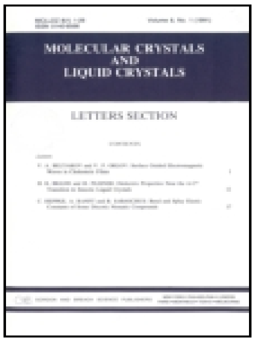


Molecular Crystals and Liquid Crystals

ISSN: 1542-1406 (Print) 1563-5287 (Online) Journal homepage: http://www.tandfonline.com/loi/gmcl20

Synthesis, Characterization and Electrical Conductance of Ferrocenylazobenzene

Tei Tagg, Siti Athirah Mohamad Jamali, Hasiah Salleh & Gurumurthy Hegde

To cite this article: Tei Tagg, Siti Athirah Mohamad Jamali, Hasiah Salleh & Gurumurthy Hegde (2014) Synthesis, Characterization and Electrical Conductance of Ferrocenylazobenzene, Molecular Crystals and Liquid Crystals, 604:1, 142-150, DOI: 10.1080/15421406.2014.968081

To link to this article: http://dx.doi.org/10.1080/15421406.2014.968081

Mol. Cryst. Liq. Cryst., Vol. 604: pp. 142–150, 2014

ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2014.968081

Synthesis, Characterization and Electrical Conductance of Ferrocenylazobenzene

TEI TAGG,[1,*] SITI ATHIRAH MOHAMAD JAMALI,[1]
HASIAH SALLEH,[2] AND GURUMURTHY HEGDE[3]

[1]School of Fundamental Science, Universiti Malaysia Terenggan,
Kuala Terengganu, Malaysia
[2]School of Ocean Engineering, Universiti Malaysia Terengganu,
Kuala Terengganu, Malaysia
[3]Faculty of Industrial Sciences and Technology, Universiti Malaysia Pahang,
Kuantan, Malaysia

Ferrocenylazobenzene was synthesized by condensing an aminoazobenzene dye with ferrocenecarboxylic acid previously treated with oxalyl chloride. The compound displayed an anticipated chemically reversible one-electron oxidation process and gave a formal potential, $E^\circ = 0.65$ *V. In the UV-Vis region, the azo* π-π^* *and* n-π^* *transitions appeared at 355 and 460 nm respectively. On oxidation of the ferrocenyl moiety, the azo* π-π^* *band was blue-shifted to 348 nm with an increase in intensity, while a new broad, lower energy absorption band assigned to the ligand-to-metal charge transfer appeared at 622 nm. The growth of this new band was concurrent with the bleaching of the metal-to-ligand charge transfer band which was largely obscured by the azo* n-π^* *band at 460 nm. The compound in the form of thin film gave an average electrical conductivity of* 0.239 ± 0.001 Scm^{-1} *and a non-linear I-V curve with knee voltage at 2.3 V in dark condition.*

Keywords Ferrocene; azobenzene; electrical; conductivity

1. Introduction

Azobenzene is a diazene (NH=NH) compound, where both hydrogens are substituted by phenyl groups. Its versatility, chemical stability and facile color tuning makes it one of the important dyes in the broad class of aromatic azo compounds [1–3]. In theory, azobenzene is a π-conjugated molecule with an electron-withdrawing effect [4], but there is no investigation using azobenzene as an electron acceptor in molecular electronics because the intramolecular electronic communication between azobenzene and adjacent chromophore can alter its original feature [5]. In contrast, azobenzene is mostly employed as a photo responsive linker between chromophores since its readily induced and reversible isomerization about the azo bond between the *trans* and *cis* geometric isomers proved useful in

---

[*] Address correspondence to Tei Tagg, School of Fundamental Science, Universiti Malaysia Terenggan, 21030 Kuala 6 Terengganu, Malaysia. E-mail: woochiat@umt.edu.my

Color versions of one or more of the figures in the article can be found online at www.tandfonline.com/gmcl.

regulating molecular motion for photo switchable devices [6,7]. However, we are interested in employing azobenzene as an acceptor by conjugating it to a redox active (electron donating) chromophore like ferrocene in a donor-acceptor array. There are a few reports on azobenzenes functionalized with ferrocenes [8–13], and they are limited to the study of photoisomerization behaviors of azobenzenes on switching the oxidation state of the ferrocenyl moieties. In this paper, we report the preparation of a new ferrocenylazobenzene (**FcAzoben**) and its spectroscopic, electrochemical and spectroelectrochemical properties. The electrical conductance studies were carried out in dark condition to omit any photo response of the azo moiety.

2. Experimental

a. Synthesis of Ferrocenylazobenzene (FcAzoben)

All chemicals were purchased and used without further purifications except for triethylamine which was distilled prior to use. All reactions were carried out under nitrogen atmosphere. Ferrocenoyl chloride was prepared by a modified literature method [14]. Preparation of ferrocenylazobenzene (**FcAzoben**): Ferrocenoyl chloride (0.43 g, 1.73 mmol) was dissolved in 30 mL of dry CH_2Cl_2, and 2.5 mL of distilled NEt_3 was added to the solution. After being stirred for 30 min at room temperature, 4-aminoazobenzene (0.11 g, 0.57 mmol) in 30 mL of dry CH_2Cl_2 was added dropwise within 1 h. The reaction mixture was stirred for 48 h at room temperature, and then heated to reflux for 2 h. Solvent was removed *in vacuo* and the residue purified by column chromatography (SiO_2, CH_2Cl_2) gave yellow solid of **FcAzoben** (0.16 g, 70%). Anal. Calcd. for $C_{23}H_{19}FeN_3O$: C, 67.50; H, 4.68; N, 10.27. Found: C, 67.32; H, 4.64; N, 9.97. EI-MS: $(M + Na)^+$, $m/z = 432.07$. ^1H NMR ($CDCl_3$), δ (ppm): 4.31 (s, 5H, C_5H_5); 4.49 (s, 2H, β-C_5H_4); 4.84 (s, 2H, α-C_5H_4); 7.48–7.56 (m, 4H, C_6H_4 + NH); 7.80 (d, $J_{HH} = 9$ Hz, 2H, C_6H_4); 7.94 (d, $J_{HH} = 7$ Hz, 2H, C_6H_4); 8.00 (d, $J_{HH} = 9$ Hz, 2H, C_6H_4). ^{13}C NMR ($CDCl_3$), δ (ppm): 68.34 (α-C_5H_4); 69.98 (C_5H_5); 71.19 (β-C_5H_4); 75.87 ($C_\alpha{-}\underline{C}{-}C{=}O$); 119.61, 122.74, 124.18, 129.08, 130.72, 140.71, 148.84, 152.75 ($C_6H_4 + C_6H_5$); 168.80 (C=O).

b. Deposition of FcAzoben on ITO Substrate

FcAzoben was deposited on the ITO substrate by electrochemical method using the Electrochemical Impedance Spectroscopy (EIS) PGSTAT302. The experimental set-up consists of an electrochemical cell, a potentiostat/galvanostat, and a General Purpose Electrochemical System (GPES). Using the GPES software, cyclic voltammetry (Staircase) method was set to be in Normal method. The cyclic process was set for 20 cycles. Deposition was completed in acetonitrile (ACN) with the following conditions; scan rate of 0.05 Vs^{-1}, potential range of 0–1.5 V, solution of $\sim 10^{-4}$ M in electroactive material and 0.1 M in lithium tetrafluroborate ($LiBF_4$) as supporting electrolyte.

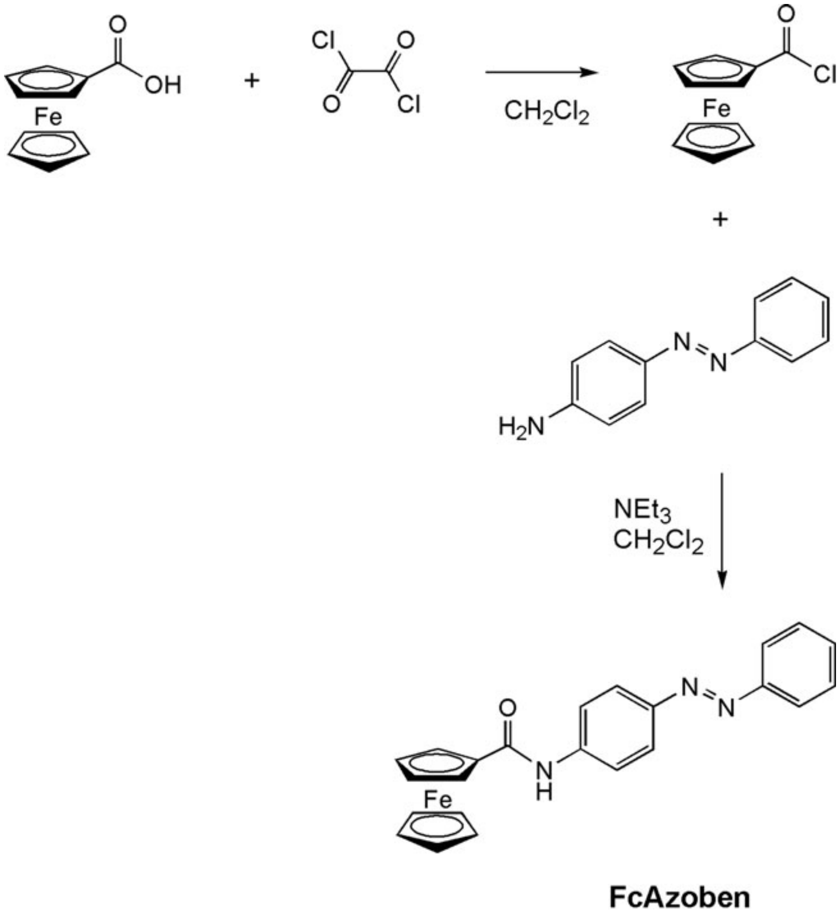
c. Characterizations

Elemental analysis was obtained using FLASH EA 1112 CHNS-O analyzer. Mass spectrum was recorded on Shimadzu LCMS-QP8000 spectrometer. ^1H and ^{13}C NMR spectra were recorded using Bruker Avance III 400 MHz spectrometer in $CDCl_3$ at 25°C. IR spectrum was recorded via FTIR Perkin Elmer 100 spectrophotometer using potassium bromide (KBr) pellet. UV-Vis spectrum was recorded on Shimadzu 1601 series in ACN using 1 cm path length quartz cell. Cyclic voltammetry was performed in ACN using Electrochemical Impedance Spectroscopy (EIS) PGSTAT302 with a three-electrode cell consisting of a polished Pt rod working electrode, Pt disc counter electrode and AgCl reference electrode. The solution was $\sim 10^{-4}$ M in electroactive material and 0.1 M in supporting electrolyte, lithium tetrafluroborate ($LiBF_4$). The scan rate employed was 0.05 Vs^{-1}. All data were recorded on the AutoLab software General Purpose Electrochemical System (GPES) manager. The UV-Vis Optically Transparent Thin Film Electrode (OTTLE) spectra were obtained using standard cells in ACN with platinum grid electrodes and Varian Carry 500 UV-Vis spectrophotometer. Electrical conductivity of the thin film was measured by four point probe system consisting of Jandel Universal Probe that was combined with Jandel RM3 test unit. The current–voltage characteristics an (I-V curve) measurement was performed by a two point probe system, which was connected to SMU-4200 SCS Keithley Characterisation System.

3. Results and Discussion

a. Synthesis

FcAzoben has been synthesized by condensing an aminoazobenzene dye with ferrocenecarboxylic acid previously treated with oxalyl chloride. The synthesis route is illustrated in Scheme 1. An additional base, such as triethylamine (NEt_3) is usually required to trap the



Scheme 1. Synthesis route for **FcAzoben**.

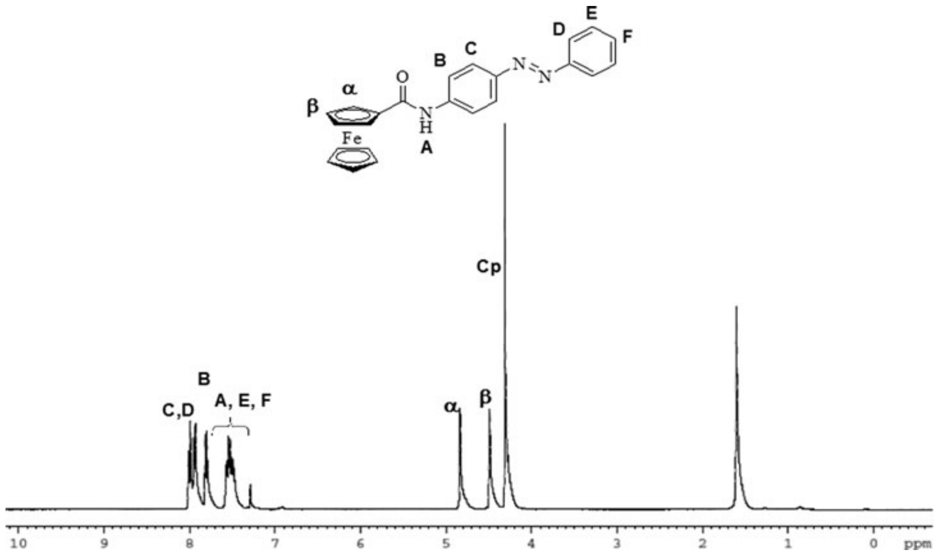


Figure 1. ^{1}H NMR spectrum for **FcAzoben** in $CDCl_3$.

formed HCl and to avoid the conversion of the amine into its unreactive HCl salt. **FcAzoben** is obtained in reasonable yield (70%) and is soluble in polar and semi polar solvents.

b. ^{1}H and ^{13}C NMR Spectroscopy

Assignments of ^{1}H and ^{13}C NMR resonances are done using homonuclear (COSY) and heteronuclear (HSQC and HMBC) techniques. The three ^{1}H NMR resonances of the ferrocenyl moiety, C_5H_5, H_β and H_α appear as a singlet at δ_H 4.31, 4.49 and 4.84 ppm. The N—H signal cannot be observed due to the overlapped signals from the phenylene protons in the range δ_H 7.48–7.56 ppm. The rest of the phenylene protons are observed as a doublet in the range δ_H 7.80–8.00 ppm. Fig. 1 shows the ^{1}H NMR spectrum for **FcAzoben**. The ^{13}C NMR resonances of the ferrocenyl moiety, C_5H_5, β-C_5H_4 and α-C_5H_4 appear at δ_C 69.98, 71.19 and 68.34 ppm respectively. Signal for the carbonyl carbon atom is detected at δ_C 168.80 ppm and the adjacent carbon atom at 75.87 ppm. The carbon resonances of the phenylene groups appear in the range δ_C 119.61– 152.75 ppm.

c. IR Spectroscopy

The IR spectrum of **FcAzoben** as shown in Fig. 2 displays ν(C =O) as a medium strong band at 1648 cm^{-1}. The decrease in the vibrational wavenumber of C =O stretching mode is possibly a result of the formation of an intermolecular hydrogen bond [15]. The hydrogen bond formation also tends to broaden out the N—H stretching vibration of amide observed at 3436 cm^{-1}. The ν(N—C =O) band at 1243 cm^{-1} is weaker than ν(C =O) band, probably due to the mixed vibration of the N - H bending modes.

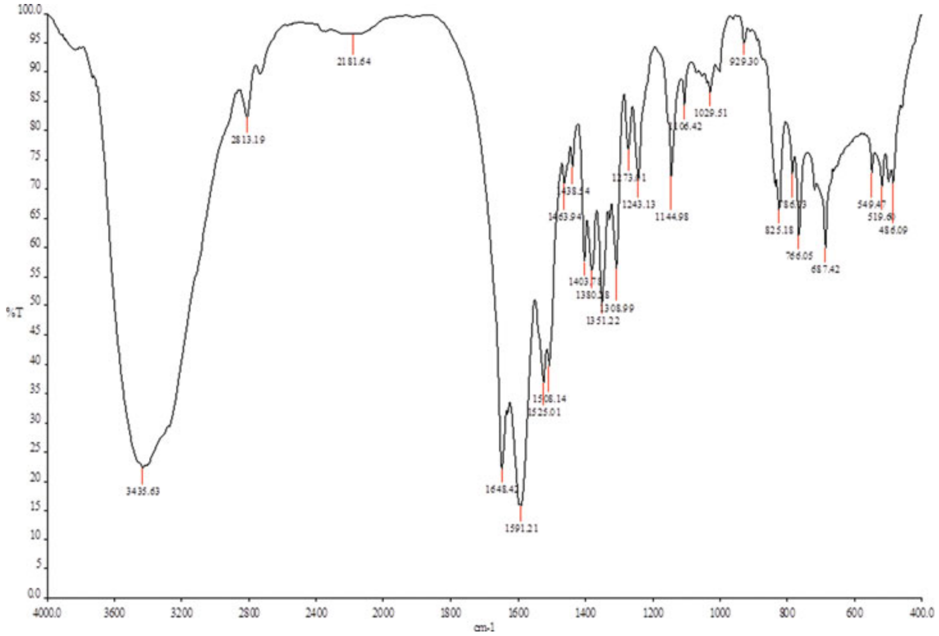


Figure 2. IR spectrum of **FcAzoben**.

d. *UV-Vis Spectroscopy*

In theory, the UV-Vis spectrum of an unsubstituted azobenzene in *trans* conformation consists of two well separated bands; the strong UV band at $\lambda_{\max} = 320$ nm ($\varepsilon_{\max} \sim 22000$ L mol^{-1} cm^{-1}) can be attributed to symmetry allowed π-π^* transition and the weaker band at $\lambda_{\max} = 450$ nm ($\varepsilon_{\max} \sim 400$ L mol^{-1} cm^{-1}) can be assigned to symmetry forbidden n-π^* transition [16–18]. Substitution of a ferrocenyl moiety on the azo ring in **FcAzoben** shifts the π-π^* (band **A**) and n-π^* (band **B**) transitions to higher wavelengths with higher extinction coefficients *i.e.* 355 nm ($\varepsilon_{\max} \sim 27000$ L mol^{-1} cm^{-1}) and 460 nm ($\varepsilon_{\max} \sim 2360$ L mol^{-1} cm^{-1}) respectively, compared to those of an unsubstituted azobenzene. The UV-Vis spectrum of **FcAzoben** is shown in Fig. 3. This phenomenon can be attributed to the increase in the π orbital (HOMO) energy and a decrease in the π^* orbital (LUMO) energy [19, 20].

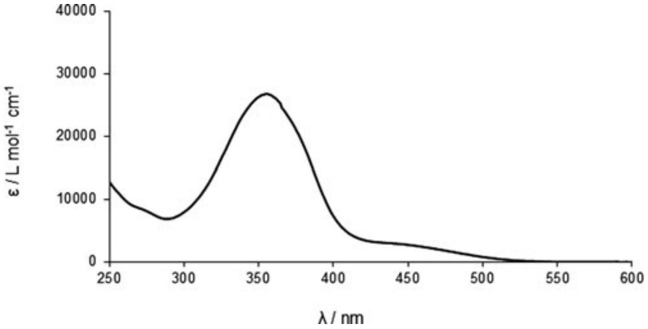


Figure 3. UV-Vis absorption spectrum of **FcAzoben** in ACN.

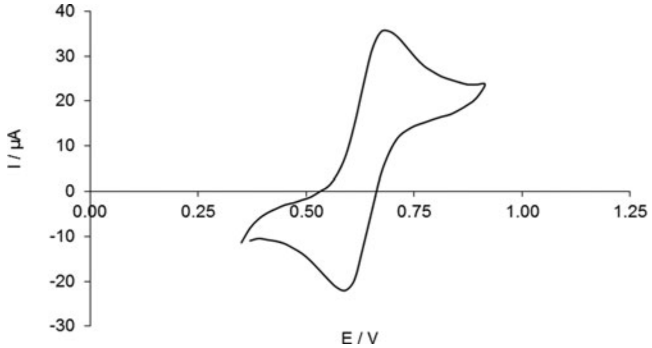


Figure 4. Cyclic voltammogram of **FcAzoben** (1×10^{-4} M in ACN, Pt, 0.1 M $LiBF_4$, 0.05 Vs^{-1}).

Although the ferrocenyl and azobenzene moieties are not fully π-conjugated, the presence of metal-to-ligand charge transfer (MLCT) transition cannot be totally disregarded. The MLCT band is obscured by the azo n-π^* band **B** and evidence for its presence can be inferred from the results of Optically Transparent Thin Layer Electrode (OTTLE) spectroscopy. Upon oxidation of the ferrocenyl moiety, there is an observable bleaching under the broad **B** envelope, *vide infra*. Undoubtedly, a stronger MLCT transition has been postulated for similar ferrocenyl and azobenzene moieties that are fully π-conjugated [9].

e. Electrochemistry

The cyclic voltammogram for **FcAzoben** in Fig. 4 displays the anticipated chemically reversible one-electron oxidation process of the ferrocenyl moiety. The anodic, E_{pa} and cathodic, E_{pc} peak potentials at 0.60 and 0.69 V respectively, give formal potential, $E^\circ = (E_{pa} + E_{pc}) / 2 = 0.65$ V. Compared to that of an unsubstituted ferrocene ($E^\circ = 0.42$ V), this anodic shift is unsurprising, due to the decreased of electron density on the substituted ferrocenyl system [21, 22].

f. Spectroelectrochemistry

On oxidation of the ferrocenyl moiety in **FcAzoben**, there are significant changes to the absorption bands as shown in the Optically Transparent Thin Layer Electrode (OTTLE) spectra in Fig. 5. Stability of the monocation **FcAzoben**$^+$ is shown by consistent isobestic points and complete reversibility upon application of the reverse potential. Complex changes to the profiles and energies of the bands are observed in the UV-Vis spectra of the monocation compared to the neutral molecule. Illustrating the complexity of these changes, the azo π-π^* transition band **A** appears to undergo a small blue-shift and an increase in intensity, while a new broad, lower energy absorption band **C** appears at 622 nm. The growth of band **C** in the visible region is concomitant with the bleaching of band **B** (MLCT that is obscured by azo n-π^*) at 460 nm in Fig. 6. Band similar to **C** has been observed previously in another ferrocenylazobenzene derivative and has been assigned to the ligand-to-metal charge transfer (LMCT) transition [9].

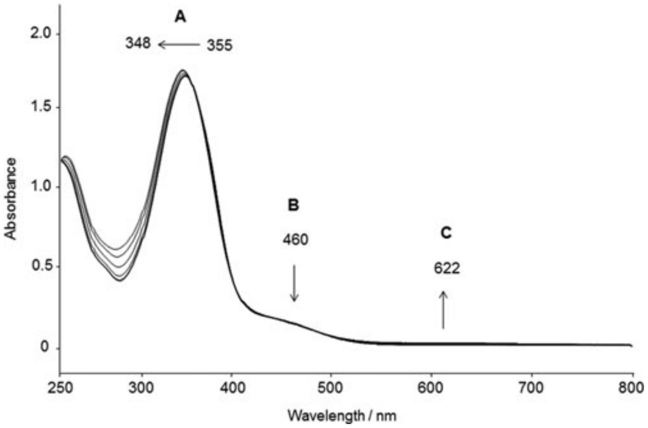


Figure 5. OTTLE spectra of **FcAzoben**$^+$ in ACN, 0 – 0.8 V.

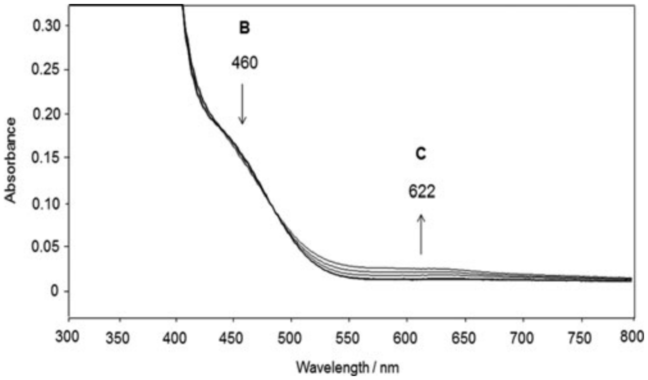


Figure 6. The growth of band **C** is concomitant with the bleaching of band **B** in OTTLE spectra.

g. Electrical Conductivity

Electrical conductivity, σ is a measure of the ability of a material to conduct an electric current. The conductivity of **FcAzoben** is measured in the form of thin film using a four point probe in dark condition, and the value can be obtained using Equation (1) and Equation

Table 1. Current, voltage and electrical conductivity data for **FcAzoben**

Voltage, V ± 0.0001 (mV)	Current, I ± 0.01 (mA)	Conductivity, σ ± 0.0001 (Scm^{-1})
1.4050	1.50	0.236
1.3762	1.50	0.241
1.3790	1.50	0.240
1.3794	1.50	0.240
	Average	0.239

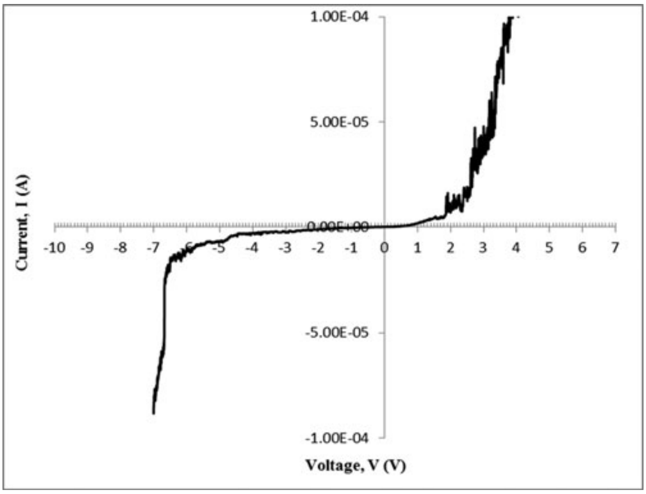


Figure 7. I-V characteristics of **FcAzoben**.

(2) based on the values of current, I and voltage, V in Table 1.

$$R_s = 4.532 \times V/I \qquad (1)$$

$$\sigma = 1/R_s \qquad (2)$$

R_s is sheet resistance for wafers and films. The average electrical conductivity of **FcAzoben** is 0.239 ± 0.001 Scm^{-1}. Based on the range of electrical conductivity in solids [23], **FcAzoben** can be identified as a semiconductor material.

h. Current-Voltage Characteristics

Figure 7 shows the I-V characteristics of **FcAzoben**. The optimum range of voltages applied into the circuit is −7.0 ± 0.1 V to 4.0 ± 0.1 V. In the forward region, the current gradually increases from 0 to 1.9 V, and then it drastically increases to 4.0 V. In the backward region, an abrupt breakdown behavior is observed, indicating the breakdown voltage at −7.0 V. The voltage at which the current starts to increase rapidly is called the knee voltage, and it is found at 2.3 V. The values of forward-bias voltage in **FcAzoben** are significantly different to those of the schottky and *pn* junction diodes [24] because the type of materials used here are very different. The materials for Schottky and *pn* junction diodes are silicon-based, while **FcAzoben** is iron-based.

Conclusion

We have shown here the synthesis and characterization of **FcAzoben**. Bathochromic shifts were observed for the azo π-π^* and n-π^* transitions on substitution of an electron donating ferrocenyl moiety on the electron accepting azobenzene unit. The presence of MLCT was evident and on oxidation of the ferrocenyl moiety, LMCT occurred. In the context of donor-acceptor array, the roles of ferrocene and azobenzene were reversed on oxidation. Ferrocene went from being a net donor to a weak acceptor with the azobenzene adopting the donor role. The electrical properties indicated **FcAzoben** as a semiconductor material with non-linear I-V characteristics. All these results showed that azobenzene can be employed as an electron acceptor in the donor-acceptor dyad for the development of molecular electronics.

Acknowledgment

We would like to acknowledge the Universiti Malaysia Pahang for providing the research facilities. We are grateful to our collaborators at the University of Otago for their assistance in OTTLE and MS.

Funding

We would like to acknowledge the Ministry of Higher Education, Malaysia for the Fundamental Research Grant Scheme (Grant No: 59177) and the Exploratory Research Grant Scheme (Grant No: 55075), MyBrain15 for the MSc scholarship, Institute of Marine Biotechnology, Universiti Malaysia Terengganu and Universiti Malaysia Pahang for providing the research facilities.

References

[1] Yoshino, J., Kano, N., & Kawashima, T. (2013). *Dalton Trans.*, *42*, 15826.
[2] Beharry, A. A., Sadovski, O., & Woolley, G. A. (2011) *J. Am. Chem. Soc.*, *133*, 19684.
[3] El Halabieh, R. H., Mermut, O., & Barrett, C. J. (2004). *Pure Appl. Chem.*, *76*, 1445.
[4] Autret, M., Le Plouzennec, M., Moinet, C., & Simonneaux, G. (1994). *J. Chem. Soc., Chem. Commun.*, 1169.
[5] Chiu, K. Y., Tu, Y.-J., Lee, C.-J., Yang, T.-F., Lai, L.-L., Chao, I., & Su, Y. O. (2012). *Electrochim. Acta*, *62*, 51.
[6] Schuster, D. I., Li, K., Guldi, D. M., Palkar, A., Echegoyen, L., Stanisky, C., Cross, R. J., Niemi, M., Tkachenko, N. V., & Lemmetyinen, H. (2007). *J. Am. Chem. Soc.*, *129*, 15973.
[7] Yamamura, T., Momotakeb, A., & Arai, T. (2004). *Tetrahedron Lett.*, *45*, 9219.
[8] Daniel, M.-C., Sakamoto, A., Ruiz, J., Astruc, D., & Nishihara, H. (2006). *Chem. Lett.*, *35*, 38.
[9] Sakamoto, A., Hirooka, A., Namiki, K., Kurihara, M., Murata, M., Sugimoto, M., & Nishihara, H. (2005). *Inorg. Chem.*, *44*, 7547.
[10] Horie, M., Sakano, T., Osakada, K., & Nakao, H. (2004). *Organomet.*, *23*, 18.
[11] Kurihara, M., Hirooka, A., Kume, S., Sugimoto, M., & Nishihara, H. (2002). *J. Am. Chem. Soc.*, *124*, 8800.
[12] Lee, S.-M., Marcaccio, M., McCleverty, J. A., & Ward, M. D. (1998). *Chem. Mater.*, *10*, 3272.
[13] Kondo, T., Kanai, T., & Uosaki, K. (2001). *Langmuir*, *17*, 6317.
[14] Cormode, D. P., Evans, A. J., Davis, J. J., & Beer, P. D. (2010). *Dalton Trans.*, *39*, 6532.
[15] Eaton, G., Symons, M. C. R., & Rastogi, P. P. (1989). *J. Chem. Soc. Faraday Trans.*, *85*, 3257.
[16] Bandara, H. M.D., & Burdette, S. C. (2012). *Chem. Soc. Rev.*, *41*, 1809.
[17] Hamm, P., Ohline, S. M., & Zinth, W. (1997). *J. Chem. Phys.*, *106*, 519.
[18] Lednev, I. K., Ye, T.Q., Matousek, P., Towrie, M., Foggi, P., Neuwahl, F.V.R., Umapathy, S., Hester, R. E., & Moore, J. N. (1998). *Chem. Phys. Lett.*, *290*, 68.
[19] Barret, C., Natansohn, C., & Rochod, P. (1995). *Chem. Mater.*, *7*, 899.
[20] Siewertsen, R., Neumann, H., Buchheim-Stehn, B., Herges, R., Nather, C., Renth, F., & Temps, F. (2009). *J. Am. Chem. Soc.*, *131*, 15594.
[21] Sarhan, A. A.O., & Izumi, T. J. (2003). *J. Organomet. Chem.*, *675*, 1.
[22] Humphrey, B. D., Castilo, R. E., Vega, A. H., Feliciano, A., & Squires, M. E. (2011). *Inorg. Chim. Acta*, *368*, 271.
[23] Tilley, R. J. D. (2004). *Understanding Solids: The Science of Materials*, John Wiley & Sons Ltd.: West Sussex, England.
[24] Neamen, D. (2006). *An Introduction to Semiconductor Devices*, McGraw-Hill: New York, USA.