New donor-acceptor material for organic solar cells with different transfer mechanism

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Abstract: This paper presents results from a new donor-acceptor material using easily available and renewable organic material. The new material was developed and tested using an idea of a new electron transfer mechanism using combined chlorophyll and ferrocene as the bulk-hetero junction active layer. This research aims to produce a binding between the chlorophyll molecule and the protein substitute using ferrocene so that the theory of electron transfer can be tested. The main objective of the research is to produce electricity from the new donor-acceptor material. It is observed that open-circuit voltage (Voc), short circuit current (Isc), fill factor (FF) and the efficiency (η) of the device were 0.1665V, 0.005A, 0.645 and 0.13%, respectively.

1. Introduction

Many of the processes in the production of Organic Solar Cells (OSC) that lead to low power conversion efficiency (PCE) remained poorly understood, posing a challenge for future research and development. To today’s knowledge, energy conversion by an OSC can be broken down into exciton generation, exciton diffusion, exciton dissociation, and charge transportation and collection. Therefore, some possible factors that may lead to the downturn of the PCE of OSC include spectrum loss, excitons loss, recombination loss, and contact loss. Although materials development always was based on energy level tuning, photocurrent production has proven to be more sensitive to morphology and fabrication conditions [1]. Besides, they are also factors that are limiting the stability and degrades the OSC such as oxygen and water oxidisation, continuous illumination, heating, and mechanical stress[2]. Despite many research, there is hardly any breakthrough for OSC[1]. It is said that Charge Transfer States (CTSS) recombination contribute to the largest loss and not well understood [1][3]. Therefore, by all means, new materials design and device engineering are needed beyond energy level tuning for this technology to be a success[1].

2. Donor- Acceptor material

The donor-acceptor material that forms the active layer in this research is the chlorophyll (Chl) extracted from spinach (Spinacia oleracea) combined with an organometallic material Ferrocene (Fc). These two materials were combined to form a donor-acceptor (Fc- Chl) bulk-hetero junction (BHJ) material. Chlorophyll was chosen since it is known due to its strong Soret and Qy bands as well as its excellent excitation energy and electron transportability [4]. The changes in the structure of Chlorophyll and its derivatives allow tunability in photochemical and photophysical properties of Chlorophylls [4]. Chlorophyll molecules can also form J-type aggregates guided by π-π stacking interaction with adjacent molecules that can improve charge carrier mobility[5][6]. Although Chl is sensitive and unstable when exposed to light, heat, and oxygen[7], the stability of Chl can be achieved through crystallization.
Chlorophyll extraction
The chlorophyll pigments were extracted from spinach (Spinacia oleracea). Spinach contains chlorophyll a and b. The spinach leaves were torn into small pieces and were mixed with acetone and left to sit for several minutes. The mixture was filtered, and saturated sodium chloride was added to form a separated two layers of liquid. The top layer, which is the organic layer, was collected and passed through a funnel of anhydrous sodium sulphate. Next, alumina was added to the solution, and the solvent was removed using rotary evaporator as in Figure 1 to produce dried powder of chlorophyll.

![Figure 1. Removing excessive solvent from Chlorophyll extract using Rotary Evaporator.](image)

Column Chromatography
Using a column, the dried sample extracted previously were added to the column with layers of materials as given in Figure 2. The fractions were collected separately based on the colour, and only the greenish fraction was taken. Then, the green fraction was dried using rotary evaporator again to produce a green chlorophyll extract shown in Figure 3. Then, the sample of the extract was tested using thin-layer chromatography (TLC) to check for the pigments that still contained in the extract. From the test, it is known that the extract contains not only Chlorophyll a and chlorophyll b, but some of the chlorophyll have degraded to become pheophytin a and pheophytin b and also contained traces of xanthophylls and β-carotene.

![Figure 2. Column Chromatography.](image)
![Figure 3. Chlorophyll extract.](image)

Ferrocene-Chlorophyll bond
Then the chlorophyll extract was added to ferrocene using the ratio of donor: acceptor of 1: 1. The
chlorophyll needed to react with the ferrocene, which is an iron centred organometallic compound. The iron centre of the ferrocene is expected to form a bond with chlorophyll a and b contained in the spinach extracts. The probable bonds are with any carbon double bond, oxygen double bond, and unpaired electron in the structure of the chlorophylls which are plenty available in chlorophyll a and b. Most probably, the bindings in chlorophyll a will involve with the double bonds located on the outer circle for chlorophyll as Figure 4. Further formations can be detected through chemical characteristics using Fourier Transform Infrared (FT-IR).

Solar cell device architecture and Electrical characterization
The device architecture of the solar cell is ITO/ PEDOT: PSS/ Fe – Chl/Ag, as shown in Figure 6. The indium-doped tin oxide (ITO)-coated glass with square resistance of 15Ω/ square is cleaned in an ultrasonic bath with detergent, deionized water, acetone, and isopropyl alcohol, and then dried in a nitrogen stream. Then the PEDOT: PSS solutions are spin-coated on top of the Ag coated silica at 3000 rpm for the 60s followed by annealing for 20 min. The active layer was spin-coated on the ITO.

3. Results and discussion

Based on thin-layer chromatography (TLC), it can be seen that the extract still contains traces of pigments from the leaves. Nonetheless, the experiment was proceeded due to a non-polar characteristics of the pigments.

Chemical Characterization of Fe – Chl
The metal centre of ferrocene is expected to combine with the ligand of chlorophyll a and b to form a complex, its vibrational spectra are also expected to change its frequencies, and new peaks are also expected to form. When the metal complex Fe- Chl spectrum is compared to the original spectra of the chlorophyll, the bonding character of the complex can be observed by looking at the change in the positions of the bands, the appearance of new bands, the splitting of bands into multi-plates and the change in relative intensities of the bands.

The difference in both the original spectrum and the Fe- Chl complex spectrum is shown in Figure 5. Some of the peaks may have been shifted to the left and right where the frequencies have changed. Some peaks also have been newly developed. The newly developed peaks and missing peaks were indicated in red circles in Figure 5, and all observations in changes were summarized in Table 1,
Figure 5. The spectrum of Chlorophyll compared to the Ferrocene-Chlorophyll complex.

From Table 1 and Table 2, comparing the original chlorophyll spectrum with the spectrum of the Fc–Chl complex, five new peaks have been observed, and two peaks have been missing. The appearance of new bands suggests different indication based on the type of ligand. First, the appearance of a new band in the region of 1493 cm\(^{-1}\) group of aromatic C= C and the considerable shift of the bond to a lower frequency suggests that the C = C coordination of the ligand to the ion metal of ferrocene. Lastly, a new strong intensity peak in the fingerprint region was observed at 700 cm\(^{-1}\) showing a formation of a C–H aromatics strong out-of-plane bend.

**Table 1.** New peaks in Ferrocene–Chlorophyll Spectrum.

| Frequency (cm\(^{-1}\)) | Type of bond | Fc-Chl complex frequency | Type of vibration | Intensity |
|------------------------|--------------|-------------------------|------------------|----------|
| 1700 - 1000            | C – H alkenes| 1003                    | bend             | strong   |
| 1600 - 1400            | C = C aromatic| 1493                    | -                | Medium- weak |
| 1250 - 1050            | C - O        | 1107                    | stretch          | strong   |
| 700                    | C – H aromatics| 700                    | Out of plane bend | strong   |

The disappearance of ligand band of C–H around 1700 – 1000 cm\(^{-1}\) from Table 2 is maybe due to hydrogen-bonded carbon indicated the coordination of carbon with the metal ion forming ferrocene. Next, the new band in 1107 cm\(^{-1}\) group supports the formation of C – O strong stretch bond in the complexes.

**Table 2.** Missing peaks in Ferrocene–Chlorophyll Spectrum.

| Frequency (cm\(^{-1}\)) | Type of bond | Fc-Chl complex frequency | Type of vibration | Intensity |
|------------------------|--------------|-------------------------|------------------|----------|
| 1700 - 1000            | C – H alkenes| 1057                    | -                | strong   |
| 1000- 700              | C–H aromatics| 868                    | Out-of-plane bend | strong   |

From Table 3, a significant shift of the benzene to a higher frequency is an indication of the participation of the carbon bond with the metal ion in ferrocene. On the other hand, the considerable shift of the bond to a lower frequency together with the appearance of a new band in the region of 1493 cm\(^{-1}\) group of aromatic C= C, suggests that the C= C coordination of the ligand to the ion metal of ferrocene. The C=C bond has demonstrated a decreasing wavenumber by approximately 9cm\(^{-1}\). The reason is that; the C= C group bond can be very weak. Conjugation with other double bonds can greatly increase the intensity as well as causing the wavenumber to decrease. Besides, the shift in the position of C= C group of ligands on complexation to lower frequency side also infers that coordination of the ligand to metal ion has taken place. Apart from that, there is also a significant shift of the ligands band of C–H to a higher frequency on complexation further confirms the participation
of carbon of the ligands in the bond formation with the metal ion. It can be seen for the C–H bond’s wavenumber has increased by approximately 14 cm$^{-1}$. Generally, any shifting frequency to a higher wavenumber means that the bond becomes more stable and stronger. Resonance could be a good interpretation for this shift. Apart from these three frequencies, other frequencies also have exhibited small changes in frequency, but the changes are not discussed here since they were not very significant.

| Original Frequency (cm$^{-1}$) | New frequency (cm$^{-1}$) | Type of bond | Shifting          |
|--------------------------------|---------------------------|--------------|-------------------|
| 1602                           | 1618                      | benzene      | Left-Increasing wavenumber |
| 1463                           | 1454                      | C = C        | Right-Decreasing wavenumber |
| 802                            | 816                       | C - H        | Left-Increasing wavenumber |

Surface characterisation of Fc– Chl
The surface of the BHJ Fc-Chl active layer was spin-coated under 1200 rpm. The thickness of the active layer is about 100nm. However, after several attempts, the spread of the Fc-Chl was not even. Some spots were measured between 100 - 200nm. Nonetheless, the measurement for electrical characterization was proceeded. Under the Scanning Electron Microscope (SEM), the active layer seen very rough and white shiny spots were seen on the surface, these are probably due to the nature of the chlorophyll and the metallic characteristics of the ferrocene.

**Figure 6.** Device architecture of Fc–Chl solar cell

**Figure 7.** The surface of Fc– Chl under Scanning Electron Microscope (SEM).

Electrical Characterisation of Fc – Chl
The electrical characterization of the solar cell was measured using a solar simulator under the standard condition of AM 1.5 and 1000Wm$^{-2}$ at an ambient temperature of 25°C. Figure 7 shows the surface of Fc-Chl under scanning. The simulator was connected to a Source Meter Unit (Keithley SMU2450), a data logger radiometer and a pyranometer. Then, the result was calculated using Equation 1 and Equation 2 for the fill factor and efficiency.

\[
FF = \frac{I_{max} \times V_{max}}{I_{sc} \times V_{oc}}
\]

\[
\eta = \frac{J_{sc} \times V_{oc} \times FF}{P_{in}}
\]
It can be seen that the efficiency is low due to the low value of open-circuit voltage ($V_{oc}$) and short circuit current ($I_{sc}$). The high fill factor is predominantly due to high hole mobility, which is beneficial for charge separation and transfer process[4]. The $J$-$V$ curve of the device has been depicted in Figure 8. However, unconventional distortions of the $J$-$V$ curve are due to the imbalanced mobilities that usually happened in planar heterojunctions, can also happen in non-homogeneous bulk heterojunction [8]. Most probably, surface recombination at the interface of the active layer and electrode due to the poor morphology of the active layer has impacted the open-circuit voltage ($V_{oc}$)[9].

4. Conclusions

In conclusion, based on the results, a new donor-acceptor was successfully fabricated and proven to produced electricity. Although, the FF is high, the value of $V_{oc}$ and $I_{sc}$ are very low due to the poor surface morphology of the active layer and the impurities content in the chlorophyll extract. This study provides a new electron transfer mechanism in OSC, but more researches are needed to further improve the performance of this new material, including interfacial layers and the crystallization of FC-Chl for stability.

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