CHAPTER 6

CONCLUSIONS AND FUTURE WORKS

6.1 Conclusions

The characterization and analysis of tris (8-hydroxyquinolinate) metals (Mq3), with Gaq3 and Alq3 as representatives, for their employment in solution-processed organic solar cells have been performed successfully. The absorption bands, optoelectronic energy gaps, and molecular energy levels (HOMO and LUMO), refractive index, along with dielectric properties of the materials have been investigated. The constant refractive index for the Gaq3 and Alq3 films was calculated to be 1.77 and 1.68, respectively. The higher refraction response of Gaq3 is attributed to the higher molecular packing density of Gaq3 compared to that of Alq3. A larger dielectric constant for Gaq3 was noticed, indicating the presence of higher density of states and accumulated space charge upon illumination in comparison to that of Alq3 film. The dissipation rate of ultraviolet electromagnetic waves in the Alq3 film was found to be considerably higher than that of Gaq3. This was correlated to the stronger optical absorption behavior of Alq3 in the ultraviolet region compared to that of Gaq3. The energy gap of 2.80 eV for Gaq3 as was seen smaller than that of 2.86 eV for Alq3, while a lower HOMO energy level for Gaq3 (5.8 eV) was determined, indicating the need of smaller potentials to oxidize Gaq3 molecules in comparison to Alq3 (6.3 eV). These relatively small differences are thought to be originated from the effects of the central metal cations of Ga^{3+} and Al^{3+} on their relative molecular quinolinate ligands. From all above investigations, it has been concluded that the application of tris (8-hydroxyquinolinate) metals in fabricating efficient solution-processed organic solar cells may be possible due to the unique photophysical features attained by Mq3 materials. Besides, the comparably high refractive index and dielectric constants of the materials revealed easily polarization of their medium upon illumination. Hence, the hypothesis of incorporating these materials into the photovoltaic devices to harvest a large amount of solar energy by the active area is reinforced. Moreover, the complementary absorption of Mq3 materials from 250 nm to 450 nm was observed, indicating their participation in harvesting the high photonic energies. Additionally, due to their relatively high optical energy gaps compared to the common organic solar cells materials, their contribution in the ternary bulk structures is become interesting to allow for the low photon energies to pass readily through the active layers so as to be absorbed by the low optical band gap components. This is where the charge carriers can be stabilized and boundaries for exciton dissociation can be enlarged instantly.

From the thermal history records of the tris (8-hydroxyquinolinate) metals, the value of glass transition temperature (T_g) for Gaq3 and Alq3 were found to be 182 ^oC and 173 ^oC, respectively. The higher T_g of Gaq3 compared to that of Alq3 indicating the presence of stronger dipolar interaction in Gaq3 than that in Alq3. The higher thermal stability for Gaq3 in comparison to Alq3 was attributed to the effect of Ga^{3+} central atom. Noteworthy, the satisfactory high T_g value of Mq3 materials is considered to have positive impacts on preserving the stability of their based devices. The photoabsorption of Mq3 materials was found to be enhanced upon thermal annealing process (with a merged broad band at 235 ^oC). This is due to the conformational changes governed by the re-arrangement of the quinolinate ligands at the high temperatures. Noteworthy, upon increasing the annealing temperature to 255 ^oC, the films showed a quenched photoluminescence (PL) response but still having a broad absorption spectrum. Such behavior was ascribed to the appearance of crystalline α-Gaq3 polymorph domains above the T_g, which was ascertained by the XRD and DSC measurements. The observed decrease in the optical energy gap (E_g) and infrared absorption bands have been attributed to the enhancement of the $\pi - \pi$ interaction and conformational changes in the films towards the increment of α-Gaq3 polymorph. A blueshift in the PL peak associated to the reconfiguration of the ligands was observed. Besides, reduced Stokes shift was noticed for the annealed films (all range of the annealing temperatures), suggesting that the structural differences between the ground and excited electronic states are mitigated in the annealed configuration of the ligands. It is concluded that Mq3 materials can be a good candidate to be applied in the organic solar cells due to their unique optoelectronic properties and high thermal stability. However, Gaq3 was seen to show better promising results over Alq3 owing to its non-monotonic change behavior in PL, absorbance, and E_g. Moreover, it has shown a higher electrochemical and thermal stability.

The studies continued with investigating the effects of Mq3 incorporation on the photovoltaic active layers and the devices electrical performance. DH6T films have been doped with various weight percentages of Mq3 to investigate its impact on the DH6T:Mq3 blends absorption energies and spectra. From the results analysis and by applying an empirical formula to fit the variation of the absorption band gap, 25% of Mq3 is found to be the optimum amount for the prescribed organic solar cells having DH6T as the host donor. The photoabsorption spectra of DH6T/Mq3/PCBM ternary bulk heterojunction blends upon incorporating the optimum amount of Mq3 revealed a considerable broadening in the absorption spectra of the films. This evidence could be referred to as the effect of Mq3 inclusion in assisting photoenergy charge transfer and increased area of the phase boundaries between the donor and acceptor moieties, thereby generating a large number of excitons in the photovoltaic active layers. The PL quenching behaviors of the ternary blend films were also supported this inherent reality. Having obtained information on the photophysical of the blend films, devices based on bilayer (BL) and bulk heterojunction (BHJ) active layers of DH6T/PCBM have been assessed. The results of the BHJ structure demonstrated an improved photovoltaic performance by a factor of 1.5 better than that of the BL structure. Nevertheless, it was found that the fill factor (*FF*) in the BHJ devices is lower compared to that of BL ones. Such phenomenon has been ascribed to the deviation in the *P-V* curves, which is thought to be originated from the morphology complexity of the donor-acceptor (D-A) phases. Consequently, the D-A blend structures are selected as a favored system to be ready for incorporating the optimum amount of Mq3 materials. Hence, the influence of Mq3 incorporation in the DH6T/Mq3/PCBM based devices on the electrical characterizations has been investigated. The *J-V* and *P-V* characteristics analysis in dark and under illumination demonstrated that the photocurrent, open circuit voltage, and the entire performance of the devices have been improved of approximately six times in comparison to the device without Mq3 incorporation. The basic contribution of Mq3 materials on this improvement route is thought to be initiated from first, the increased number of exciton generation, and their dissociation into free charge carriers. This is because of the enlarged area of the donor-acceptors boundaries among each of DH6T/Mq3 and DH6T/PCBM moieties. And second, the stabilization of charge carriers' mobility within the DH6T donor and Mq3/PCBM acceptors. This may assist to achieve the charge carriers balance between the holes and electrons transportation within the donor and acceptor components, respectively, as a consequence of Mq3 incorporation. Ultimately, the realization of tris (8-hydroxyquinolinate) metals for solution-processed organic solar cells has been obtained.

6.2 Future Works

The unique optoelectronics, photo-physical and thermal properties of Mq3 followed by their successful application in solution-processed organic solar cells based on DH6T/Mq3/PCBM ternary bulk heterojunction suggest the following research studies that should be undertaken as future works:

- Studying the optimization and effects of thermal annealing on the performance of solution-processed organic solar cells based on DH6T/Gaq3/PCBM blends. This can be done by varying the ratio of PCBM and thickness of the active layers, then for each set of devices, the effect of post thermal annealing upon the devices is carried out.
- Assessing the overall performance of solution-processed organic solar cells based on DH6T/Gaq3/PCBM blends by referring to their fabrication under different ambient conditions (e.g., room temperature and within glove boxes), then testing the devices in laboratory and outdoor conditions.
- Incorporating Gaq3 into the state of art of the solution-processed all polymer based solar cells, then studying its effect on the charge transport properties, morphological phase separation between D-A components and photovoltaic performance of the devices.