SYNTHESIS AND CHARACTERIZATION OF ALKOXY SUBSTITUTED THIOUREA WITH *Curcuma longa* AS ACTIVE LAYER IN ORGANIC SOLAR CELL

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MASTER OF SCIENCE
UNIVERSITI MALAYSIA TERENGGANU
MALAYSIA
2014

A THESIS ENTITLED

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(CHEMICAL SCIENCES)

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Challenging work need self efforts along with hard working and respect.

I would like to dedicate my thesis to:

My superb and awesome supervisor,

'Associate Prof. Dr Wan Mohd Khairul Wan Mohamed Zin'

My beloved parents,

'Mak and Ata'

Thank you for support, trust and Du'a...

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Thesis Submitted in Fulfillment of the Requirement for the Degree of Master of Science in the School of Fundamental Science Universiti Malaysia Terengganu

July 2014

Abstract of thesis presented to the Senate of Universiti Malaysia Terengganu in fulfillment of the requirement for the degree of Master of Science.

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Supervisor : Associate Professor Wan Mohd Khairul Wan Mohamed Zin, Ph.D.

School : School of Fundamental Science

Organic solar cells based on single molecular system have attracted considerable attention because of their great potential to convert solar energy into electrical energy efficiently at low cost. The exploitation of conjugated thiourea molecular system combined with natural dyes are surprisingly unexplored in this distinctive area although the well-known rigid π-systems enhance the development of molecular wire architecture to be applied as potential active layer in organic solar cell. Therefore, in the present research, interest has been focused on the design, synthesis, fabrication and evaluation of the performance of essentially linear thiourea derivatives based on Donor (**D**)-π-Acceptor (**A**) system incorporated with *Curcuma longa* as an active layer in organic solar cell. The compounds were spectroscopically characterized via Infrared Spectroscopy (IR), UV-Visible Absorption Spectroscopy (UV-Vis), CHNS elemental analysis, ^{1}H and ^{13}C Nuclear Magnetic Resonance Spectroscopy (NMR), Thermogravimetric Analysis (TGA), X-ray diffraction (XRD) as well as Cyclic Voltammetry (CV) analysis. In addition, curcumin were extracted from fresh *Curcuma longa* as promising alternative sensitizers to improve photoelectric conversion efficiency (PCE). In turn, it was fabricated on ITO substrate prior the conductivity behaviour, efficiency and OSC parameter were evaluated by Four Point Probe, Semiconductor Characterisation System and Probe Station. The performance of thin films doping with and without natural dyes onto the ITO substrate investigated in order to compare its conductivity performance. Besides that, the compounds were evaluated theoretically via Gaussian 09 software employing DFT approach with set of basis function B3LYP/6-31G (d,p). Based on IR results, the synthesized compounds revealed all the expected frequency region of bands of interest namely ν(N-H), ν(C-H), ν(C=O), ν(C-N), ν(C-O) and ν(C=S). The data for the UV-Vis analysis shows the important electronic transitions of $\pi \rightarrow \pi^*$ and forbidden $n \rightarrow \pi^*$ which indicate the presence of important chromophores occupied in the molecular system. In ^{1}H and ^{13}C NMR spectra, they exhibit all expected resonances which are in good agreement with the proposed structure. Based on TGA analysis, the synthesized compounds show good potential of thermal stability under high temperature and it is proven these compounds can act as great potential coating material for the fabrication of solar cells. The X-ray diffractograms show that the diffraction peak of synthesized compound become broader and less intense which indicating its semi crystalline nature. Whilst, the energy bandgap (E_g) also was measured and calculated. It has been found that the compounds exhibit 2.92 to 4.10eV. The quantum mechanical calculation involves the

geometry optimization to the minimum energy and the result revealed the predicted value was in agreement with experimental result. In the figure of electrical conductivity, it revealed the layer of curcumin/TU (**3a/3b**)/ITO thin films performed better and exhibits the increasing conductivity, 0.2308Scm^{-1} to 0.2370Scm^{-1} with the presence of dyes under maximum light intensity of 100Wm^{-2}. Moreover, from the efficiency and OSC parameters, single layer OSC of thiourea with natural dyes exhibited better performance in the range of 0.08 to 0.38%. With the outstanding approach and performance, further investigation on photovoltaic studies on the same molecular system is suggested to be applied as organic molecular wire for the development of microelectronic devices.

Abstrak tesis yang dikemukakan kepada Senat Universiti Malaysia Terengganu sebagai memenuhi keperluan untuk Ijazah Sarjana Sains.

SINTESIS DAN PENCIRIAN TIOUREA TERGANTI ALKOKSI DENGAN *Curcuma longa* SEBAGAI LAPISAN AKTIF SEL SOLAR ORGANIK

RAFIZAH BINTI RAHAMATHULLAH

Julai 2014

Penyelia : **Profesor Madya Wan Mohd. Khairul Wan Mohamed Zin Ph.D.**

Pusat Pengajian : **Pusat Pengajian Sains Asas**

Sel solar organik berasaskan sistem molekul tunggal telah menarik perhatian kerana berpotensi tinggi dalam penukaran tenaga solar kepada tenaga elektrik dengan cekap pada kadar kos yang rendah. Walaubagaimanapun, pengeksploitasian sistem molekul tiourea terkonjugat dengan penggabungan pewarna semulajadi masih belum diterokai sepenuhnya dalam bidang ini walaupun ia sangat dikenali sebagai sistem-π utuh di mana dapat meningkatkan perkembangan rekabentuk wayar molekul yang berpotensi untuk diaplikasikan sebagai lapisan aktif pada sel solar organik. Oleh yang demikian, dalam kajian ini, perhatian difokuskan kepada reka bentuk, sintesis, fabrikasi dan penilaian prestasi bagi terbitan thiourea linear menggunakan sistem penderma (**D**)-π-penerima (**A**) dengan penggabungan *Curcuma longa* sebagai lapisan aktif sel solar organik. Sebatian yang telah disintesis kemudiannya dicirikan secara spektroskopi melalui Sinar Inframerah (IR), Analisis Ultra-Lembayung Sinar Nampak (UV-Vis), Analisis Unsur CHNS, ^{1}H and ^{13}C Multi Resonan Magnetik Nukleus (NMR), Analisis Termogravimetri (TGA), Analisis Pembelauan Sinar-X (XRD) dan juga Analisis Voltametri Kitaran (CV). Di samping itu, curcumin telah diekstrak daripada *Curcuma longa* segar sebagai salah satu alternatif pewarna untuk meningkatkan kecekapan penukaran fotoelektrik. Kemudiannya, sebatian ini telah difabrikasikan pada substrat ITO sebelum ciri-ciri kekonduksian, kecekapan dan parameter OSC dinilai menggunakan Penduga Empat Titik dan Sistem Pencirian Semikonduktor. Prestasi filem nipis terdop dan tidak terdop dengan pewarna semulajadi pada substrat ITO telah dikaji untuk membandingkan prestasi kekonduksian. Selain itu, sebatian ini juga telah dinilai secara teori menggunakan perisian Gaussian 09 dan pendekatan DFT dengan set fungsi asas B3LYP/6-31G (d,p). Daripada keputusan IR, sebatian yang telah disintesis menunjukkan kesemua frekuensi regangan yang telah dijangka iaitu ν(N-H), ν(C-H), ν(C=O), ν(C-N), ν(C-O) dan ν(C=S). Selain itu, data bagi analisis sinar UV menunjukkan peralihan elektronik bagi $\pi \rightarrow \pi^*$ dan $n \rightarrow \pi^*$ yang mana membuktikan kehadiran kromofor-kromofor penting dalam sistem molekul tersebut. Dalam spektra ^{1}H dan ^{13}C NMR, mereka menunjukkan kesemua resonan yang dijangka di mana sangat bertepatan dengan struktur yang dicadangkan. Daripada analisis TGA, sebatian yang disintesis menunjukkan potensi yang tinggi dalam kestabilan terma pada suhu yang tinggi di mana ia membuktikan bahawa sebatian ini sangat berpotensi sebagai bahan sadur untuk fabrikasi sel solar. Difraktogram sinar-X pula menunjukkan puncak belauan pada sebatian yang disintesis menjadi semakin lebar dan kurang keamatannya yang mana ini membuktikan sifat separa hablurnya. Sementara itu, jurang jalur tenaga

(E_g) juga telah diukur dan dikira. Sebatian ini telah menunjukkan nilai di antara 2.92-4.10eV. Pengiraan mekanik kuantum melibatkan pengoptimuman geometri pada tenaga keupayaan minimum dan keputusannya menunjukkan nilai yang selari di antara nilai teori dan keputusan eksperimen. Daripada kajian kekonduksian, ia menunjukkan lapisan filem nipis curcumin/TU(**3a/3b**)/ITO memberikan prestasi lebih baik dengan peningkatan nilai kekonduksian, $0.2308Scm^{-1}$ kepada $0.2371Scm^{-1}$ dengan kehadiran pewarna di bawah keamatan cahaya maksimum iaitu $100Wm^{-2}$. Tambahan pula, daripada kecekapan sel solar organik, lapisan tunggal tiourea dengan pewarna menunjukkan prestasi yang baik iaitu di antara 0.08-0.38%. Dengan pendekatan dan prestasi yang menggalakkan, penyelidikan lanjut mengenai kesan fotovoltaik pada sistem molekul yang sama perlu dilaksanakan untuk perkembangan di dalam bidang peranti-peranti mikroelektronik.