

SYNTHESIS AND CHARACTERISATION OF FERROCENYL-  
AZOBENZENE DERIVATIVES FOR THE DEVELOPMENT  
OF DIODES

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MASTER OF SCIENCE  
UNIVERSITI MALAYSIA TERENGGANU

2013



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

**December 2013**

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

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Photochromic azobenzene derivatives have attracted much attention recently due to their potential applications in the electronic and photonic devices. Introduction of a redox active unit to the azobenzene derivatives provides the opportunity for charge separation in the excited state of the systems. In this study, two series of ferrocenyl-azobenzene derivatives were synthesised. The first are a series of four ferrocenyl-azobenzene derivatives (**1-4**) in which the spacer is an amide moiety and the substituents, R = -NO<sub>2</sub>, -N(CH<sub>3</sub>)<sub>2</sub>, -H and -NH<sub>2</sub>. The second are a series of two ferrocenyl-azobenzene derivatives (**5** and **6**) with acyl thiourea spacer and substituents, R = -NO<sub>2</sub> and -N(CH<sub>3</sub>)<sub>2</sub>.

The synthesised compounds were characterised via elemental analysis, electrochemical techniques and spectroscopic methods including mass, NMR, IR, UV-Vis, photoisomerisation and OTTL. In elemental analysis, the experimental values of C, H and N were comparable to the calculated theoretical values. This indicated that the synthesised compounds were reasonably pure. In <sup>1</sup>H NMR spectroscopy, the effects of R substituents on the azobenzene protons are dominant. The proton resonances of azobenzene moieties containing the electron-withdrawing substituents, R = -NO<sub>2</sub> and -H appeared further downfield than those containing the electron-donating substituents, R = -N(CH<sub>3</sub>)<sub>2</sub> and -NH<sub>2</sub>. However, the proton resonances of ferrocenyl unit are independent of the nature of R substituents. The  $\nu(\text{N-H})$ ,  $\nu(\text{C=O})$ ,  $\nu(\text{C-N})$ ,  $\nu(\text{N-C=O})$  and  $\nu(\text{C=S})$  for compounds **1-6** were observed at *ca.* 3400, 1600, 1300, 1250 and 1130 cm<sup>-1</sup>, respectively.

In UV-Vis analysis, the type of spacers employed in the compounds had a minor influence on the azo  $\pi \rightarrow \pi^*$  transition. However, the bathochromic shifts observed for azo  $\pi \rightarrow \pi^*$  transition could be attributed to the effect of R substituents. The azo  $\pi \rightarrow \pi^*$  bands were more red-shifted for compounds with electron-donating substituents compared to those with electron-withdrawing substituents. The MLCT bands were displayed for compounds **1** and **3** as a shoulder under the tail of azo  $\pi \rightarrow \pi^*$  band. However, for compounds **2**, **4**, **5** and **6**, the MLCT bands could not be observed as they were obscured by the azo  $\pi \rightarrow \pi^*$  envelope. Additional n- $\pi^*$  and  $\pi \rightarrow \pi^*$  transitions of C=S in compounds **5** and **6** containing the acyl thiourea spacer were also observed. From the energy band gap data, compounds with stronger electron-

donating substituent,  $R = -N(CH_3)_2$  gave the lowest energy compared to other compounds.

All compounds exhibited the reversible one-electron oxidation process of the ferrocenyl moiety. The nature of R substituents and the type of spacers employed had a minor influence on the  $Fc^+/Fc^0$  couples as they appeared in similar magnitudes. On oxidation of the ferrocenyl unit, the bleaching of MLCT band was observed and the growth of a new band in the visible region could be assigned to the LMCT transition. In photoisomerisation, the *trans-cis-trans* processes were dependent on the nature of R substituents. Compounds **2** and **4** containing the electron-donating substituents showed shorter conversion time of *trans-cis-trans* process compared to **1** and **3** that contain the electron-withdrawing substituents.

All compounds were then fabricated on ITO substrates as thin films. Investigation on the electrical conductivity and I-V characteristic were carried out. The electrical conductivity for compounds **1-6** were observed in the range of semiconductor materials. Compounds **1** and **2** with the electron-withdrawing and electron-donating R substituents respectively have been selected for the measurement of I-V characteristic because of their high electrical conductivities. The non-linear I-V curves for diodes **1** and **2** showed knee voltages at 2.9 and 2.3 V respectively. The breakdown voltages were approximately -7.0 V under the reverse bias of both diodes.

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

## SINTESIS DAN PENCIRIAN TERBITAN FEROSENIL-AZO BENZENA UNTUK PEMBANGUNAN DIOD

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Terbitan azobenzena yang bersifat fotokromik kini semakin mendapat perhatian disebabkan kebolehnya untuk diaplikasikan dalam peralatan elektronik fotonik. Pengenal unit aktif redoks kepada terbitan azobenzena memberi peluang bagi sistem tersebut untuk mengalami pemisahan cas pada keadaan teruja. Dalam kajian ini, dua siri terbitan ferosenil-azobenzena telah disintesis. Siri yang pertama mengandungi empat terbitan ferosenil-azobenzena (1-4) di mana unit penyambungan yang digunakan adalah amida moiety dan penukarganti R = -NO<sub>2</sub>, -N(CH<sub>3</sub>)<sub>2</sub>, -H and -NH<sub>2</sub>. Siri kedua adalah ferosenil-azobenzena (5 dan 6) yang menggunakan acil tiourea moiety sebagai unit penyambungan dan penukarganti R = -NO<sub>2</sub> and -N(CH<sub>3</sub>)<sub>2</sub>.

Sebatian yang telah disintesis dicirikan melalui analisis unsur, teknik elektrokimia dan kaedah spektroskopi seperti jisim, resonans magnetik nuklear (RMN), inframerah, ultralembayung-nampak, pengisomeran cahaya and elektrod lapisan nipis optik lutsinar (OTTLE). Di dalam analisis unsur, nilai yang diperolehi dari eksperimen menunjukkan kadar yang hampir sama dengan nilai teori. Ini membuktikan sebatian yang disintesis adalah tulen. Manakala, dalam spektroskopi <sup>1</sup>H RMN penukarganti R menunjukkan kesan yang dominan terhadap proton azobenzena. Resonans bagi proton azobenzena yang mengandungi kumpulan penukarganti penerima elektron, R = -NO<sub>2</sub> and -H muncul pada medan yang rendah berbanding sebatian yang mempunyai kumpulan penukarganti penerima elektron, R = -N(CH<sub>3</sub>)<sub>2</sub> and -NH<sub>2</sub>. Walau bagaimanapun, resonans proton bagi unit ferosenil tidak bergantung kepada sifat penukarganti R. Berdasarkan keputusan spektrum inframerah, kesemua regangan  $\nu(\text{N-H})$ ,  $\nu(\text{C=O})$ ,  $\nu(\text{C-N})$ ,  $\nu(\text{N=O})$ ,  $\nu(\text{N-C=O})$  dan  $\nu(\text{C=S})$  masing-masing dapat dilihat pada nilai 3400, 1600, 1300, 1250 and 1130 cm<sup>-1</sup>.

Bagi analisis ultralembayung-nampak, jenis unit penyambungan dalam sebatian memberikan sedikit kesan terhadap peralihan  $\pi \rightarrow \pi^*$  kumpulan azo. Walau bagaimanapun peralihan batokromik yang di perhatikan bagi peralihan  $\pi \rightarrow \pi^*$  kumpulan azo dipengaruhi oleh sifat penukarganti R. Anjakan merah untuk jalur  $\pi \rightarrow \pi^*$  kumpulan azo ini lebih menonjol bagi sebatian yang mempunyai kumpulan

penukarganti elektron penderma berbanding electron penerima. Jalur MLCT bagi **1** dan **3** diperhatikan pada penghujung jalur azo  $\pi \rightarrow \pi^*$ . Manakala bagi sebatian **2**, **4**, **5** dan **6**, jalur MLCT tidak dapat dilihat kerana berada di bawah jalur azo  $\pi-\pi^*$ . Kumpulan peralihan tambahan  $n-\pi^*$  and  $\pi-\pi^*$  yang merujuk kepada C=S dalam sebatian **5** dan **6** yang mengandungi kumpulan asil tiourea penyambungan juga diperhatikan. Data jurang tenaga yang diperolehi menunjukkan sebatian yang mengandungi sifat kumpulan penukarganti penderma elektron yang kuat iaitu R = -N(CH<sub>3</sub>)<sub>2</sub> memberikan bacaan jurang tenaga yang lebih rendah berbanding sebatian-sebatian yang lain.

Semua sebatian mempamerkan proses pengoksidaan berbalik satu elektron bagi moiety ferosenil. Sifat penukarganti R dan jenis unit penyambungan yang digunakan hanya memberi sedikit kesan terhadap pasangan  $Fc^+/Fc^0$  kerana menunjukkan bacaan magnitud yang hampir serupa. Semasa pengoksidaan unit ferosenil, penurunan jalur 'MLCT' dikesan dan diikuti dengan kemunculan jalur baru pada rantau nampak yang dikenali sebagai 'LMCT'. Semasa proses pengisomeran cahaya, pertukaran isomer *trans-cis-trans* sangat dipengaruhi oleh sifat penukarganti R. Sebatian **2** dan **4** yang mempunyai elektron penderma menunjukkan masa pertukaran yang lebih pendek berbanding sebatian **1** dan **3** yang mengandungi kumpulan pengganti penerima elektron.

Semua sebatian kemudiannya diaplikasikan di atas substrat ITO sebagai filem nipis. Kajian kekonduksian elektrik dan pencirian graf I-V dilaksanakan. Kekonduksian elektrik bagi sebatian **1-6** menunjukkan bacaan di dalam julat bahan semikonduktor. Sebatian **1** dan **2** yang masing-masing mempunyai kumpulan penukarganti, R penerima elektron dan penderma elektron telah dipilih untuk pencirian graf I-V kerana mempunyai bacaan kekonduksian elektrik yang tertinggi. Graf I-V yang diperolehi bagi diod **1** and **2**, masing-masing menunjukkan bacaan voltan 'knee' pada 2.9 V dan 2.3 V. Manakala bacaan bagi pemecahan voltan di dapati menghampiri -7 V dalam lingkungan pincangan songsang bagi kedua-dua jenis diod.