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Assessment on Heck-Immine Derivatives as Organic Semiconductor Materials

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Abstract

This paper reports the synthetic, characterization and theoretical evaluation of new class of hybrid Heck-immine system involving mixed moieties of vinylene (C=C) and azomethines (CH=N) which has been successfully integrated into an addition of organic semiconducting materials. The assessment of 4-[(hexyloxyphenyl)methylene]amino)-4'-chlorostilbene (**HEXCS**) based on Donor (D)- π -Acceptor (A) was evaluated as active semiconductor material candidates via several spectroscopic and analytical techniques. In turn, the investigation of its potential as dopant system in conductive film was successfully deposited on indium tin oxide (ITO) coated substrate via spin coating method. The relationship between electronic and optical properties, chemical modelling at molecular interactions and electrical performances of the designated system were evaluated. In addition, the quantum mechanical calculation proved that the value of energy separation of **HEXCS** between HOMO and LUMO exhibits 3.09 eV which was in good agreement with the experimental result of optical band gap 3.10 eV. The findings from the thermal and conductivity analysis revealed that the developed film **HEXCS** exhibited good stability at high temperature and electrical performance with an increasing conductivity up to 0.1531 Scm⁻¹ under maximum light intensity of 100 Wm⁻². Therefore, this proposed type of molecular framework has given an ideal indication to act as semiconductor material candidates potentially use in any designated electronic application.

Abstract

Penilaian Turunan Heck-Immine sebagai Material Organik Semikonduktor. Penelitian ini melaporkan tentang kajian sintetik, karakterisasi dan evaluasi teoritis bagi kelas baru dari sistem hibrid Heck-imina yang melibatkan perpaduan unsur vinilen (C=C) dan azometina (CH=N) yang telah berhasil diintegrasikan sebagai bahan tambahan pada material semikonduktor organik. Penilaian 4-[(heksiloksifenil)metilena]amino)-4'-kloro-stilben (HEXCS) berdasarkan donor (D)- π -penerima (A) dievaluasi sebagai kandidat bahan semikonduktor aktif melalui beberapa teknik spektroskopi dan analitis. Selanjutnya, penelitian mengenai potensinya sebagai sistem dopan pada film konduktif, HEXCS berhasil diendapkan pada substrat yang dilapisi *indium tin oksida* (ITO) melalui metode *spin coating*. Hubungan antara sifat elektronik dan optik, pemodelan kimia pada interaksi molekuler dan kinerja elektrik dari sistem ini juga telah dievaluasi. Sebagai tambahan, perhitungan mekanikal kuantum membuktikan bahawa nilai pemisahan energi **HEXCS** di antara HOMO dan LUMO adalah 3.09 eV, dimana nilai tersebut mendekati nilai eksperimen dengan nilai 3.10 eV. Temuan dari analisis termal dan konduktivitas menunjukkan bahawa film **HEXCS** yang dikembangkan menunjukkan stabilitas yang baik pada suhu tinggi dan kinerja elektrik yang baik dengan peningkatan nilai konduktivitas 0.1531 Scm⁻¹ menggunakan intensitas cahaya maksimum sebesar 100 Wm⁻². Oleh karena itu, kerangka molekul yang diusulkan ini ideal digunakan sebagai kandidat material semikonduktor yang berpotensi digunakan dalam berbagai aplikasi elektronik.

Keywords: bandgap, conductivity, heck-immine, semiconductor

1. Introduction

The research on organic semiconductor materials has been arousing continuous attention for decades due to their unique characteristics and potential towards low cost of production, lightness, mechanical flexibility and chemical versatility [1]-[3]. It is widely known that these promising systems have opened wide range opportunities in molecular electronics such as organic photovoltaic (OPVs), organic light emitting diode (OLEDs) and organic field effect transistors (OFETs) [4]-[6]. The chemistry of these active materials offers extensive electronic delocalization in π -orbital system and contains fair number of alternating single and double bonds which the electron can easily flow from one reservoir to another that resulted into the effective properties of electrical conductivity. Within this concern, exploitation of organic semiconducting materials based on electron push and pull structure (also called donor-acceptor (D-A) have been rapidly developed to finely tune the energy level, solubility and planarity in optimizing the efficiencies of these systems in optoelectronic devices [7]-[9]. Nevertheless, the quest on designing ideal molecular system with simple processing techniques as photoactive layer in organic electronic devices that possess high conjugated and multi donor sites framework system is big challenging.

Therefore, building a fundamental understanding of the material properties, structure-function relationships and device performance parameters are the key requirements in the progress of designing new materials for organic electronics [10]-[12]. By inserting the electron donation and withdrawing groups in the molecule itself, the molecules are becoming more efficient because the electrons can be generated in-situ on the conjugated system. In addition, the correlations between chemical modeling, physical alteration and synthesis, it is possible to modulate the required electronic and mechanical properties of these molecules.

Regarding this matter, in the present research, the effort is given on an extensive study of new class of hydrid Heck-immine system namely4-[(hexyloxyphenyl) methylene]amino)-4'-chloro-stilbene (HEXCS) as organic semiconducting material candidates to be applied as active layer in conductive film as shown in Figure 1. Considering their versatile properties such as having delocalized ground state electronic structure with extensive π -conjugation system and relatively high thermal stabilities are anticipated to transform into new semiconductor materials in this work. Additionally, Heckimmine system has turned out to be a great candidate to construct D-A molecular wire compounds, which can act as excellent transporters. Thus, they can act as the simplest electronic component for the conduction of current along its molecular backbone. Therefore, the devotions of this contribution has been actively focused on the design, synthesis and investigation on its electronic and optical properties, including HOMO-LUMO energy gaps of π -conjugated systems of new Heck-immine derivative in order to evaluate how

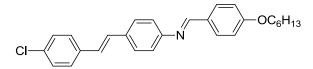


Figure 1. Molecular Structure of 4-[(hexyloxyphenyl) methylene]amino)-4'-chloro-stilbene (HEXCS)

2. Experimental

purification and the reactions were carried out under an ambient atmosphere and no special attention was taken to exclude air or moisture during experimental work-up. The infrared (IR) spectra were recorded on Perkin Elmer Spectrum 100 Fourier Transform Infrared Spectrometer by using potassium bromide (KBr) pellets, or from neat liquids in the spectral range of 4000-400 cm⁻¹. The UV-Vis spectra were recorded using a Shidmadzu UV-1800 UV-Vis spectrophotometer in 1 cm path length quartz cell with dichloromethane solution with concentration of 1×10^{-5} M in the spectral range of 200-500 nm. NMR spectra were recorded on Bruker Avance III 400 Spectrometer ¹H (400.11 MHz) and ¹³C (100.61 MHz) using deuterated chloroform (CDCl₃) acting as the solvent and TMS an internal standard within the ranges between $\delta_{\rm H}$ 0-15 ppm (¹H) and $\delta_{\rm C}$ 0-200 ppm (¹³C). The theoretical study was evaluated via Gaussian 09 software employing DFT approach with set of basis function B3LYP/6-31G (d,p) with required physical parameters such as total energy and energy band gap. Thermogravimetric analysis was performed using Perkin-Elmer TGA Analyzer from 30 °C to 700 °C at a heating rate of 10 °C/min under nitrogen atmosphere.

far these types of molecular framework systems could be applied as photoactive semiconducting material.

Materials and instrumentation. All chemicals, materials.

and solvents used in the experimental process were

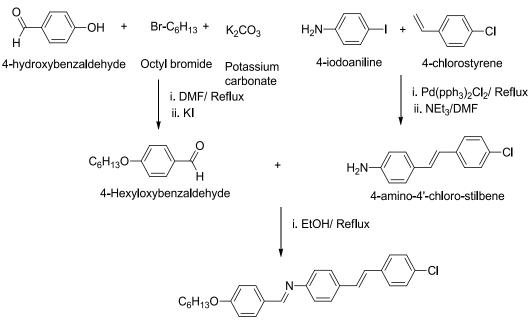
commercially purchased from standard suppliers namely

Sigma Aldrich, Merck, Fisher Scientific and R&M

Chemical. They were used as received without further

General overview of synthetic work. The synthesis work up process comprised three major parts which were the synthesis of 4-hexyloxy benzaldehyde (1) and the Heck cross-coupling protocols derivative, 4-amino-4'-chloro-stilbene (2) to act as precursor compound. From precursor, the preparation of Heck-immine, **HEXCS** was accomplished via Schiff base reaction as focalpoint compound in this study. However, the experimental details with regard to the synthesis of precursor have been reported before in literatures [13],[14]. However, some modifications in synthetic work and further characterization on the spectroscopic and analytical tasks was carried out and are discussed further in this report. The synthetic approach for the prepara tion of **HEXCS** is summarized in Scheme 1.

Synthesis of 4-hexyloxybenzaldehyde (1). The synthesis of 4-hexyloxybenzaldehyde (1) was done via Williamson ether synthesis. 4-hydroxybenzaldehyde (2.62 g, 21.45 mmol), hexyl bromide (3.54 g, 21.45 mmol), K₂CO₃ (2.96 g, 21.45 mmol) and KI (1.00 g, 6.00mmol) were put at reflux with constant stirring in 100 mL of DMF for ca. 24 h. After the reaction was adjudged completed by Thin Layer Chromatography (TLC) using



4-[(hexyloxyphenyl)methylene]amino)-4'-chloro-stilbene (HEXCS)

Scheme 1. The Synthetic Pathway for the Preparation of HEXCS

the solvent system of (hexane:ethyl acetate; 3:2), the reaction mixture was allowed to come to room temperature. Then, the reaction mixture being partitioned between diethyl ether (100 mL) and water (100 mL) for thrice, the organic layer was washed with 5 mL of NaOH (5% w/v), followed by neutralization using *ca*. 100 mL of water for thrice. The organic layer was dried over anhydrous MgSO₄ and the solvent was removed *in vacuo* to attain pale yellow oily liquid of **1** (85% yield).

Heck cross-coupling reaction: Preparation of 4-amino-4'-chloro-stilbene (2). A mixture of 4-iodoaniline (0.5 g, 2.28 mmol), 4-chlorostyrene (0.63 g, 4.57 mmol) and Pd(PPh₃)₂Cl₂ (0.1 mol%) were charged to 100 mL round bottom flask. The reaction was carried out at reflux at 80 °C using DMF as solvent and triethylamine (Et₃N) as base for *ca.* 8 hours under ambient atmosphere to give two layers of solution. After adjudged completed by TLC (hexane: ethyl acetate; 3:2), the solution was cooled at room temperature prior to extraction of the organic layer. The organic layer was separated, dried over MgSO₄ and solvent was removed *in-vacuo*. The residue was purified by silica gel column chromatography (n-hexane:ethyl acetate; 7:3) to afford title compound (55% yields).

Preparation of 4-[(hexyloxyphenyl) methylene]ami no)-4'-chloro-stilbene (HEXCS). The synthesis of **HEXCS** involved the addition of equimolar reaction between 1 (0.1g, 0.44mmol) and 2 (0.1 g, 0.44 mmol) in ethanolic solution fitted with a Dean-stark condenser. Then, it was put at reflux at 70 °C with constant stirring for *ca.* 6 hours and the progress was monitored by using TLC (hexane: ethyl acetate) (4:1). Once the reaction was complete, the solvent was removed *in-vacuo* and the crude product was recrystallised from acetonitrile to afford the yellow precipitate of the title compound (75% yield).

Fabrication and Electrical Studies of thin film of HEXCS on ITO Substrate. The fabrication of **HEXCS** was deposited on the ITO substrate by spin coating method via Spin Coater Model WS-400B-6NPP-LITE with sample concentration of 1x10⁻³ M. For electrical conductivity characterization, Four Point Probe system was used to determine the conductivity of **HEXCS** in the form of thin film under various intensity of light, 30 Wm⁻², 50 Wm⁻² and 100 Wm⁻². The sheet resistivity in produced films was measured by using Four Point Probing System consists of Jandel Universal Probe combined with a Jandel RM3 Test Unit.

Sheet resistance for wafer and film;

$$R_S = 4.532 \ x \ V/I \tag{1}$$

Where, R_S is the sheet resistance (resistivity), 4.532 is the correction factor, V is the voltage measured and I is the current applied from the test unit. Thus, electrical conductivity can be determined which it is the reciprocal (inverse) of the electrical resistivity, σ as shown in Eq. 2.

$$\sigma = 1/R_S \tag{2}$$

Where, σ = electrical conductivity and R_s= sheet resistance (resistivity).

3. Results and Discussion

Infrared (IR) Spectroscopy Analysis. The IR spectrum of **1** showed four absorption bands of interest namely v(C-H), v(C=O), v(C(=O)H) and v(C-O) (ether) ranging from moderate to strong intensities. The absorption band for alkyl group, v(C-H) was observed in the range of 2859 cm⁻¹ to 2932 cm⁻¹. The bands at around 2800-2735 cm⁻¹ correspond to v(C(=O)-H) band of aldehyde moiety. Meanwhile, a strong absorption band of v(C=O) was assigned at around 1694 cm⁻¹ that related to the resonance and mesomeric effect of phenyl ring. Additionally, the presence of v(C-O) (ether) stretching vibration can be observed at 1157 cm⁻¹ respectively, in which it is highly indicated the compound was indeed aldehyde derivative and are in close agreement with previously studied system [15],[16].

Meanwhile, 2 showed four major distinctive bands of v(NH), v (C=C alkene), v(C=C aromatic), v(C-N) and v(C-Cl). Two bands of v(N-H) can be identified at 3456 cm⁻¹ and 3376 cm⁻¹ which represented the asymmetric and symmetric N-H stretching vibrations of the terminal primary amine (NH₂) moieties. A prominent C=C alkene stretch was observed with an absorption band at 1653 cm⁻¹ which confirmed the formation of alkene moiety [17]. In addition, the band identified at 1280 cm⁻¹ was corresponded to v(C-N) in the Heck-amine linkage of 2. The presence of v(C-Cl) stretching vibration was observed in the range of 600-500 cm⁻¹ and can be assigned at low frequency of 533 cm⁻¹. IR spectrum of targeted compound, HEXCS revealed all the expected bands of interest namely v(C-H), v(C=C alkene), v(C=C aromatic) and v(C=N). The bands at around 2930 cm⁻¹ to 2872 cm⁻¹ correspond to C-H stretching of alkyl substituent and attributed to the symmetry stretching vibration of (Ar-O-CH₂). Meanwhile, the absorption band for v(C=C) alkene and aromatic stretching vibration occurred at 1604 cm⁻¹ and 1582 cm⁻¹ for the formation of stilbene moieties with moderate intensity. The presence of v(C=N) stretching vibration can be observed at 1605 cm⁻¹ respectively, in which it is highly indicated to Schiff base formation and are in close agreement with previously studied system [18],[19].

Optical Properties. The absorption spectrum of **1** revealed three principal bands which were expected to arise from C=O, phenyl and Ar-O-R. The broad absorption band was observed in range of λ_{max} 284 nm which arose from mixed of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions due to the overlapping and π -conjugation of effect of the molecule. Whilst, the electronic transition of **2** showed two major bands which were expected to be contributed from Ar-NH₂ and C=C alkene system. Strong absorption band can be identified at λ_{max} 338 nm which can be assigned as the mixed transition of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$. Meanwhile, electronic transition spectrum of targeted compound, HEXCS showed three principal

bands which were believed arising from phenyl, C=C alkene and C=N moiety at λ_{max} 357 nm which can be attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions due to the existence of overlapping between C=C and C=N moiety.

Then, the optical band gap (E_g^{opt}) was calculated using Eq. 3 where E_g^{opt} expressed in eV and $\lambda_{off\text{-set}}$ obtained from the cut off wavelength which is the intercept of the linear portion of the UV-Vis spectrum expressed in nm [20].

$$E_{\rm g}^{\rm opt} = 1240 \,/\,\lambda_{\rm off-set} \,\mathrm{eV} \tag{3}$$

According to UV-Vis spectrum of **HEXCS**, the cut off wavelength ($\lambda_{off-set}$) was found to be 400 nm which led to experimental optical energy band gap of 3.1 eV as illustrated in Figure 2. To investigate further into the energy separation between the difference of highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO), the molecular geometry of **HEXCS** was optimized via density functional theory (DFT) calculations with set of basis function B3LYP/6-31G (d,p). The HOMO-LUMO level of **HEXCS** was depicted in Figure 3 which derived

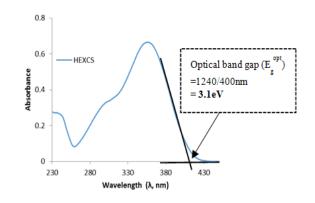


Figure 2. UV-Vis Spectrum of HEXCS Recorded in Dichloromethane

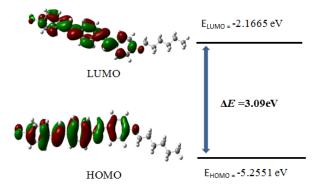


Figure 3. Energy Level between HOMO and LUMO of HEXCS

from quantum chemical calculations. From the data analysis, it is clearly observed that the value of energy separation between the HOMO and LUMO of HEXCS with the energy band gap value 3.09 eV was in good agreement with the experimental result of optical band gap from UV-Vis absorption spectroscopy, 3.1 eV. Notably, the electron withdrawing group from the chloro moiety to the conjugated backbone during the HO-MO→LUMO transition which the HOMO of HEXCS corresponded to a π bonding system localised at the phenyl ring moiety of the extensively π -conjugated into the stilbene-Schiff base aromatic system. Meanwhile, its LUMO has π symmetry with antibonding nature delocalized throughout the electron donating effect from the alkoxy moieties to the conjugated backbone of azomethine (CH=N) moiety.

Thus, a good relation between the experimental and theoretical data provide strong support of **HEXCS** being a potential candidate in organic semiconductor application, particularly in the respect of film owing to their low and good stability of HOMO-LUMO energies.

¹H and ¹³C Nuclear Magnetic Resonance (NMR) Analysis. The ¹H NMR spectrum for 1 showed methyl resonance at $\delta_{\rm H}$ 0.91 ppm while protons for the alkoxy group were observed in the range of $\delta_{\rm H}$ 0.92-1.82 ppm. For R-O-CH₂, the signal for the proton was detected at $\delta_{\rm H}$ 4.0 ppm because the hydrogen on the carbon attached to the oxygen was deshielded due to the contribution of electronegativity of the oxygen atom [21]. Whilst, aromatic protons were observed around the range of $\delta_{\rm H}$ 6.96-7.82 ppm which showed pseudo-doublet of system and the resonance was strongly affected by parasubstituted of phenyl ring. In addition, the aldehyde protons were observed at $\delta_{\rm H}$ 9.85 ppm characterized by their unique singlet resonance at downfield. For 2, NMR spectrum showed ¹H NMR where a significant =CH protons were observed in range δ_H 6.83-7.07 ppm as doublet-doublet of alkene system strongly influenced by the position of para substituent on the phenyl rings. The aromatic protons were assigned in the range $\delta_{\rm H}$ 7.32-7.83 ppm as multiple resonances respectively. The ¹H NMR spectrum for **HEXCS** showed methyl resonance at $\delta_{\rm H}$ 0.88 ppm while protons for the alkoxy group were observed in the range of $\delta_{\rm H}$ 1.25-1.83 ppm. For R-O-CH₂, the signal for the proton was detected at $\delta_{\rm H}$ 4.01 ppm because the hydrogen on the carbon attached to the oxygen was deshielded due to the contribution of electronegativity of the oxygen atom. Whilst, the aromatic protons of the para-substituted aromatic rings can be clearly observed at around δ_H 6.99-7.53 ppm as pseudodoublet resonances. For instances, the disappearance of amine and aldehyde protons that accompanied with the appearance azomethine proton (CH=N) was also observed at δ_H 8.41 ppm which confirming that amine have been condensed with aldehyde to produce targeted compounds of HEXCS.

The ¹³C NMR of **HEXCS** was consistent with the proposed molecular structure. The methyl resonance can be clearly observed at $\delta_{\rm C}$ 14.03 ppm and carbon resonances for alkyl were detected in the range of $\delta_{\rm C}$ 22.60-31.58 ppm, which revealed a good agreement with the previous reports on the similar systems. Whilst, the chemical shift for R–CH₂-O- can be found at $\delta_{\rm C}$ 68.26 ppm due to the deshielding effect in the presence of oxygen atom that withdrew certain amount of electron density from the alkyl chain. Meanwhile, the resonances for both aromatic ring carbons were assigned in the range of $\delta_{\rm C}$ 114.77 to 130.61 ppm which corresponded to the phenyl rings in these compounds. The C=N was also observed in the spectrum at $\delta_{\rm C}$ 162.04 ppm where this chemical shift is comparable to the literature [22].

Thermal Stability. Thermal stability of the material is important to be investigated for fabrication of any designated thin films. Thermal properties of the synthesized compounds were evaluated via thermogravimetric analysis (TGA) at heating rate of 10 °C/min under nitrogen atmosphere with temperature range of 30–700 °C as shown in Figure 4.

The thermogram revealed no mass loss occurred below 100 °C which indicated there was no trace of water molecule or solvent presence in the sample. The degradation process of precursor 2 showed two stages of major mass loss. Initial degradation took place at around 200 °C (Tonset) and ended at around 240 °C (Toffset) and second stage started to degrade at 300 °C (Tonset) and ended at 650 °C (Toffset). Meanwhile, the degradation process of **HEXCS** started to degrade at 290 °C (T_{onset}) and ended around 400 °C (T_{offset}) which higher than its precursor. Whilst, second stage started to degrade at 410 °C (Tonset) and ended at 850 °C (Toffset) showed that the targeted compound exhibited thermal stability at high temperature and it gave good indications for the potential of thin film fabrication be applied as conductive film for it displays remarkable performance under prolonged thermal stress.

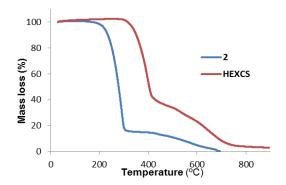


Figure. 4. Thermogravimetric Thermogram Analysis of Synthesized Compounds

Electrochemical properties. The electrochemical properties of HEXCS was investigated by using cyclic voltammetry analysis in order to determine the redox reaction and potential range of different electrochemical processes. The cyclic voltammogram of HEXCS exhibit irreversible redox processes with the presence of oxidation and reduction peaks respectively. The oxidation peak occurred at $\Delta E_{\rm pa}$ = 1.70V with $I_{\rm pa}$ = 2.95x10⁻⁸A while the reduction peak occurred at ΔE_{pc} = 1.65V with I_{pc} = 2.72x10⁻⁸A. Thus, it showed that the redox potential of HEXCS appeared in the positive region with its electro-oxidation stage as an anodic peak with a separation about 1V. The irreversible behavior of this reaction and the existence of redox potential that subsequently gave good sign for potential of the fabrication of conducting thin film.

Electrical Conductivity of Thin Film under Intensity of Light. In order to investigate its conductivity in various conditions, as shown in Figure 5, the electrical conductivity (EC) study of HEXCS in thin film form coated on the Indium Tin Oxide (ITO) glass was measured under various intensities of light conditions (Wm⁻²) by using Four-Point Probe. It showed that the electrical conductivity increased by the increasing amount of light intensities. The highest conductivity was observed for **HEXCS** under maximum light intensity (100 Wm⁻²) with the conductivity value, 0.1531 Scm⁻¹. In this case, the increasement of conductivity value might be due to the properties of the system which possessed number of alternating single and double bonds where the electron can easily flow from one reservoir to another that resulted into the effective properties of electrical conductivity.

As a conclusion, the electrical conductivity showed positive results under various intensity of light which revealed the film was successfully coated on the ITO substrate. Thus, based on the resulting conductivity, the **HEXCS** system can be applied as an active layer in conducting material.

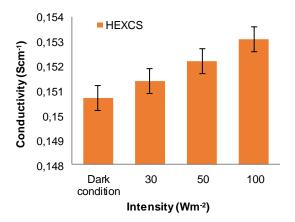


Figure. 5. Electrical Conductivity Values under Various Intensity of Light

4. Conclusions

The role and performance of new class of hybrid Heckimmine system namely 4-[(hexyloxyphenyl) methylene]amino)-4'-chloro-stilbene (HEXCS) based on Donor (D)- π -Acceptor (A) has been successfully synthesized and characterized as active semiconductor material candidates in conductive film. The optical band gap of HEXCS exhibited 2.8 eV which showed good relation between the experimental and theoretical data where provides strong support of being a potential candidate in organic semiconductor application, particularly in the optoelectronic devices. In fact, ITO/HEXCS thin film can conduct electricity better under maximum light intensity which exhibited up to 0.1531 Scm⁻¹. From these findings, further investigation on the similar molecular system is suggested to be applied as organic molecular wire for the development and application in any microelectronic devices.

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