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Cu(II) 5,10,15,20-tetrakis(4-isopropylphenyl) porphyrin based photo capacitive Detectors

By

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Abstract:

In this study a photosensitive 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 sublimation on a glass substrate with preliminary deposited metal electrodes and Al/CuTIPP/Al and Au/CuTIPP/Au surface type photocapacitive detectors were fabricated. Thickness of the CuTIPP films was equal to 100 nm in the Al/CuTIPP/Al and Au/CuTIPP/Au detectors. Length and width of the semiconducting channel between metallic electrodes were equal to 40 μm and 15 mm, respectively. It was observed that under filament lamp illumination of up to 4000 lx the capacitance of the Al/CuTIPP/Al and Au/CuTIPP/Au 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.

Keywords:

Organic semiconductor, Cu(II) 5,10,15,20-tetrakis(4′-isopropylphenyl) porphyrin (CuTIPP), detector, surface-type photocapacitor, polarization, photoconductivity

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1. Introduction:

At present organic semiconductors have attracted much attention due to their interesting properties and potential applications for solar cells, light emitting diodes, field effect transistors and different kinds of detectors [1-4]. Fabrication and investigation of a self-charging photocapacitor for direct conversion and storage of solar energy has been reported by Miyasaka and Murakami [5]. The photocapacitor was constructed on a multilayred photoelectrode comprising dye-sensitized semiconductor TiO_2 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. 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 have been investigated by Murakami et al. [6]. As far as capacitive detector is concerned investigations have been made of a piezocapacitive detector with poly-O-phthalanthracenate under uniaxial compression [7]. The photosensitive organic semiconductors such as poly-N-epoxypropylcarbazole (PEPC) that have the potential for applications in electronic engineering, photoelectric converters such as solar cells, an electrophotographic material and electronic switch [8,9] was used for fabrication of photocapacitive detectors. In [10,11,12] Complexes of poly-N-epoxypropylcarbazole (PEP)with oligomeric salt of perily (OSP) and tetracyanoquinodimethane (TCNQ) were prepared. Using these complexes as photoactive materials CG/PEPC-OSP/Ag and CG/PEPCTCNQ/Al sandwhich-type photocapacitive detectors were fabricated and their properties were investigated. They were observed sensitive in the visible spectral region. In another study, a surface-type copper phthalocyanine (CuPc) based photocapacitive detector [13] was reported. This detector had the following structure: Ag/CuPc/Ag. The photocapacitance of the detector increased continuously up to 20% at 1000 lx relative to the dark condition. In this article, we report the results of investigations of an organic semiconductor Cu(II) 5,10,15,20-tetrakis(4′-isopropylphenyl) porphyrin (CuTIPP) surface-type photocapacitive detectors.

2. EXPERIMENTAL:

Cu(II) 5,10,15,20-tetrakis(4′-isopropylphenyl) porphyrin was synthesized from 5,10,15,20-tetrakis(4′-isopropylphenyl) porphyrin [14] by acetate method [15] and the molecular structure of CuTIPP is shown in figure 1. Thin film of CuTIPP, of thickness 100 nm, were thermally sublimed on glass substrates of sizes of $25x25x1\ mm^3$ with gold or aluminum surface-type electrodes at 10^{-4} Pa and Al/CuTIPP/Al and Au/CuTIPP/Au detectors were fabricated. Gap between electrodes was equal to 40 μm, the length of the gap was 15 mm. Aluminum or gold 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 [16].

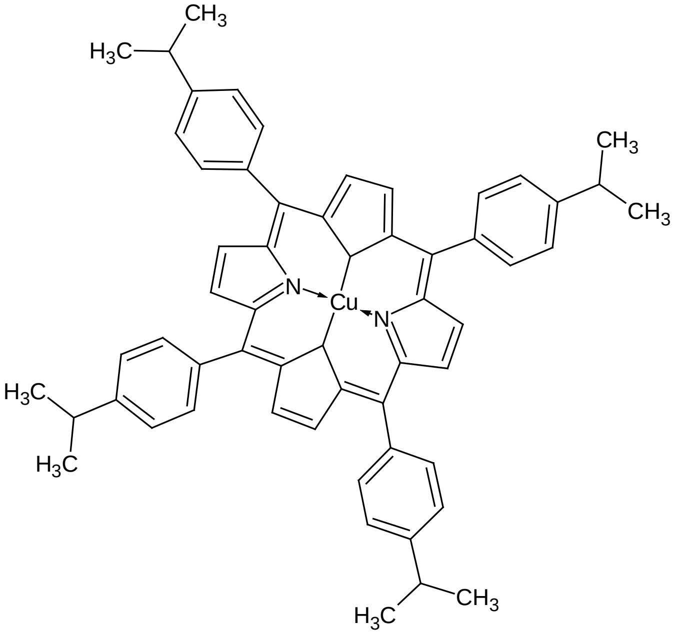


***Figure (1):** Molecular structures of CuTIPP*

Figure 2 shows 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.

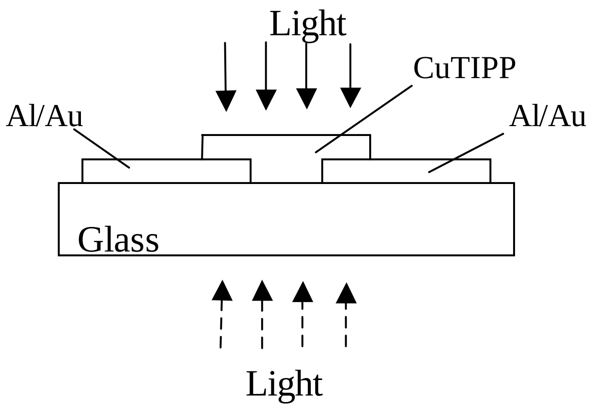


***Figure (2):** Cross-sectional view of the Al/CuTIPP/Al and Au/CuTIPP/Au surface-type photocapacitive detectors*

3. RESULTS AND DISCUSSION:

Figure 3 shows relative capacitance–illumination relationships for the Al/CuTIPP/Al and Au/CuTIPP/Au 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 Au/CuTIPP/Au detectors, respectively. It is seen from Figure 3 that photocapacitances of the Al/CuTIPP/Al and Au/CuTIPP/Au detectors increase with increase of illumination of 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.

In the effect of light concentration of charge carriers may increase exponentially. Therefore the polarizability due to the transfer of charge carriers as electrons and holes may increase as well.

Figure 3 shows that the response of Al/CuTIPP/Al detector is higher than of Au/CuTIPP/Au one. It is well-known that Al forms usually Schottky-type rectifying junction and Au forms ohmic junction with organic semiconductors [1,3,9,17]. It means that in the case of Al electrode depletion region is formed in 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 of better performance of the Al/CuTIPP/Al detector with respect of the Au/CuTIPP/Au one.

As is known [17,18] the capacitance value depends on polarizability of the material and basically there are several sources of it such as dipolar α_{dip}, ionic α_i and electronic α_e polarizability. In this case we may neglect the dipolar (α_{dip}) polarizability due to absence of visible dipoles in molecular structures of the CuTIPP. 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 polarizabilities probably affect the dark capacitance at low frequency (1 kHz) measurements of capacitance. In [19-21] it was investigated the polarizability due to the transfer (α_{td}) of charge carriers as electrons and holes that are present at normal, including at dark conditions. Therefore we may write for the total polarizability at dark conditions (α_d):

$$\alpha_d = \alpha_i + \alpha_e + \alpha_{td} \quad (1)$$

For the illuminated samples the total polarizability (α) may be the following

$$\alpha = \alpha_i + \alpha_e + \alpha_t \quad (2)$$

where α_t is polarizability under illumination due to the transfer of electrons/holes as charge carriers. Here we take into consideration that concentration of charge carriers and total polarizability (α) are illumination dependent.

In general, the relationship between relative dielectric constant and molecular concentration, N, (or N_d as concentration of the electron/holes at dark conditions) and polarizability of the molecule is determined by Clausius-Mosotti relation [18] :

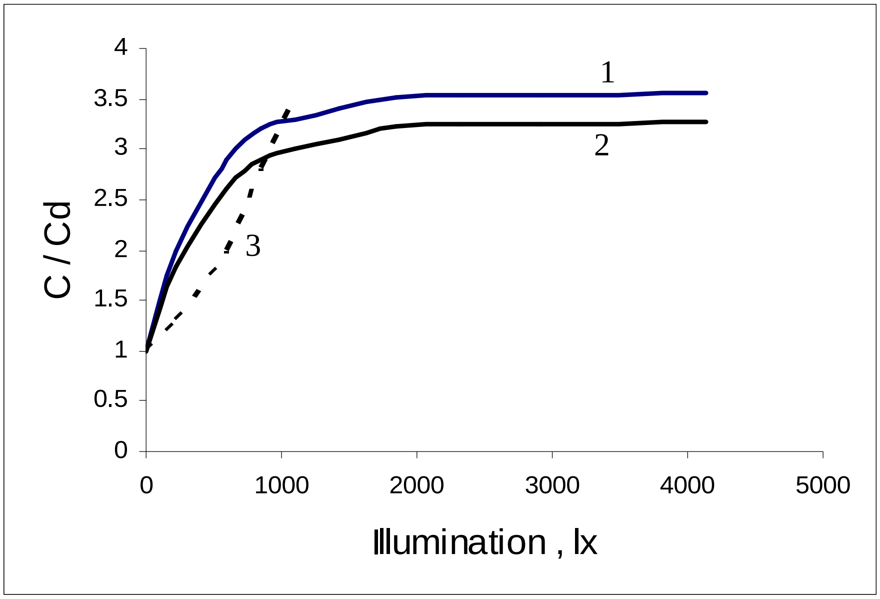


Figure (3): *Relative capacitance versus illumination for the Al/CuTIPP/Al (1) and Au/CuTIPP/Au (2) surface-type photocapacitive detectors, (3) calculated result.*

$$(\varepsilon_d - 1) / (\varepsilon_d + 2) = N_d \alpha_d / 3\varepsilon_o \qquad (3)$$

where ε_d is relative permittivity, ε_o is permittivity of free space. On the base of this equation the following expression was derived [12,13]:

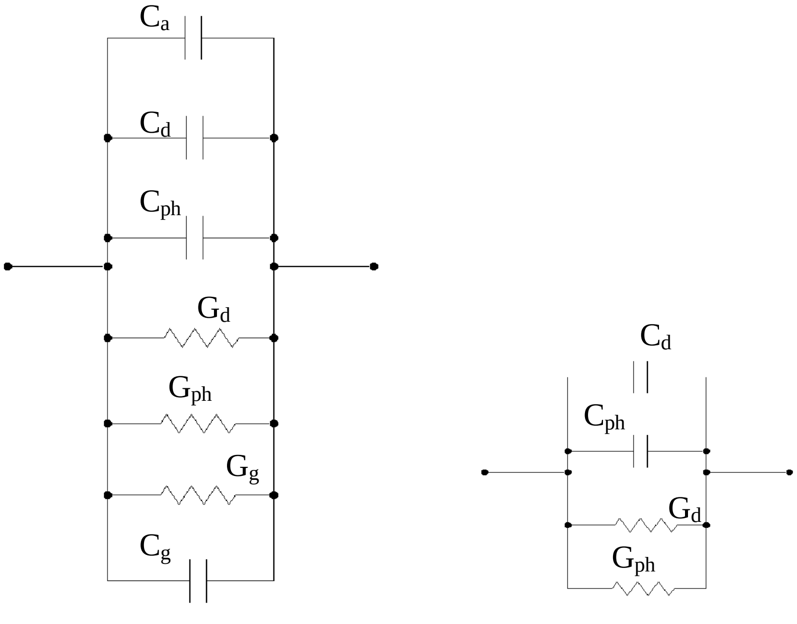
$$C / C_d = [1 + 2N_d\, \alpha_d\, (1+ kJ) / 3\, \varepsilon_o] / [1 - N_d\, \alpha_d\, (1 + kJ) /3\, \varepsilon_o]\varepsilon \qquad (4)$$

where C is photocapacitance (capacitance under illumination), C_d is capacitance at dark condition, k is photocapacitive factor, J is intensity of light or illumination.

From Eq. 4 it may be calculated in the case of dark conditions, $J=0$, $C=C_d$, the product $N_d\, \alpha_d = 1.3\times10^{-11}$ F/m. Here we assumed that $\varepsilon_d = 4$, it is average value for low molecular organic semiconductors [13,17,19].

Figure 4 shows the experimental relative capacitance versus illumination relationship and the simulated results by Eq. 4. It is seen that both graphs show reasonable agreement at low illumination range only (up to 500 lx). In this case $k = 6.6\times10^{-4}$ (1/lx).

Assuming that properties of the surface-type capacitive detector, first of all, depend on properties of photosensitive organic semiconductor CuTIPP, we developed simplified equivalent circuit (Figure 4b) as well. The equivalent circuit reflects the point that photocapacitance and photoconductivity phenomena have a common physical reason as photogeneration of electrons/holes under illumination. From the point of technology, fabrication of surface-type photocapacitive detectors is more simple than of sandwich-type ones.



(a) (b)

Figure (4): *Detailed (a) and simple (b) equivalent circuits of the Al/CuTIPP/Al and Au/CuTIPP/Au 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).*

4. Conclusions:

The properties of the surface-type Al/CuTIPP/Al and Au/CuTIPP/Au 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 Au/CuTIPP/Au 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.

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