue was purified by chromatography (20% EtOAc-Hexane) to afford the product as white solid (5.6 g, 95%).

<sup>1</sup>HNMR(400 Mz, CDCl<sub>3</sub>): δ 7.31 (t, 1H, *J*=7.6Hz), 7.38 (t, 1H, *J*=7.04Hz), 7.43-7.49 (m, 3H), 7.53 (t, 1H, *J*=7.03Hz), 7.63 (s, 1H), 7.90 (d, 2H, *J*=7.98Hz), 8.02 (d, 1H, *J*=8.26).

<sup>13</sup>CNMR(100Mz,CDCl<sub>3</sub>):δ 99.9, 113.7, 120.2, 124.1 124.8, 125.9, 126.9, 129.5, 129.9, 134.3, 134.4, 137.9. EI-MS: 335(100%), 194(76%).

### 3-bromo-2-iodo-1-(phenylsulfonyl)-1H-indole (**4**)<sup>4</sup>

To a solution of **3** (3g, 8.9mmol) in dry THF(50mL), LDA (lithium diisopropylamide) 2M 4.8mL was added via syringe over 3min under Argon at -78°C. After being stirred for 1.5h at -78°C, the golden yellow solution was treated dropwise over 4min with a solution of iodine (2.8g, 11.1mmol) in dry THF (20mL) and the mixture was allowed to warm slowly to room temperature overnight. The reaction mixture was cooled to 0-5°C and treated with 5% aqueous sodium thiosulfate (200mL) and CH<sub>2</sub>Cl<sub>2</sub> (200mL). The layer was separated, and the organic phase was washed again with sodium thiosulfate (200ml) and CH<sub>2</sub>Cl<sub>2</sub> (200mL). the combined aqueous portions were extracted with CH<sub>2</sub>Cl<sub>2</sub> (2×100mL) and the combined organic phase were dried with Sodium sulfate. The solvent was removed by evaporator, and then the residue was casted on silica column to afford **4**(3.2g, 80%).

<sup>1</sup>HNMR(400Mz, CDCl<sub>3</sub>): δ 7.28-7.35 (m, 2H), 7.42-7.46 (m, 3H), 7.57 (t, 1H,

$J=7.15\text{Hz}$ ), 7.9 (d, 2H,  $J=8.0\text{Hz}$ ), 8.3 (d, 1H,  $J=8.0\text{Hz}$ )

$^{13}\text{CNMR}(100\text{Mz}, \text{CDCl}_3)$ :  $\delta$  115.6, 115.8, 120.1, 124.7, 126.2, 126.9, 127.3, 19.4, 129.5, 130.2, 134.4, 137.9, 138.3.

### **3-bromo-2-iodo-1*H*-indole (5)**

A solution of NaOH (3.2g, 40mL) was added to a stirring solution of **4** (3g, 6.5mmol) in 30mL of methanol and heated to reflux at 85°C under nitrogen overnight until starting material was consumed as monitored by TLC. Methanol was removed in vacuum and product was extracted with ether(5×20mL), washed with brine, and dried over  $\text{MgSO}_4$ . Then the solvent was removed by evaporation, and then the residue was casted on silica column to afford **5** (1.9g, 92%).

$^1\text{HNMR}(400\text{Mz}, \text{CDCl}_3)$ :  $\delta$  7.81(m, 2H), 7.32 (d, 1H,  $J=6.02\text{Hz}$ ), 7.51 (d, 1H,  $J=6.48\text{Hz}$ ), 8.21 (s, 1H, N-H).

$^{13}\text{CNMR}(100\text{Mz}, \text{CDCl}_3)$ :  $\delta$  138.3, 127.8, 123.5, 121.2, 119.0, 110.7, 102.4, 80.4

EI-MS: 321 (100%).

Melting point: 85°C (decomposition).

Elemental analysis calcd (%) for **5**: C, 29.85; H, 1.57; N, 4.35 Found: C, 29.76; H, 1.49; N, 4.32.

### **3-bromo-1-hexyl-2-iodo-1*H*-indole (6)**

To a suspension of KOH (1g, 13mol) in 100mL of DMF was added 3-bromo-2-iodo-1*H*-indole (1.15g, 3.6mmol). After the solution was stirred for 1h, 1-bromopropane(1.19g, 7.2mmol) was added. The reaction mixture was then warmed to 50°C and stirred overnight. The resulting suspension was poured into water and extracted with  $\text{CH}_2\text{Cl}_2$ . The combined organic layers were washed with water, dried over anhydrous  $\text{MgSO}_4$ , and filtered. Then the solvent was removed in vacuum. The crude product was purified by column to afford **6** as colorless oil(1.3g, 92%).

<sup>1</sup>HNMR(400Mz, CDCl<sub>3</sub>): δ 0.90 (t, 3H, J=6.87Hz), 1.30-1.39 (m, 6H), 1.71-1.78(m, 2H), 4.20 (t, 2H, J=7.64Hz), 7.13-7.19 (m, 2H), 7.31 (d, 1H, J=7.97Hz), 7.52 (d, 1H, J=7.51Hz); <sup>13</sup>CNMR(100Mz,CDCl<sub>3</sub>): δ 14.14, 22.66, 26.59, 30.12, 31.58, 48.58, 88.87, 100.65, 119.23, 120.56, 122.79, 128.07, 137.21. EI-MS:405(100%), 334(100%), 320(35%).

Elemental analysis calcd (%) for **6**: C, 41.41; H, 4.22; N, 3.45 Found: C, 41.35; H, 4.30; N, 3.40.

### **3-bromo-1-hexyl-2-(phenylethynyl)-1H-indole (7)**

A mixture of **6** (1.3 g, 3.2 mmol), phenylacetylene (408 mg, 450 μL), 40 mg of (PPh<sub>3</sub>)<sub>2</sub>PdCl<sub>2</sub> and 20 mg of CuI in 30 mL of Et<sub>2</sub>NH was heated in Ar atmosphere for 13 h at 50°C up to the disappearance of **6**, then the mixture was poured into ether, washed with water, brine, and dried over anhydrous MgSO<sub>4</sub>. The solvent was removed in vacuum, and the crude product was purified by column to afford the **7** as light yellow viscous oil (1.1 g, 90%).

<sup>1</sup>HNMR(400Mz, Acetone-D<sub>6</sub>): δ 0.83 (t, 3H, J=6.8Hz), 1.27-1.41(m, 6H), 1.87-1.9 (m, 2H), 4.44 (t, 2H, J=7.2Hz), 7.21 (t, 1H, J=7.3Hz), 7.33 (t, 1H, J=7.6Hz), 7.48-7.55 (m, 5H), 7.65-7.68 (m, 2H); <sup>13</sup>CNMR(100Mz, Acetone-D<sub>6</sub>): δ 14.23, 23.21, 27.16, 30.80, 32.17, 45.90, 79.99, 96.46, 99.63, 111.30, 119.93, 121.77, 123.06, 125.13, 121.21, 129.70, 120.13, 132.25, 136.96. EI-MS: 379(100%), 308(70%), 229(70%).

Elemental analysis calcd (%) for **7**: C, 69.48; H, 5.83; N, 3.68 Found: C, 69.42; H, 5.75; N, 3.62.

### **N, N-dihexyl-3,6-diphenyl-pentaleno[1,2-b:4,5-b]diindole (IB1)**

Under nitrogen atmosphere, to the solution of **7** ( 0.9 g, 2.4 mmol) in 1,4-dioxane (10 mL) was added hydroquinone (0.6 g, 5.1 mmol), Cs<sub>2</sub>CO<sub>3</sub> (1.6 g, 4.9 mmol), CsF (0.85

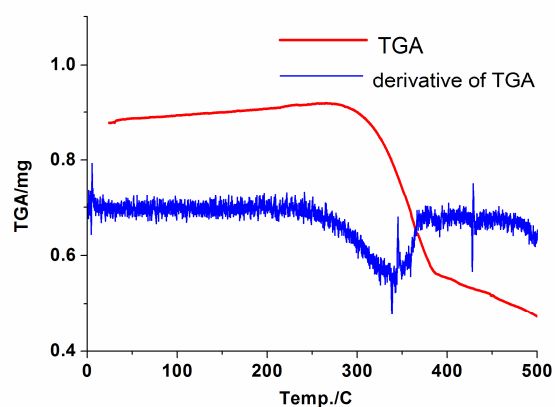
g, 5.6 mmol), and then stirred for 20 min. Subsequently,  $P^tBu_3$  (1 mL, 10% in hexane), and  $Pd_2(dba)_3$  (10.7 mg, 0.012 mmol) was added into the mixture, and the suspension was immediately heated to 130-140°C. After heating for 24 h the reaction mixture was diluted with toluene (25 mL), filtered through celite, and then evaporated to dryness to yield a deep red oil. Purification via column chromatography (hexane: dichloromethane= 5:1) on Alumina N afforded 90 mg of a dark purple solid (Crude yield 12%). MALDI-TOF: 600.5. Melting Point: 185-187 °C.

$^1H$ NMR(400Mz, Acetone-D6):  $\delta$  0.69-0.73 (m 4H), 0.83 (t, 6H,  $J=8$ Hz), 1.0-1.05 (m 4H), 1.07-1.11 (m, 4H), 1.14-1.18 (m, 4H), 3.28 (t, 4H,  $J=8$ Hz), 6.45 (m, 2H), 6.55 (m, 4H), 6.77 (d, 2H,  $J=8$ Hz), 7.49-7.54 (m, 10H)

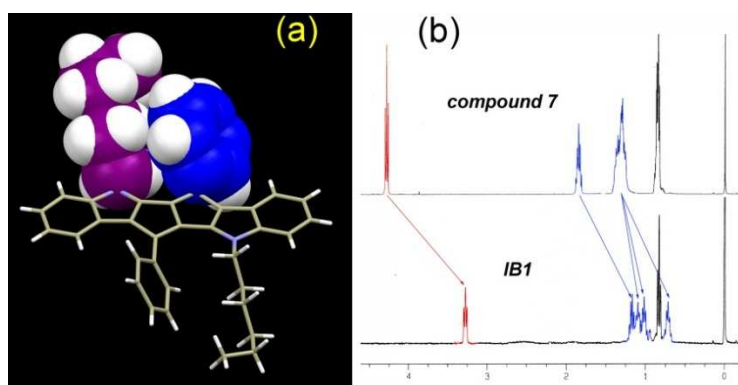
$^{13}C$ NMR(100Mz, Acetone-D6):  $\delta$  0.61, 13.48, 22.4, 25.76, 31.35, 45.04, 127.73, 128.35, 129.43, 129.78.

Elemental analysis calcd (%) for **IB1**: C, 87.96; H, 7.38; N, 4.66 Found: C, 87.79; H, 7.33; N, 4.64.

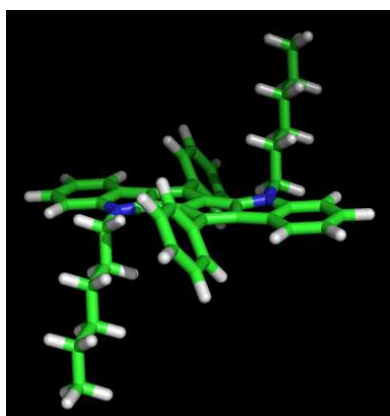
### §3. Figures and data



**Figure S1.** TGA (red) and its derivative data of **IB1**.



**Figure S2.** (a) Crystal structure shows the interaction between benzene and alkyl chain; (b) NMR changes from **7** to **IB1** (<sup>1</sup>H-NMR, Bruker 400MHz).



**Figure S3.** Fully optimized structure of **IB1** by Gaussian 03 B3LYP/6-31+G\*

**Table S1.** Experimental and calculated bond lengths of **IB1**

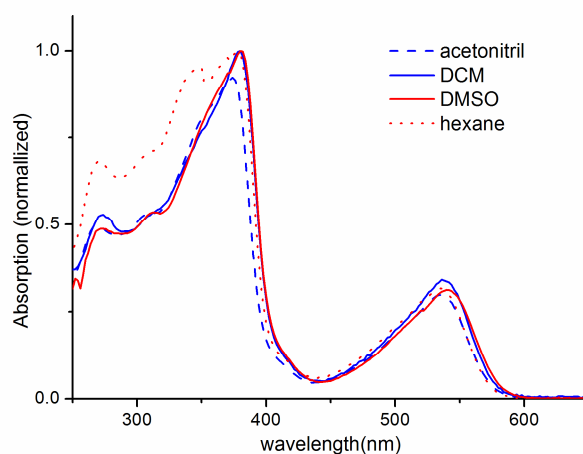
Bond	X-ray	DFT-cal*	Bond	X-ray	DFT-cal*
C1-C2	1.398	1.403	C3-C6	1.436	1.436
C1-C1A	1.46	1.46	C5-C6	1.421	1.43
C2-C3	1.442	1.441	C5-N1	1.403	1.409
C3-C4	1.405	1.412	C4-N1	1.368	1.367
C1A-C4	1.443	1.446	Benzene(avg)	1.396	1.403

\* Performed using Gaussian 03 at the B3LYP/6-31+G\* level of theory.

**Table S2.** NICS values of different position over the **IB1**

	a*	b*	c*
NICS(5) <sup>§</sup>	-0.1	0.29	0.6
NICS(4) <sup>§</sup>	-0.4	0.39	1.3
NICS(3) <sup>§</sup>	-1.1	0.43	3
NICS(2) <sup>§</sup>	-3.3	-0.39	8
NICS(1) <sup>§</sup>	-8.2	-3.3	23
NICS(0) <sup>§</sup>	-7.8	-3.1	28

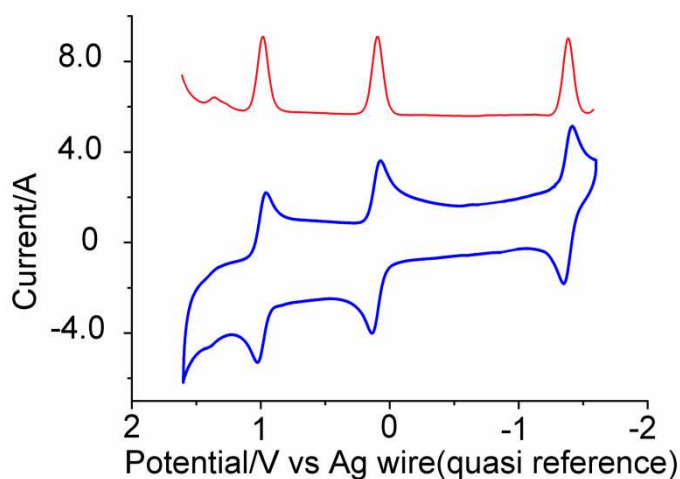
\* a: benzene of indole, b: pyrrole of indole, c: pentalene. §: NICS(n) means the point we calculated at n Å over the a/b/c perpendicularly.

**Figure S4.** UV-Vis spectra of **IB1** in different solvents



**Table S3.** Absorption wavelengths and oscillator strength of **IB1** evaluated by the TD-DFT (B3LYP/6-31+G\*) calculation

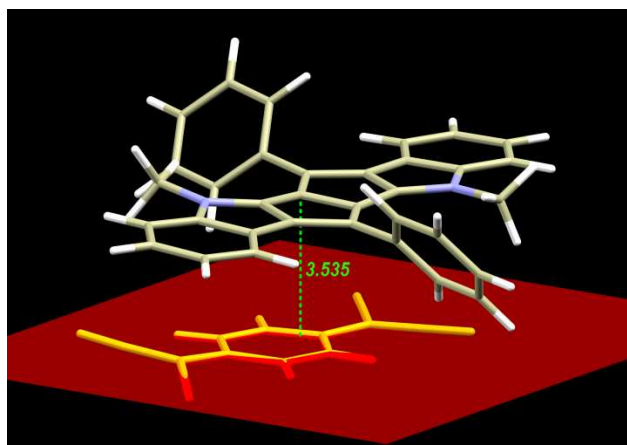
Excitation energies	Absorption[nm] (oscillator strength)	Assignments (%)
0.99 eV	1248.29 (0.00)	HOMO→LUMO (67)
2.37 eV	523.69 (0.21)	HOMO-1→LUMO (62)
3.21 eV	386.43 (0.22)	HOMO→LUMO+1 (62)
3.54 eV	350.20 (0.26)	HOMO-4→LUMO (65)
3.77 eV	328.67 (0.82)	HOMO→LUMO+5 (62) HOMO→LUMO+1 (16)



**Figure S5.** Cyclic voltammograms and differential pulse voltammograms of **IB1** in 0.1 M  $n\text{Bu}_4\text{NPF}_6/\text{CH}_2\text{Cl}_2$ . Reference electrode: Ag wire; working electrode: glassy carbon; counter electrode: Pt. <sup>[a]</sup> Half-wave potentials versus  $\text{Fc}^+/\text{Fc}$ .  $E_{\text{Fc}^+/\text{Fc}}^{1/2} = 0.37 \text{ V}$ .

**Table S4.** Data of cyclic voltammetry experiment of **IB1** (versus  $\text{Fc}^+/\text{Fc}$ )

	$E_{\text{IB}^{2+}/\text{IB}^+}$	$E_{\text{IB}^+/\text{IB}}$	$E_{\text{IB}/\text{IB}^-}$
$E_{1/2}$	0.61V <sup>[a]</sup>	-0.27V <sup>[a]</sup>	-1.76V <sup>[a]</sup>
$\Delta E_p(E_{pa}-E_{pc})$	66mV	61mV	70mV



**Figure S4.** The structure of [IB][TCNQ] optimized by Gaussian 03 at B3LYP/6-31+G\* level.

**Table S5.** Crystal data for **IB1**

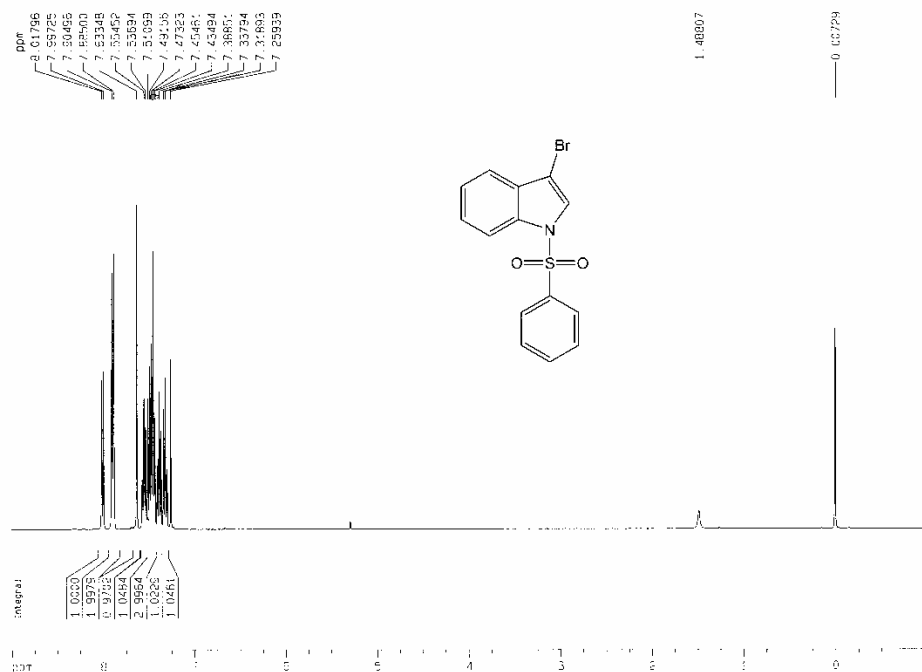
Compound	<b>IB1</b>
Formula	C <sub>44</sub> H <sub>44</sub> N <sub>2</sub>
Formular weight	600.81
T/K	173(2)
Crystal system, space group	Monoclinic, P2(1)/c
<i>a</i> , Å	5.4753(11)
<i>b</i> , Å	22.659(5)
<i>c</i> , Å	13.406(3)
$\alpha$ , deg	90
$\beta$ , deg	96.93(3)
$\gamma$ , deg	90
Volume, Å <sup>3</sup>	1651.0(6)
Z	2
Calculated density, g/cm <sup>3</sup>	1.209
Absorption coefficient, mm <sup>-1</sup>	0.069
F(000)	644
Crystal size, mm	0.40 × 0.34 × 0.31
$\theta$ range, deg	3.06 to 27.48
Reflections collected / unique	7941/3831
Absorption correction	Semi-empirical from equivalents
Data/restraints/parameters	3831/1/425
Goodness-of-fit on $F^2$	1.054
Final <i>R</i> indices [ $I > 2\sigma(I)$ ]	$R1 = 0.0503$ , $wR2 = 0.1148$
<i>R</i> indices (all data)	$R1 = 0.0550$ , $wR2 = 0.1188$
Largest diff. peak and hole, e/Å <sup>3</sup>	0.212 and -0.185

**Table S6.** Absorption wavelengths and oscillator strength of **IB1 radical cation** evaluated by the TD-DFT (UB3LYP/6-31+G\*) calculation

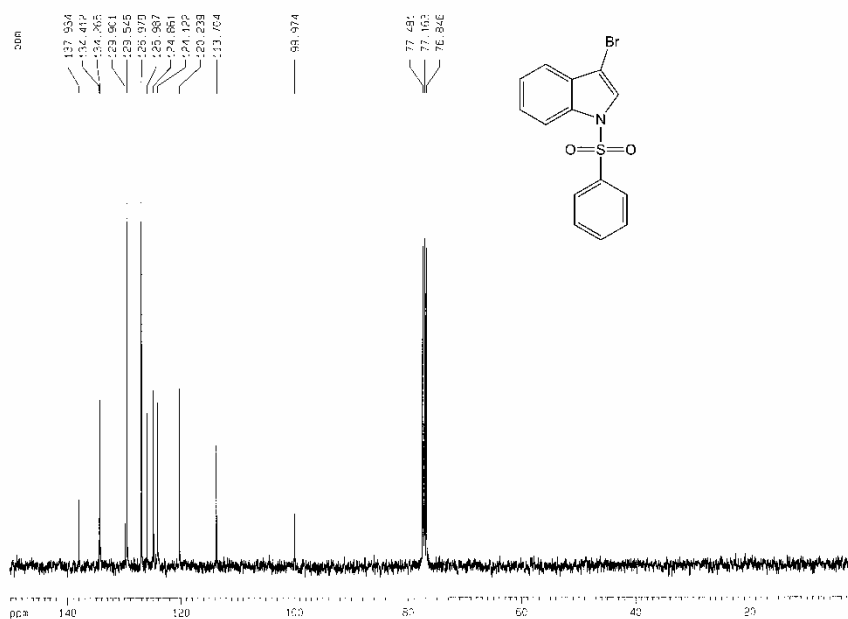
Excitation energies	Absorption[nm] (oscillator strength)	Assignments (%)
1.73 eV	716.09 (0.05)	159B→161B (90)
2.38 eV	519.81 (0.12)	159B→162B (77) 161A→163A (11)
2.59 eV	477.9 (0.46)	160A→162A (51) 159B→162B (38)
3.09 eV	400.54 (0.28)	158A→162A (70) 157B→162B(29)

## § 4. NMR data

### <sup>1</sup>HNMR of 3



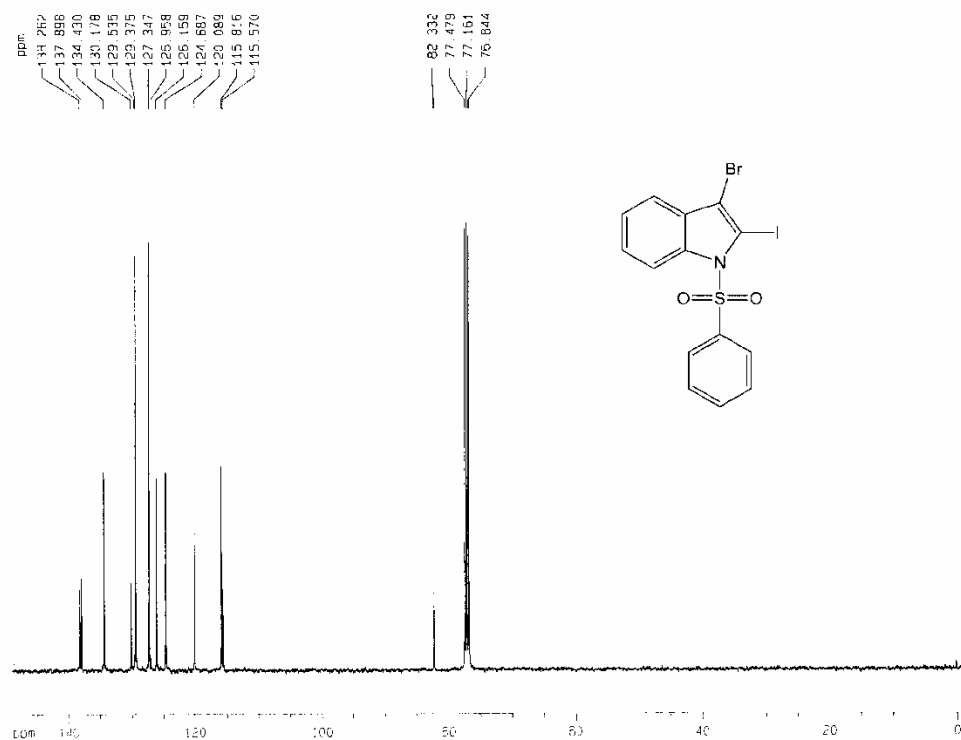
### <sup>13</sup>CNMR of 3



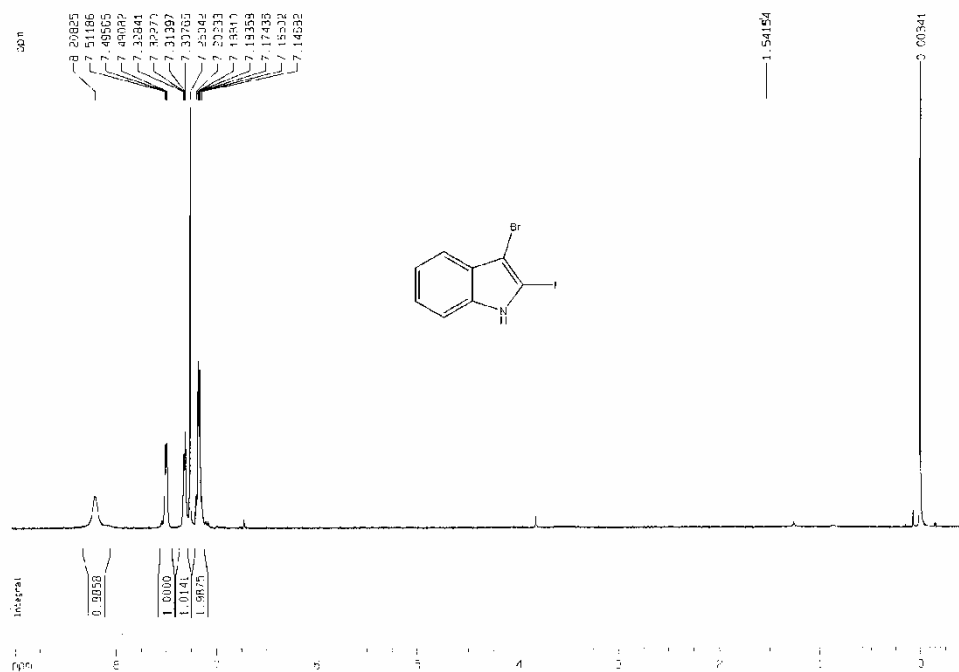
# <sup>1</sup>HNMR of 4

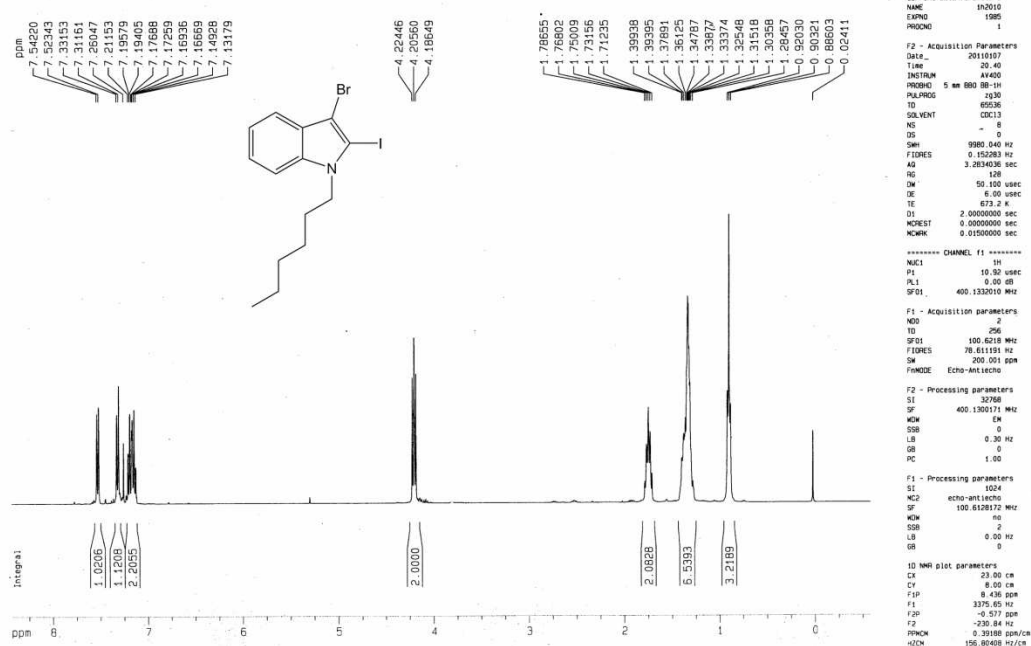


# <sup>13</sup>CNMR of 4

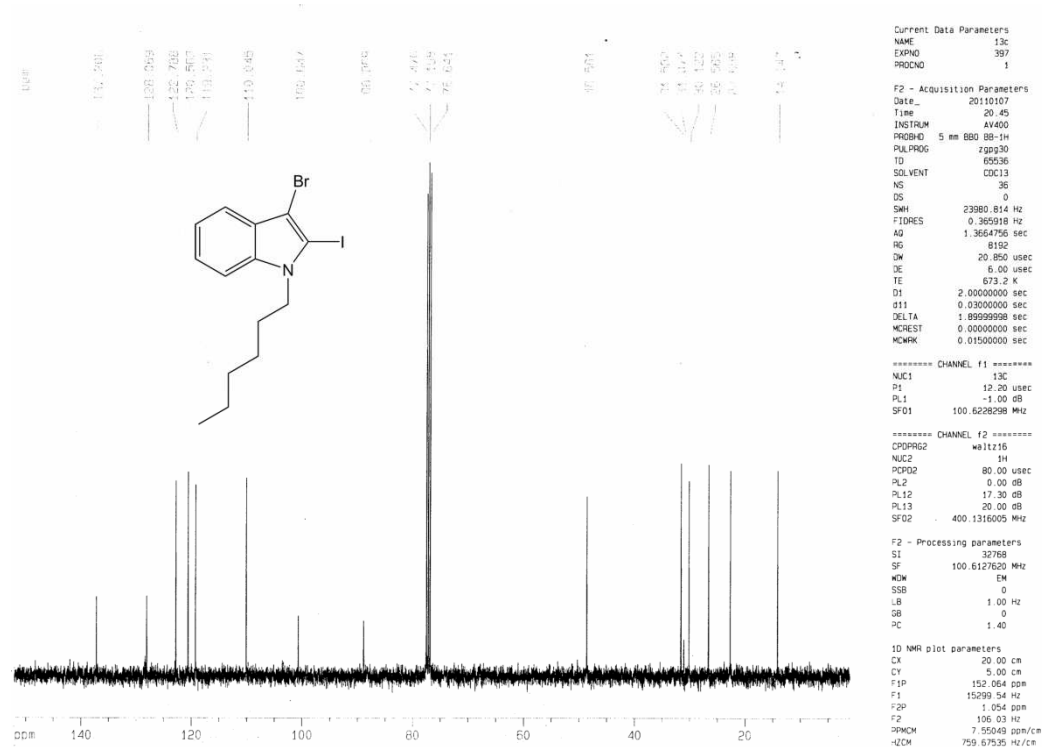


# <sup>1</sup>HNMR of 5





## <sup>13</sup>CNMR of 6

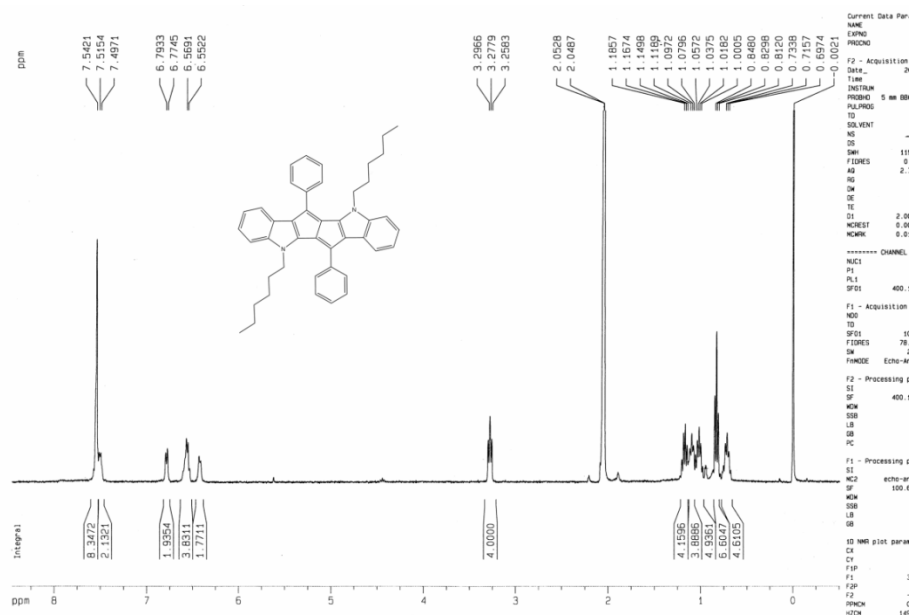


## <sup>1</sup>HNMR of 7

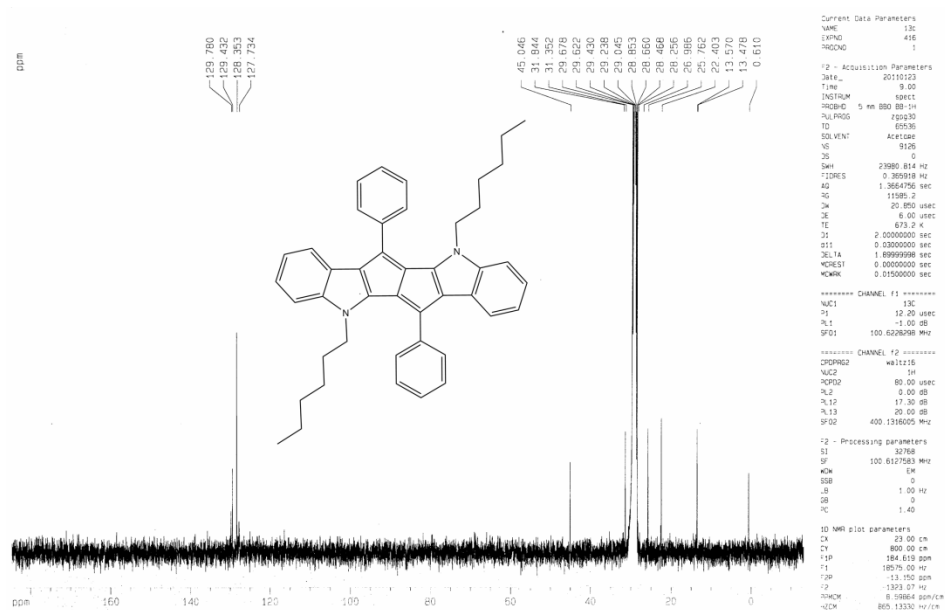




## <sup>1</sup>HNMR of IB1



## <sup>13</sup>CNMR of IB1



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