JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 10, No. 6, June 2008, p. 1468 - 1472

# Synthesis and photocapacitive studies of Cu(II) 5,10,15,20-tetrakis(4′-isopropylphenyl) porphyrin

M. SALEEM [a], M. H. SAYYAD [a,*], K. S. KARIMOV [a,b], Z. AHMAD [a],
M. SHAH [a], M. YASEEN [c], I. KHOKHAR [c], M. ALI [d]
[a]*GIK Institute of Engineering Sciences and Technology, Topi, District Swabi, N.W.F.P. 23640, Pakistan.*
[b]*Physical Technical institute of Academy of Sciences, Rudaki Ave, 33, Dushanbe 734025, Tajikistan.*
[c]*Institute of Chemistry, University of the Punjab, Lahore 54000, Pakistan.*
[d]*Government College of Science, Wahdat Road, Lahore, Pakistan.*

An organic semiconductor Cu(II) 5,10,15,20-tetrakis(4′-isopropylphenyl) porphyrin (CuTIPP) was synthesized and investigated as an active material in photocapacitive detectors. Thin films of the CuTIPP were deposited by thermal evaporator on a glass substrate with preliminary deposited metal electrodes and Al/CuTIPP/Al and Ag/CuTIPP/Ag surface type photocapacitive detectors were fabricated. Thickness of the CuTIPP films was equal to 100 nm in both detectors. Area of the semiconducting channel between metallic electrodes was equal to 40 μm × 15 mm. It was observed that under filament lamp illumination of up to 4000 lx the capacitance of the Al/CuTIPP/Al and Ag/CuTIPP/Ag photocapacitive detectors increased by 2.6 and 2.2 times, respectively, with respect to the dark conditions. The photoconductivity of the detectors increased with illumination as well. It is assumed that the photocapacitive response of the detectors is associated with polarization occurring due to the transfer of photo-generated electrons and holes. The equivalent circuit of the photocapacitive detectors is presented. Data obtained by simulation showed reasonable matching with experimental results.

(Received April 14, 2008; accepted June 4, 2008)

*Keywords:* Organic semiconductor, Cu(II) 5,10,15,20-tetrakis(4′-isopropylphenyl) porphyrin (CuTIPP), Detector, Surface-type photocapacitor, Polarization, Photoconductivity

## 1. Introduction

Organic semiconducting materials are being extensively studied for the fabrication of electric, electronic and optoelectronic devices [1-4]. Most of these devices are usually fabricated in sandwich configuration and this structure requires the deposition of organic thin films on transparent conductive electrodes using vacuum evaporator or spin coater. On top of these films, metallic electrodes are deposited, which often damage the active material.

Surface type organic thin film structures represent a simple, low cost and versatile alternative to the devices built in sandwich configuration. Because of these advantages, there is a growing interest in the fabrication and study of surface type optoelectronic devices employing organic semiconductors [5-7]. Also the surface type devices are very suitable for exploring the low cost and simple device fabrication techniques, such as spin or drop-coating, screen printing, inkjet printing, etc.

Surface type structures offer simple and low cost technology for investigating the different properties of organic materials, such as light sensitivity, electroluminescence [6], effect of humidity [7], charge transport [5] etc. The materials possessing these properties are then employed in the fabrication of a wide range of electric, electronic and photonic devices.

In [5], surface-type organic photodetector has been studied. Organic photocapacitors have been investigated for the direct storage of energy and as a light sensor [8-10]. The fabrication and study of a polymer light emitting surface cell has been reported in [6].

In order to investigate solar energy generation and its direct storage, a photocapacitor has been constructed on a multilayered photoelectrode, comprising dye-sensitized semiconductor nanoparticles/hole-trapping layer/activated carbon particles in contact with an organic electrolyte solution, in which photogenerated charges are stored at the electric double layer [8].

A high voltage photo-rechargeable photocapacitor of three-electrode configuration, comprising a dye sensitized mesoporous $TiO_2$ electrode, two carbon coated electrodes and two liquid electrolytes has been reported by Murakami *et al.* [9]. A sandwich type and a surface type photocapacitive detector employing poly-N-epoxyprophyl carbazole complexes and copper phthalocyanine respectively has been investigated by Karimov *et al.* [7,10].

Porphyrins have attracted a great deal of attraction in the fabrication of electroluminescence and solar cell devices [11-14] because of its natural role in photosynthesis, solution processability and the relative ease with which functional groups can be attached to its basic structure [15]. Thin films of different metalloporphyrins have been used as sensing materials for the development of optical sensors for the detection of different volatile organic compounds [16]. In this work, we reported the synthesis of CuTIPP and fabrication and study of a surface-type photocapacitor employing CuTIPP as a light sensitive organic semiconductor.

## 2. Experimental

### 2.1 Active material

Cu(II) 5,10,15,20-tetrakis(4′-isopropylphenyl) porphyrin was synthesized from 5,10,15,20-tetrakis(4′-isopropylphenyl) porphyrin [17] by acetate method [18]. 5,10,15,20-tetrakis(4′-isopropylphenyl) porphyrin (1 mmole, 782 mg) was dissolved in refluxing chloroform (250 ml) and a saturated solution of copper acetate in methanol (5 ml) was added. The mixture was refluxed for 4 hours and allowed to cool at room temperature and left overnight. The solvent was evaporated in vacuole to give crude solid (815 mg). The crude solid was dissolved in carbon tetrachloride and solution was passed through a column of flash silica (1 cm dia x 10 cm) eluting with carbon tetrachloride. The major red colour band was collected. The solvent was removed and a red colour solid was obtained. The product was recrystallized from a dichloromethane/methanol (2:1) mixture to afford pure crystals of 5,10,15,20-tetrakis (4′-isopropylphenyl) porphyrinatocopper (II).

### 2.2 Device fabrication

Molecular structure of the CuTIPP is presented in Fig. 1. Thin film of CuTIPP, of thickness 100 nm, were thermally sublimed on glass substrate (of sizes of 25x25x1 mm$^3$) with silver or aluminum surface-type electrodes. Gap between electrodes was 40 μm and length of the gap was 15 mm. Aluminum or silver electrodes of thickness of 200 nm, were also deposited by vacuum evaporation technique. Thickness of the CuTIPP films was measured by crystal-controlled thickness monitor [19]. All depositions were made under vacuum pressure of $10^{-4}$ Pa.

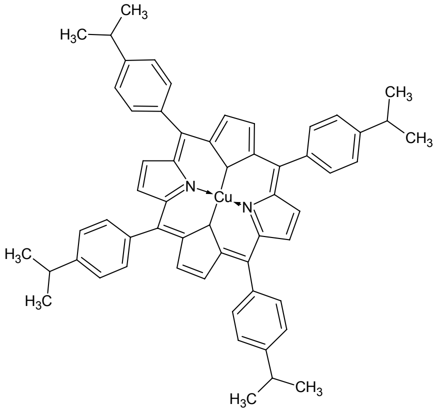


*Fig. 1. Molecular structures of CuTIPP.*

UV-VIS absorption spectrum was obtained using Lambda 19 PERKIN ELMER UV/VIS/NIR Spectrometer.

## 3. Results and discussion

Fig. 2 shows absorption spectrum of the CuTIPP film deposited by vacuum evaporation on the glass substrate. Spectrum consists of strong transitions to the second excited state ($S_0 \rightarrow S_2$) at about 423.93 nm (the Soret or B band) and weak transitions to the first excited state ($S_0 \rightarrow S_1$) at about 542.69 nm (the Q band). $S_2$ to $S_1$ internal conversation is rapid. The Soret and Q bands both arise from $\pi \rightarrow \pi^*$ transitions [20].

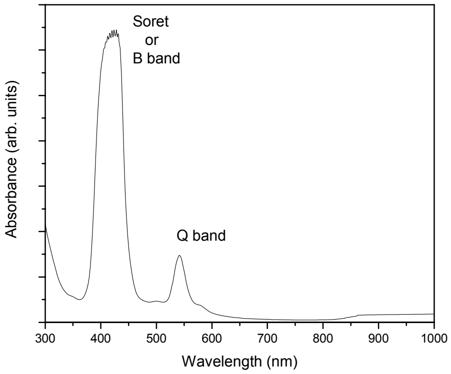


*Fig. 2. Absorption spectrum of the CuTIPP.*

Fig. 3 displays cross-sectional view of the fabricated photocapacitive detectors. Measurement of the capacitance was done by conventional instruments at the frequency of 1 kHz, at room temperature (25 ± 0.5 °C). The capacitive detectors were illuminated by filament lamp.

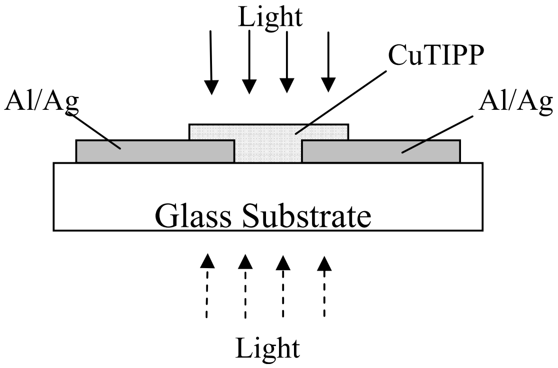


*Fig. 3. Cross-sectional view of the Al/CuTIPP/Al and Ag/CuTIPP/Ag surface-type photocapacitive detectors.*

Fig. 4 shows relative capacitance–illumination relationships for the Al/CuTIPP/Al and Ag/CuTIPP/Ag surface-type photocapacitive detectors. Here $C_{ph}$ is photocapacitance (capacitance under illumination), $C_d$ is capacitance at dark condition. $C_d$ was equal to 11 pF and 12 pF for the Al/CuTIPP/Al and Ag/CuTIPP/Ag detectors, respectively. It is seen from Fig. 4 that photocapacitances of the Al/CuTIPP/Al and Ag/CuTIPP/Ag detectors increase with increase of illumination up to 4000 lx by 2.6

and 2.2 times, respectively, with respect to dark conditions. The response of the detectors at illumination from the face and back sides approximately was the same.

The charge carriers may increase exponentially, with increase in the intensity of light. Therefore the polarizability due to the transfer of charge carriers as electrons and holes may increase as well.

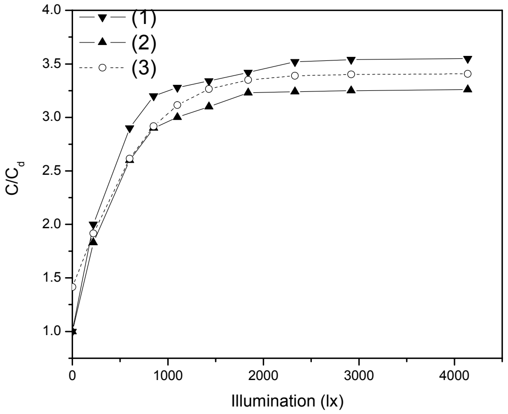


*Fig. 4. Relative capacitance–illumination relationships for the Al/CuTIPP/Al (1) and Ag/CuTIPP/Ag (2) surface-type photocapacitive detectors, (3) is calculated result.*

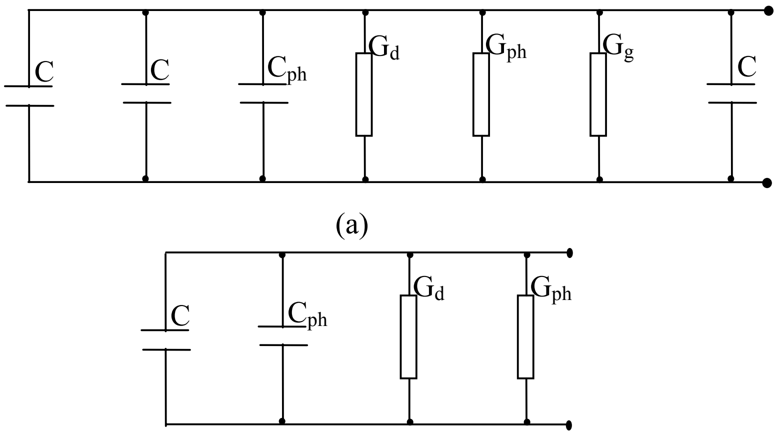
Fig. 4 indicates that the response of Al/CuTIPP/Al detector is higher than that of Ag/CuTIPP/Ag one. It is well-known that Al forms usually Schottky-type rectifying junction and Ag forms ohmic contact with organic semiconductors [21]. It means that in the case of Al electrode, depletion region is formed at the junction interface. Therefore, the ratio of concentration of photo-induced charges to concentration of charges at dark condition is higher for depletion region with respect to other sides of semiconductor under illumination. Probably it is the main reason for better performance of the Al/CuTIPP/Al detector with respect to Ag/CuTIPP/Ag one.

The capacitance value depends on polarizability of the material [21,22] and basically there are several sources of it as dipolar $P_{dip}$, ionic $P_i$ and electronic $P_e$ polarizability. In this case we may neglect dipolar $(P_{dip})$ polarizability due to absence of visible dipoles in the molecular structures of the CuTIPP (Fig. 1). Electronic polarizability is most universal and arises due to relative displacement of the orbital electrons. As the CuTIPP may comprise internal charge-transfer complex we can assume that ionic polarization takes place as well in this organic semiconductor. The ionic and electronic polarizability probably affect to dark capacitance at low frequency (1 kHz) measurements of capacitance. In earlier studies [23-25], it was investigated that polarizability $(P_{td})$, due to the transfer of charge carriers, is present both at illuminated and under dark conditions. Therefore we may write for the total polarizability at dark conditions $(P_d)$ as:

$$P_d = P_i + P_e + P_{td} \tag{1}$$

Charge carriers increase due to illumination. Thus the polarizability due to transfer of charge carriers also increase. For the samples under illuminated conditions, the total polarizability $(P)$ may be as following:

$$P = P_i + P_e + P_t \tag{2}$$



(a)

(b)

*Fig. 5. Detailed (a) and simple (b) equivalent circuits of the Al/CuTIPP/Al and Ag/CuTIPP/Ag surface-type photocapacitive detectors: $C_a$ is capacitance with air dielectric, $C_d$ is capacitance with CuTIPP dielectric at dark condition, $C_{ph}$ is capacitance with CuTIPP dielectric due to illumination, $G_d$ is dark conductance of CuTIPP, $C_g$ and $G_g$ are capacitance and conductance due to glass dielectric (substrate).*

where $P_t$ is polarizability under illumination due to the transfer of electron/holes charge carriers. Here we take into consideration that concentration of charge carriers and total polarizability $(P)$ are illumination dependent.

In general, the relationship between relative dielectric constant, molecular concentration $(N)$, (or $N_d$ as concentration of the electron/holes at dark conditions) and polarizability $(P)$ of the molecules is determined by Clausius-Mossotti Equation [22]:

$$\frac{\varepsilon_{rd}-1}{\varepsilon_{rd}+2}=\frac{N_d P_d}{3\varepsilon_\circ} \qquad (3)$$

where $\varepsilon_{rd}$ is relative permittivity or dielectric constant at dark condition and $\varepsilon_\circ$ is permittivity of free space.

From Eq. (3), relative dielectric constant at dark conditions may be written as:

$$\varepsilon_{rd}=\frac{3\varepsilon_\circ+2N_d P_d}{3\varepsilon_\circ-N_d P_d} \qquad (4)$$

Similarly, relative dielectric constant $(\varepsilon_r)$ under illumination conditions can be obtained as:

$$\varepsilon_r=\frac{3\varepsilon_\circ+2NP}{3\varepsilon_\circ-NP} \qquad (5)$$

Hence, relative capacitance relationship can be written as:

$$\frac{\varepsilon_r}{\varepsilon_{rd}}=\frac{C}{C_d}=\frac{3\varepsilon_\circ+2NP}{(3\varepsilon_\circ-NP)\varepsilon_{rd}} \qquad (6)$$

where $C$ is photocapacitance (capacitance under illumination), $C_d$ is capacitance at dark condition. The concentration of charge carriers i.e. electrons and holes $(N)$, is sensitive to illumination. Thus the factor $NP$ in Eq. 6 depends on intensity of light $J$. Here we assume their relationship as:

$$NP=N_d P_d(1.5-0.5e^{\frac{-J}{439}}) \qquad (7)$$

By substitution of this assumption into Eq. 6, following empirical expression can be obtained:

$$\frac{C}{C_d}=\frac{3\varepsilon_\circ+2N_d P_d(1.5-0.5e^{\frac{-J}{439}})}{[3\varepsilon_\circ-N_d P_d(1.5-0.5e^{\frac{-J}{439}})]\varepsilon_{rd}} \qquad (8)$$

This expression can be used for simulation of the relative capacitance $(\frac{C}{C_d})$-illumination intensity $(J)$ relationship for photocapacitive detector.

From Eq. 8, the product $N_d P_d = 1.33\times10^{-4}$ F/m may be calculated in the case of dark conditions $(J=0, C=C_d)$. Here we assumed that $\varepsilon_{rd}=2.75$, it is average value for low molecular weight organic semiconductors [21,23].

Comparison of experimental and simulated results (by Eq. 8) of relative capacitance-illumination relationship is presented in Fig. 5. It is seen that both results show reasonable agreement.

A detailed equivalent circuit of the surface-type photocapacitive detectors is given in Fig. 5(a). Assuming that properties of the surface-type capacitive detector depend on properties of photosensitive organic semiconductor CuTIPP, we developed simplified equivalent circuit (b) as well. The equivalent circuit reflects the point that the phenomena of photocapacitance and photoconductivity have a common physical reason and both are due to photogeneration of charge carriers (electron/holes) under illumination. From the point of technology, fabrication of surface-type photocapacitive detectors is more simple than that of sandwich-type ones.

## 4. Conclusions

The properties of the surface-type Al/CuTIPP/Al and Ag/CuTIPP/Ag photocapacitive detector were investigated. It was observed that under filament lamp illumination of up to 4000 lx the capacitance of the Al/CuTIPP/Al and Ag/CuTIPP/Ag photocapacitive detectors increased by 2.6 and 2.2 times, respectively. It is assumed that in general the photocapacitive response of the detector is associated with polarization due to the transfer of photo-generated electrons and holes. Calculated results reasonably matched with experimental. Equivalent circuit of the detector was developed.

### Acknowledgements

We are thankful to GIK Institute of Engineering Sciences and Technology and Institute of Chemistry, University of the Punjab for the support extended to this work. Four of us, Muhammad Saleem, Zubair Ahmad, Mutabar Shah and Muhammad Yaseen acknowledge Higher Education Commission Pakistan for fellowship.

## References

[1] M. Saleem, M. H. Sayyad, Zubair Ahmad, Kk. S. Karimov, Optoelectronic Adv. Mater. – Rapid Comm. **1**(9), 477 (2007).

[2] M. H. Sayyad, K. ul Hasan, M. Saleem, Kh. S. Karimov, F. A. Khalid, M. Karieva, Kh. Zakaullah, Zubair Ahmad, Eurasian Chem. Tech. Journal **9,** 57 (2007).
[3] A. Elahi, M. H. Sayyad, Kh. S. Karimov, Kh. Zakaullah, M. Saleem, Optoelectronic Adv. Mater. – Rapid Comm. **1**(7), 333 (2007).
[4] Kh. S. Karimov, M. H. Sayyad, M. Ali, M. N. Khan, S. A. Moiz, K. B. Khan, H. Farah, Z. M. Karieva, J. Power Sources **155**, 475 (2006).
[5] T. Agostinelli, M. Caironi, D. Natali, M. Sampietro, P. Biagioni, M. Finazzi, L. Duó, Journal of Applied Physics **101**, 114504 (2005).
[6] G. Mauthner, K. Landfester, A. Köck, H. Brückl, M. Kast, C. Stepper, E. J. W. List, Organic Electronics **9**, 164 (2008).
[7] Kh. S. Karimov, I. Qazi, T. A. Khan, P. H. Draper, F. A. Khalid, M. M. Tahir, Eviron Monit Assess, DOI 10.1007/s10661-007-9898-5 .
[8] T. Miyasaka, T. Murakami, Applied Physics Letters **85**, No.17, 3932-3934 (2004).
[9] T. Murakami, N. Kawashima, T. Miyasaka, Chem. Commun. 3346-3348 (2005).
[10] Kh. Karimov, K. Akhmedov, I. Qazi, T. A. Khan, J. Optoelectron. Adv. Mater. **9**(9), 2867-2872 (2007).
[11] M. H. Andreasson, J. Mårtensson, T. G. Andersson, Current Applied Physics **8**, 163-166 (2008).
[12] H. S. Kim, C. H. Kim, C. S. Ha, J. K. Lee, Synthetic Metals **117**, 289 (2001).
[13] A. Chowdhury, J. Chowdhury, P. Pal, A. J. Pal, Solid State Communications **107**(12), 725 (1998).
[14] N. C. Maiti, M Ravikanth, Journal of Photochemistry and Photobiology A: Chemistry **101**, 7 (1996).
[15] M. P. Balanay, C. V. P. Dipaling, S. H. Lee, D. H. Kim, K. H. Lee, Solar Energy Materials and Solar Cells **91**, 1775 (2007).
[16] C. D. Natalea, D. Salimbenia, R. Paolesseb, A. Macagnanoa A. D'Amicoa, Sensors and Actuators B: Chemical , **65**(1-3), 220 (2000).
[17] A. D. Alder, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, L. Korsakoff, J. Org. Chem. **32**, 476 (1967).
[18] M. F. Hudson, K. M. Smith, Tetrahedron Lett. 2223 (1974).
[19] M. Madou, Fundamentals of Microfabrication, CRC Press, Boca Raton, New York (1995).
[20] H. L. Anderson, Chem. Commun. 2323-2330 (1999).
[21] F. Gutman, L. E. Lyons, Organic Semiconductors, Robert E. Kriege Publishing Company, Malabar, Florida (1980).
[22] M. Ali Omar, Elementary Solid State Physics: Principles and Applications, Published by Pearson Education (Singapore) Pte.Ltd. (2002).
[23] Organic Semiconductors, Edited by V. A. Kargin, Nauka, Moscow (1968).
[24] M. Iwamoto, T. Manaka, Proc. Int. Symp. Super-Functionality Organic Devices, IPAP Conf. Series 6, 2005, pp. 63-68.
[25] F. Amy, C. Chan, A. Kahn, Organic Electronics **6**, 85(2005).

---

*Corresponding author: sayyad@giki.edu.pk,
hsayyad62@hotmail.com