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Research paper

Synthesis and Surface Morphology of The Precursors of the N-Alkylated Isoindigo

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Abstract

Isoindigo has been longly applied as the dying agent and recently introduced as an electron accepting unit of the conjugated polymers. For the later purpose, the isoindigo was generally alkylated before undergone polymerization. The purity, chemical structure, and the surface morphology of the alkylated isoindigo and its precursors was confirmed and studied through the thin layer chromatography, FTIR, NMR and SEM. Based on the micrograms, the straw-liked regular structure of oxindole has been transformed into irregular box-shaped isoindigo when two oxindole were coupled with each other at the particular position.

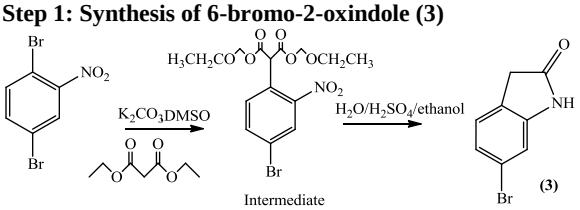
Keywords: *Alkylation, isoindigo, oxindole*

1. Introduction

Energy highly needs as most of industries and domestic usage constantly operating with aid of energy. However, recently these fact initiate worries in worldwide consumers as energy came from fossil fuel reduced in amount [1]. Hence, massive debate and multiple studies conducted to address these issue for the purpose to sustain continuous supply of energy which more eco-friendly and cost-efficient. It was rapidly realized that such solar cells were a convenient way of generating power in remote locations example for powering communications equipment or weather monitoring stations and ideal for supplying power for the satellites and vehicles being developed for the rapidly expanding space industry [2].
Science and technologies advanced rapidly over years bring about the optimization of a range of organic-based solid state devices such organic light emitting diodes, field-effect transistors photodiodes, photo detectors, non-volatile memory including solar and photovoltaic cells [3]. Polymers solar cell dominantly became academia and researcher's choice for innovation of new-types of conjugated backbone systems as it satisfy criteria include proper band gaps for purpose of effective absorption of solar energy [4], low-lying highest occupied molecular orbital energy levels for a high open circuit voltage (V_{oc}) value [5] and strong $\pi-\pi$ stacking for excellent charge carrier mobility [4]. In particular, organic solar cells or known as organic photovoltaic have the potential for harnessing low-cost solar energy due to their advantages in materials and manufacturing processes [6].
Organic semiconductors development for organic photovoltaic (OPV) applications has advanced rapidly in these recent years. In polymer-based photovoltaic devices, photoactive layer between two conducting electrodes composed of a blend of an electron-donor (p-type conjugated polymer) and electron-acceptor (n-type polymer) and which has been the widely used configuration of polymer-based solar cells. A push–pull strategy are typically used to design polymeric electron donor materials where electron-rich and electron-deficient π conjugated motifs alternate along the polymer backbone, where molecular orbital hybridization results in a narrow band gap material with excellent spectral overlap with the solar spectrum [7].
The isoindigo core was recently introduced as an acceptor unit for designing molecular and polymeric semiconductors for applications in organic electronic. Isoindigo along with indigo and indirubin is a representative of indigoid bis-indoles which in the last decade have attracted great attention as pharmaceuticals and as the components of functional material. Heeger's group was the first to report the use of isoindigo in Optical Solar Cell (OSC) to isoindigo acceptor [8]. High photophysical data short current (J_{sc}), open-circuit voltage (V_{oc}), fill-factor (FF) and power conversion efficiency (PCE) show that isoindigo is perspective acceptor group for photovoltaics application. With electron-deficient character and outstanding absorption property, isoindigo has become an important monomer for the synthesis of conjugated polymers [9]. In this work, the target compound is N-alkylated dibromoisoindigo and interested to outcome the surface morphology of the oxindole before and after the aldol dimerization reaction.

2. Materials and methods

Step 1: Synthesis of 6-bromo-2-oxindole (3)

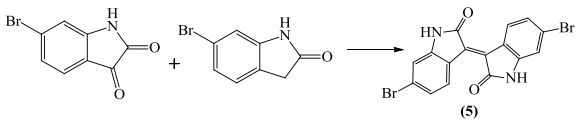


Scheme 1: Preparation of 6-bromo-2-oxindole **(3)**.

Commercially available 2, 5-dibromonitrobenzene is an alternative to synthesis sufficient amount oxindole since the cost of small amount of compound 6-bromo-2-oxindole is quite high. First, dibromonitrobenzene (16.86 g, 60 mmol) and potassium carbonate anhydrous (82.93 g, 600 mmol) added together with 89.89 mL of dry dimethyl sulfoxide (DMSO) under nitrogen atmosphere. After

that, the reaction heated up to 50ºC .In mean time, set of solution mixture prepared by placing diethylmalonate (48.05 g; 300 mmol) into 44.94 mL of DMSO after which this solution mixture will be added dropwise into the heated reaction mixture for more than an hour. The reaction allowed to react for 18 h. The collected organic phase then wash with distilled water and light yellow oil mixture. This mixture contained diethyl-2-(4-bromo-2-nitrophenyl) malonate and diethyl malonate. This mixture then will be dissolved in another prepared solution mixture that contain water (110 mL), sulphuric acid (110 mL), and ethanol (330 mL) in ratio 1:1:3 after which the mixture heated under reflux.
During reflux, zinc powder (39.24 g, 600 mmol) added slowly into the mixture. After that, the reaction mixture continued to reflux for an hour after which another batch of zinc powder with same amount again added slowly. The mixture left to react for another 2 hours and the product obtained furthered mixed into 1.5 L of distilled water. The solution product that left overnight for crystallization then filtered and white solid material obtained washed with distilled water [10]. The final product, i.e. pure 6-bromooxindole tested both physical and chemical characterization.

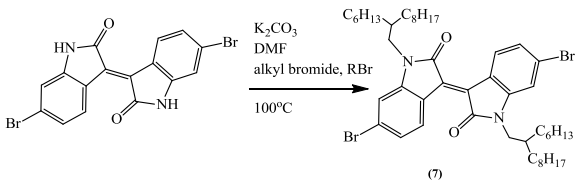
Step 2 Synthesis of 6, 6'-dibromoisoindigo (5)



Scheme 2: Preparation of 6, 6'-dibromoisoindigo **(5)**.

The pioneers of the 6, 6'-dibromoisoindigo stated that the precursors of this aldol condensation reaction are isatin and oxindole .According to [11] both commercially available 6-bromoisatin (or IUPAC name: 6-bromo-1H-indole-2,3-dione) and 6-bromo-2-oxindole were undergo acid-catalyzed aldol reaction and followed by dehydration to obtain brown 6,6'-dibromoisoindigo in c.a. 95% quantitative yield.
First, 6-bromoisatin (226 mg, 1.0 mmol) and 6-bromooxindole (212 mg, 1.0 mmol) added together into 8mL glacial acetic acid. After that, 0.05 mL of 37% concentrated HCl solution (12 M) added as acid catalyst to suspense both isatin and oxindole in acetic acid.The mixture then heated under reflux for 24 hours in the temperature range of 100 ºC -120 ºC [12] and need to be cool at room temperature. The cooled mixture filtered and washed with water, ethanol (EtOH) and ethyl acetate (AcEt) successionally. Next, solid product dried in vacuum oven. The product formed was deep red solid in colour compound. The final compound must be analyzed through both physical and chemical characterization.

Step 3 Synthesis of 6, 6'-dibromo-N, N'-(2-hexyldecyl)-isoindigo (7)



Scheme 3: Preparation of 6, 6'-dibromo-N, N'(2-hexyldecyl)-isoindigo (7).

The *N, N'*-alkylation of 6, 6'-dibromoisoindigo under basic condition began when 6,6'-bromoisoindigo (350 mg, 0.83 mmol) synthesized from the previous step add together with anhydrous potassium carbonate, K_2CO_3 (691 mg, 5 mmol) and 30 mL of N,N-dimethylmethanamide (DMF) into a three neck round bottom flask. Purpose of K_2CO_3 in DMF to act as base for the heterogenous reaction [12].
Next, the nitrogen supply connected and the nitrogen gas allowed to flow in and out of the round bottom flask. 1-bromo-2-hexyldecane (559 mg, 1.83 mmol) added into the mixture through a spectrum under nitrogen atmosphere. The mixture reflux at 100 ºC and stirred for 24 hours [13]. The reaction mixture cooled to room temperature and the three neck round bottom flask removed from the reflux condenser under reduced pressure [13-14]. The mixture then transferred into a separating funnel and 200 mL distilled water added into the reaction mixture. The reaction mixture further extracted with dichloromethane, CH_2Cl_2 for three times.
The extracted organic layers then combine together and washed with brine followed by dry over anhydrous $MgSO_4$. Finally, deep - red residue purified through silica gel column chromatography which eluted by CH_2Cl_2: Hexane with 1:1 by volume to give the 6, 6'-dibromo-N, N'-(2-hexyldecyl)-isoindigo (c.a. 456 mg, ϒ-85 %) [10-11][14].

3. Results and discussion

The melting point and the yield percent of the synthesized compounds were tabulated in the **Table 1**. The functional groups of the synthesized compounds were identified through the Fourier Transform Infra-Red (FTIR) and their chemical structures were further confirmed through Nuclear Magnetic Resonance (NMR).
The surface morphology of the solid products of oxindole **(3)** and isoindigo **(5)** were studied through Scanning Electron Microscope (SEM). The obtained FTIR, NMR data and SEM micrograms are listed in this section while the FTIR and NMR spectra are attached in the supplementary data of this article.

Melting Point and Yield

Table 1: The melting point and percentage of yield for the synthesized compounds.

Compounds	Melting Point (ºC)	Yield (%)
6-bromo-2-oxindole **(3)**	217-221	71
6, 6'-dibromoisoindigo **(5)**	>360	89
6, 6'-dibromo-N, N'-(2-hexyldecyl)-isoindigo **(7)**	49-52	82

Fourier Transform Infra-red (FTIR)

*6-bromo-2-oxindole **(3)***
3108, 3030, 2836, 1694, 1614, 1485, 1459, 1379, 1331, 1302, 1254, 1234, 1203, 1113, 1053, 922, 875, 844, 814, 780, 682, 588, 559, 516.

*6, 6'-dibromoisoindigo **(5)***
3113, 3031, 1685, 1607, 1451, 1319, 1255, 1196, 1124, 1065, 883, 848, 814, 774, 729, 685, 599, 589, 524.

*6, 6'-dibromo-N, N'-(2-hexyldecyl)-isoindigo **(7)***
2923, 2854, 1732, 1596, 1535, 1465, 1351, 1224, 1176, 1112, 1066, 872, 840, 815, 723, 643, 589, 507, 458.

Nuclear Magnetic Resonance (NMR)

*6-bromo-2-oxindole **(3)***
^{1}H-NMR (600 MHz, CD_3CN, ppm) δ 8.58 (s, N-H, 1H), 7.09 (s, 1H), 7.00 (s, 1H), 5.42 (s, 1H), 3.36 (s, 2H). **^{13}C-NMR** (125 MHz, CD_3CN, ppm) δ 176.29 (1C), 144.96 (1C), 126.13 (1C), 125.29 (1C), 124.30 (1C), 120.36 (1C), 112.33 (1C), 35.24 (1C)

*6, 6'-dibromoisoindigo **(5)***
^{1}H-NMR (500 MHz, DMSO-d_6, ppm) δ 11.10 (s, 2H), 8.99 (d, J= 8.65 Hz, 2H), 7.19 (dd, J_1=8.65Hz, J_2=2.0 Hz, 2H), 7.00 (d, J=1.95 Hz, 2H).
^{13}C-NMR (125 MHz, DMSO-d_6, ppm) δ 174.06 (2C), 150.73 (2C), 137.88 (2C), 136.14 (2C), 130.93 (2C), 129.21 (2C), 125.97 (2C), 117.59 (2C)

6, 6'-dibromo-N, N'-(2-hexyldecyl)-isoindigo ***(7)***

^{1}H-NMR (600 MHz, $CDCl_3$, ppm) δ 9.10 (d, J= 8.94 Hz, 2H), 7.20(d, J= 8.28 Hz, 2H), 6.94 (s, 2H), 3.66 (d, J= 7.56 Hz, 4H), 1.91 (sp, J= 5.52 Hz, 2H), 1.65 (s, 8H), 1.20-1.45 (m, 40H), 0.90 (m, 12H).

^{13}C-NMR (125 MHz, $CDCl_3$, ppm) δ 168.23 (2C), 146.29 (2C), 132.71 (2C), 131.08 (2C), 126.77 (2C), 125.21 (2C), 120.47 (2C), 111.67 (2C), 44.76 (2C), 36.16 (2C), 31.96 (2C), 31.89 (2C), 31.54 (4C), 30.06 (2C), 29.74 (2C), 29.64 (2C), 29.39 (2C), 26.43 (2C), 26.40 (2C), 22.76 (2C), 22.73 (2C), 14.22 (2C), 14.19 (2C).

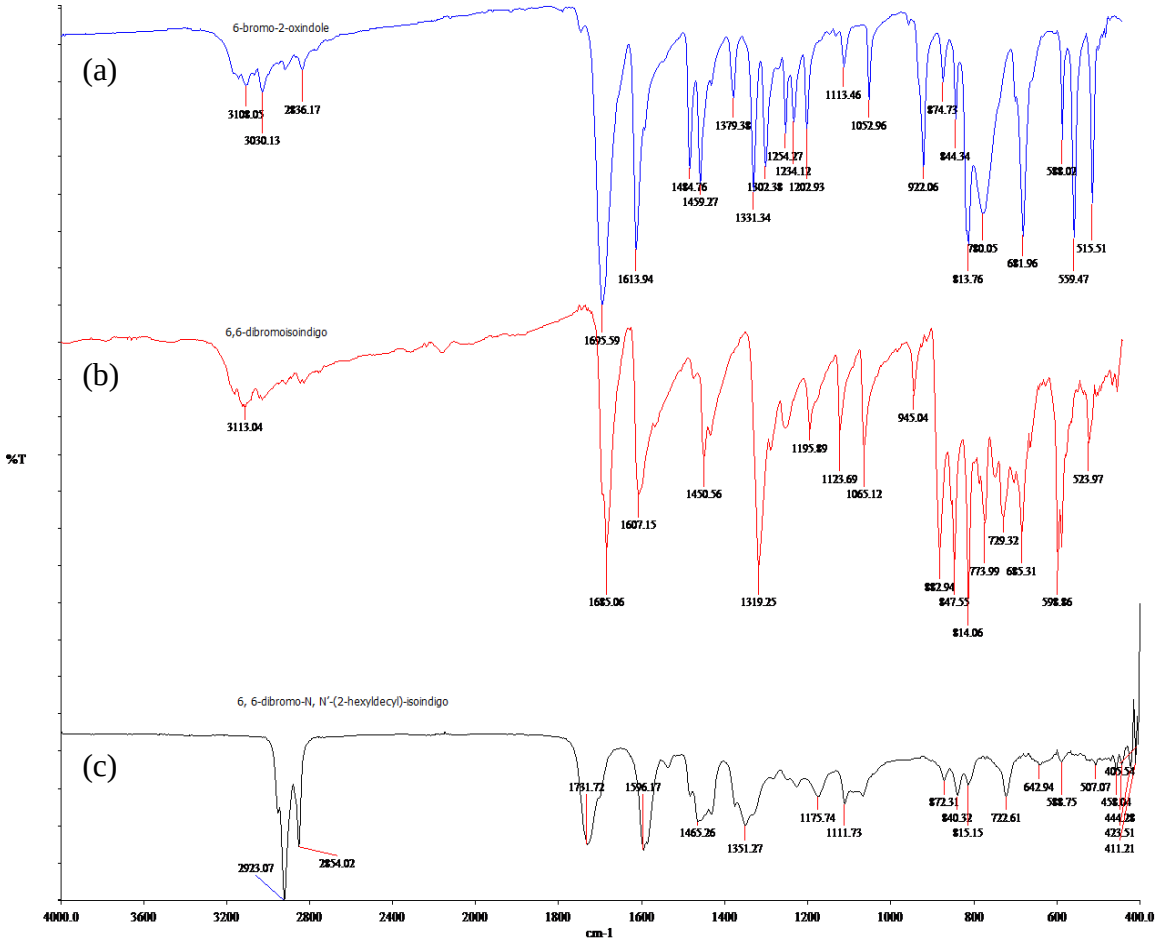


Figure 1. The FTIR spectra of compounds (a) *6-bromo-2-oxindole*, (b) *6, 6'-dibromoisoindigo*, and (c) *6, 6'-dibromo-N, N'-(2-hexyldecyl)-isoindigo*.

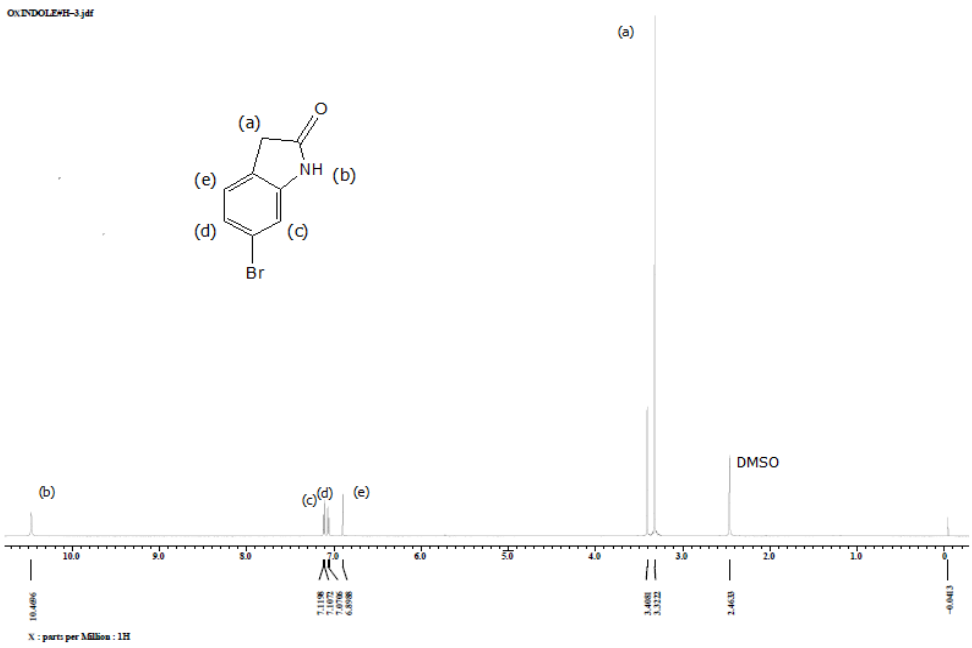


Figure 2: The ^{1}H-NMR spectrum of 6-bromo-2-oxindole **(3)**.

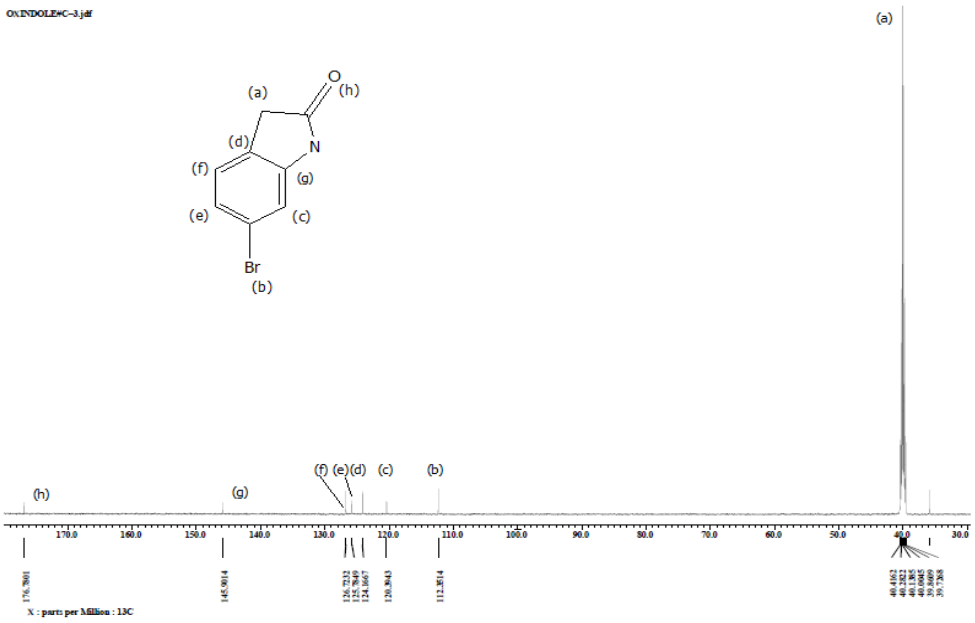


Figure 3: The ^{13}C-NMR spectrum of 6-bromo-2-oxindole **(3).**

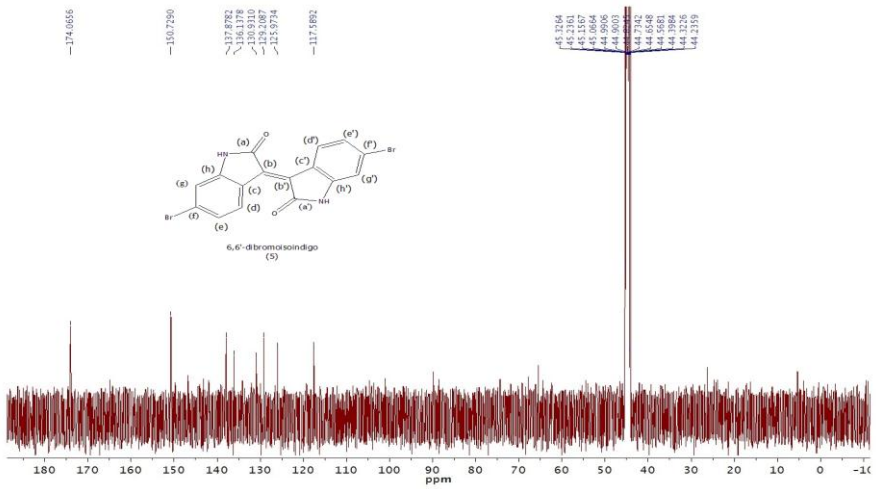


Figure 4: The ^{1}H-NMR spectrum of 6,6'-dibromoisoindigo **(5).**

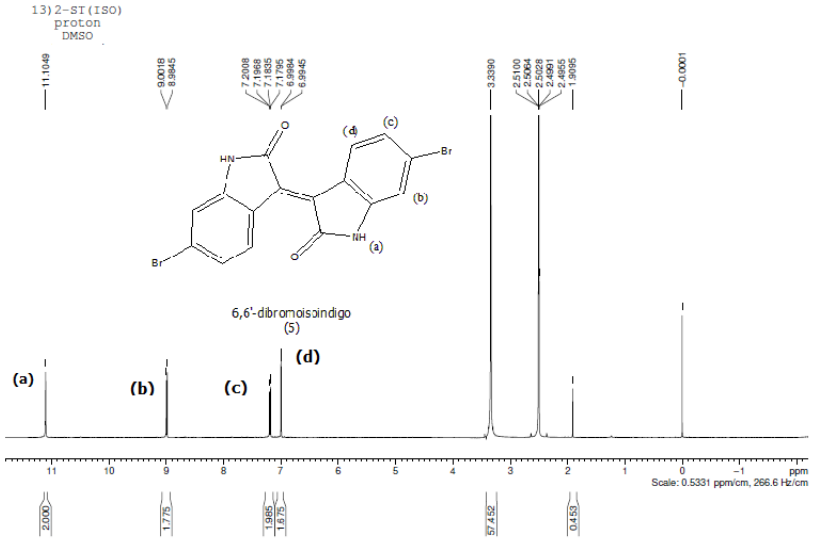


Figure 5: The ^{13}C-NMR spectrum of 6,6'-dibromoisoindigo **(5)**.

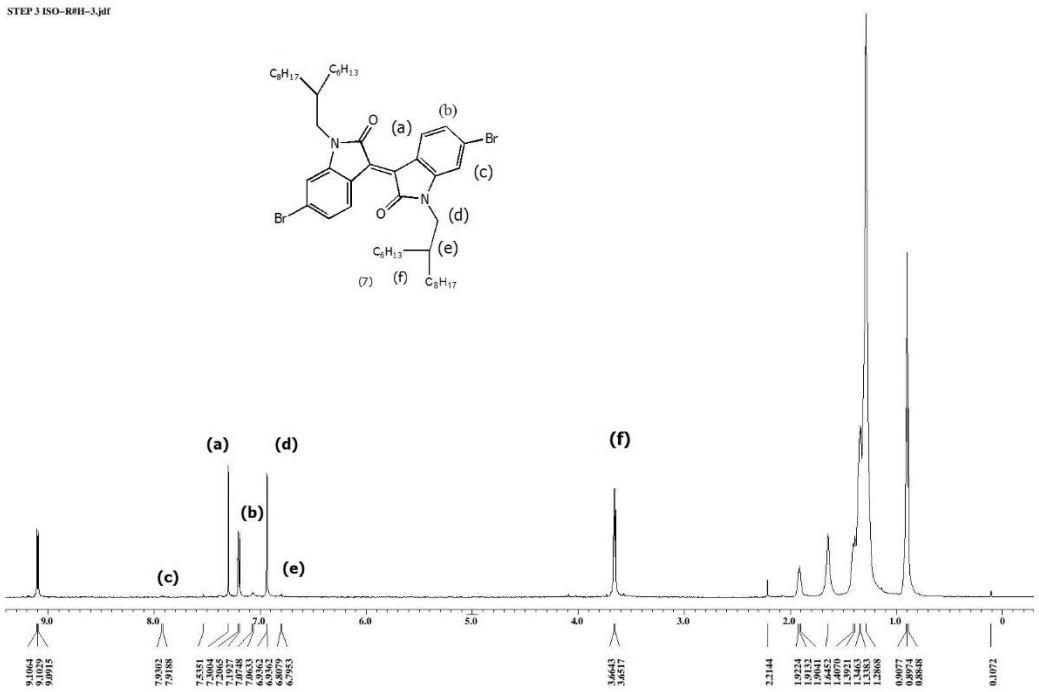


Figure 6: The ^{1}H-NMR spectrum of 6, 6'-dibromo-N, N'-(2-hexyldecyl)-isoindigo **(7)**.

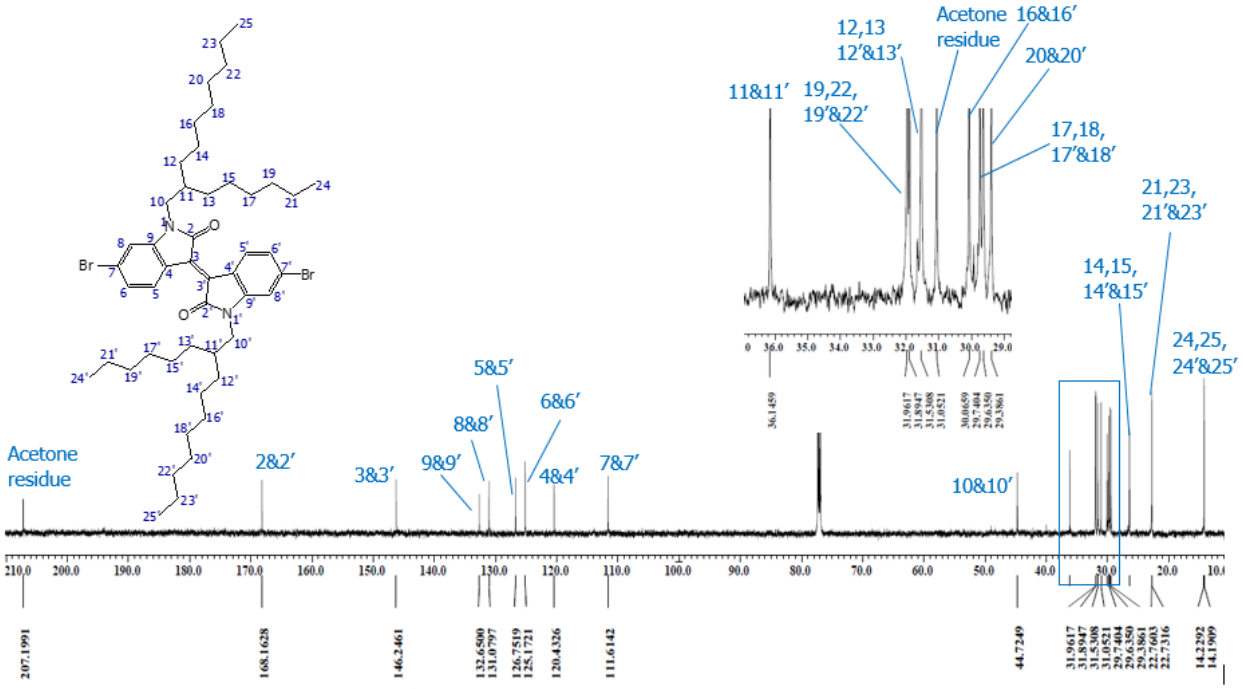


Figure 7: The ^{13}C-NMR spectrum of 6, 6'-dibromo-N, N'-(2-hexyldecyl)-isoindigo (7).

Scanning Electron Microscope (SEM)

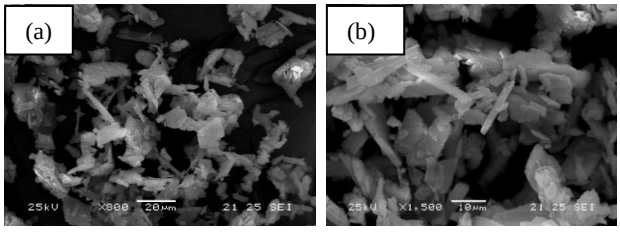


Figure 8: The SEM micrographs of 6-bromo-2-oxindole **(3)** in magnification (a) 800 X; (b) 1500 X.

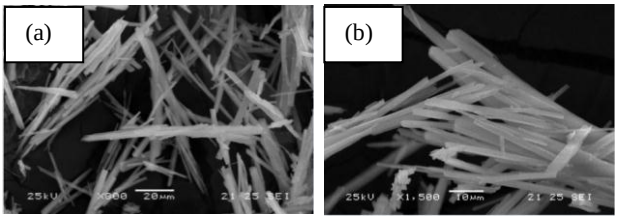


Figure 9: The SEM micrographs of 6,6'-dibromoisoindigo **(5)** in magnification (a) 800 X; (b) 1500 X.

4. Conclusion

The targeted N-alkylated dibromoisoindigo has been successfully synthesized from the 2,5-dibromonitrobenzene. An interesting outcome of this work is the surface morphology of the oxindole before and after the aldol dimerization.

Acknowledgement

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