

# Organic Photodetectors Based on Phthalocyanine and Fullerenes: Dielectric Properties

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Fabrication and characterization of organic photodetectors based on copper phthalocyanine and fullerenes are presented. We study current–voltage and impedance characteristics of the devices under dark and varied illumination conditions. The current–voltage characteristics in the reverse bias show little or no dark current and large photocurrent. The results show that photocurrent in the devices is associated with a decrease in bulk resistance and an increase in dielectric constant of the active material.

**Keywords:** Organic Photodetectors, Impedance Spectroscopy, Donor/Acceptor Interfaces, Copper Phthalocyanine, Fullerenes.

## 1. INTRODUCTION

In recent years, organic photodetectors<sup>1–8</sup> and photovoltaic devices<sup>7–13</sup> show great interest because of their potential in electronic and optoelectronic applications. In organic photodetectors, photogenerated excitons are dissociated at donor/acceptor interfaces. Under reverse bias, the carriers move to the opposite electrodes to result in photocurrent in the external circuit. In general, dark current in a photodetector should be low in a sensitive photodetector.

The advantages of using organic materials in photodetectors are broadly two-fold. With a suitable organic-metal combination, carrier-injecting barriers can be increased to reduce the dark current that would increase the sensitivity of the detectors. Secondly, spectral response of the device can be tuned by selecting organic materials with suitable absorption spectra. In general, conjugated polymers or organic dyes with low ionization potential are used as donors to transport the holes. Fullerenes with high electron affinity, on the other hand, are used as acceptor materials to transport electrons to the other electrode. In such cases, molecular orbitals at the interface energetically favor exciton dissociation to result in free-electrons and free-holes to yield photocurrent in the external circuit.

Impedance or dielectric spectroscopy is a powerful tool to study relaxation and loss processes in organic and inorganic materials. Impedance spectroscopy of organic light-emitting and photovoltaic devices provided information about transport properties, bulk resistance, and dielectric

parameters of the active material.<sup>14–17</sup> In addition, equivalent circuit of different device architectures can also be formulated from the dielectric measurements. Formation of any depletion region near the interface, which provides the necessary field for exciton dissociation, can also be analyzed from the dielectric spectroscopy.

In this respect, impedance spectroscopy of organic photodetectors is novel. In this article, we present results on the fabrication and characterization of photodetectors based on a phthalocyanine and fullerenes to study their electrical and dielectrical properties under dark and illumination conditions.

## 2. EXPERIMENTAL DETAILS

Copper (II) phthalocyanine (CuPc) and buckminsterfullerenes (C<sub>60</sub>, C<sub>70</sub>) were purchased from Aldrich and MER Corporation, Tucson, respectively. Thin films were thermally evaporated in vacuum on indium tin oxide (ITO) coated glass substrates. Sequential evaporation of CuPc and C<sub>60</sub> (or C<sub>70</sub>) from dual filaments resulted donor/acceptor-type bilayer heterostructures. Finally, aluminum (Al) as top electrode was thermally evaporated to result in ITO/CuPc/C<sub>60</sub>/Al and ITO/CuPc/C<sub>70</sub>/Al devices. For all the thermal evaporations, vacuum was less than 10<sup>−6</sup> Torr. Thickness of CuPc and buckminsterfullerenes were 100 nm each. Area of the devices, as defined by the cross-section of the electrodes, was 6 mm<sup>2</sup>.

For electrical characterization, the devices were kept in a shielded vacuum chamber with an optical window. Current–voltage (*I*–*V*) characteristics were recorded under

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dark and illumination conditions. Illumination was provided through a xenon lamp. Intensity of white light was varied between 10–100 mW/cm<sup>2</sup> with the help of neutral density filters. A Yokogawa 7651 dc voltage source and a Keithley 486 Picoammeter were interfaced to record *I*–*V* characteristics. Bias was applied with respect to Al electrode and was varied in steps of 50 mV. Current was recorded after 1 to 10 s, so that displacement current due to voltage scan speed remains low. Additionally, voltage was scanned to both directions to eliminate any trace of displacement current. Impedance characteristics of the devices under dark and different illumination conditions were recorded through a Solartron 1260 impedance analyzer. While the amplitude of test voltage was 100 mV rms, its frequency was varied from 1 Hz to 100 kHz.

### 3. RESULTS AND DISCUSSION

#### 3.1. Current–Voltage Characteristics

Electronic absorption spectra of the individual components of the photodetectors, and the heterostructures are shown in Figure 1. The spectra show the range over which the device should remain active. Reported values of highest-occupied molecular orbitals (HOMO) and lowest-unoccupied molecular orbitals (LUMO) of CuPc are 5.0 and 3.0 eV, respectively. They, in conjunction with HOMO and LUMO values of 7.5–7.3 and 2.6–2.7 eV for fullerenes, favored exciton dissociation at the CuPc/fullerene interface. The energy band diagram is also favorable for hole and electron transport through the HOMO of CuPc and LUMO of fullerenes, respectively, to the opposite electrodes to yield photocurrent in the external circuit. In other words, the carriers did not face large barriers at the respective metal electrodes.

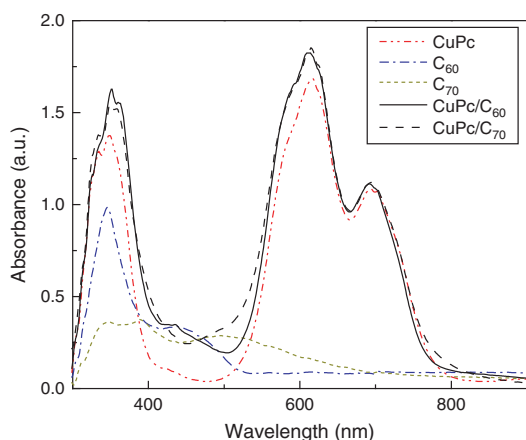


**Fig. 1.** Electronic absorption spectra of CuPc, C<sub>60</sub>, C<sub>70</sub>, CuPc/C<sub>60</sub>, and CuPc/C<sub>70</sub> films.

The CuPc/C<sub>60</sub> and CuPc/C<sub>70</sub> devices under dark condition, as shown in Figures 2(a) and (b), respectively, display very little current in the reverse bias direction. This shows that the injecting contacts from the metals were blocking in nature. Such a contact in general favors photodetection. Upon photoexcitation, the devices showed a large response for the whole voltage range studied. The *I*–*V* characteristics of the CuPc/C<sub>60</sub> and CuPc/C<sub>70</sub> devices under dark and at different illumination conditions are shown in Figures 2(a) and (b), respectively. Photocurrent increased with an increase in bias amplitude and illumination intensity.

In a photovoltaic device, the internal field at the donor/acceptor interface is the only driving force to dissociate excitons. In a photodetector, the external electric field due to the applied voltage is the additional parameter that augments exciton dissociation. Hence, with an increase in the amplitude of reverse bias, more and more photogenerated-excitons are dissociated into electrons and holes. Since the charge carriers do not face any

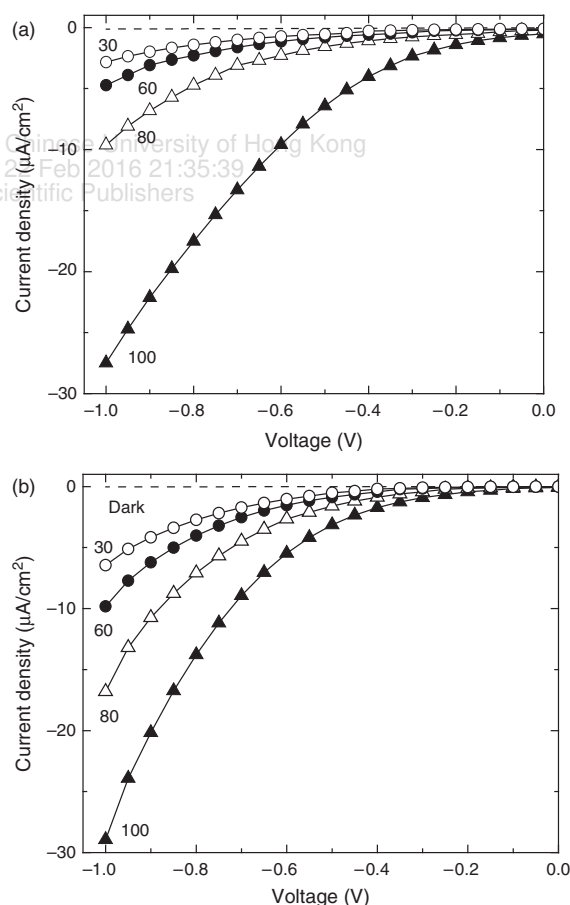


**Fig. 2.** Reverse bias section of current–voltage characteristics of (a) CuPc/C<sub>60</sub> and (b) CuPc/C<sub>70</sub> devices under dark and different illumination intensities. Legends specify illumination intensities in mW/cm<sup>2</sup>.

barrier at the opposite electrodes, amplitude of photocurrent increases with that of the external (reverse) bias. This is in contrast to the scenario under dark condition, where the amplitude of dark-current shows very little increase with that of the applied voltage. Such a low dark-current is in general due to large carrier-injecting barriers (from the electrode) at the reverse bias.

To compare the results presented in Figure 2, they have been summed in Figure 3 as plots of photocurrent at  $-1$  V versus light intensity. The photocurrent increased with an increase in the light intensity. The plot in Figure 3 shows that the photocurrent response was higher in the CuPc/C<sub>70</sub> device as compared to the one with CuPc/C<sub>60</sub>. This was however due to higher dark current in the former case as evidenced by higher intercept with the y-axis. The photocurrent increased linearly with the light intensity. The slope however differed from the low intensity region to the high one. For light intensities below  $70$  mW/cm<sup>2</sup>, the slope was around unity for both the devices. Since with an increase in photoexcitation intensity, higher excitons (and hence higher carriers) are generated, photocurrent increased with the intensity with a slope of unity. This additionally implies that the fraction of the photogenerated carriers that contributed to photocurrent in the external circuit did not change with increase in the illumination intensity. Such a linear behavior is ideal and prerequisite for a photodetector, so that a straightforward readout of light intensity from the photocurrent becomes possible. At higher light intensity region, the slope of plots rose to 2. Such a dependence may be due to an increase in the carrier mobility at higher concentration of charge carriers in the device.<sup>18</sup> The higher carrier mobility, in addition to higher dissociable excitons, can lead to a superlinear slope in the photocurrent versus light intensity plot (above  $70$  mW/cm<sup>2</sup>).

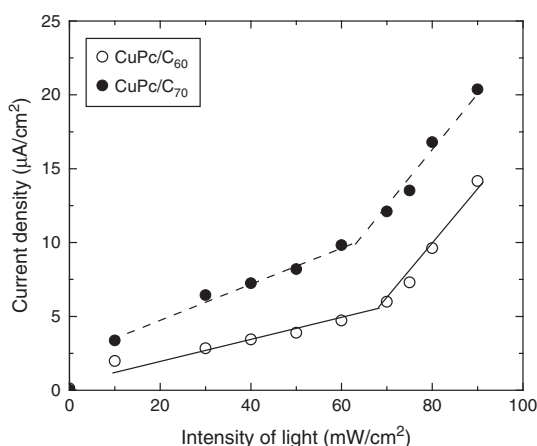


**Fig. 3.** Current density at  $-1$  V versus illumination intensity of CuPc/C<sub>60</sub> and CuPc/C<sub>70</sub> devices. The line segments are best fits to the experimental points below  $70$  mW/cm<sup>2</sup> and above illumination range.

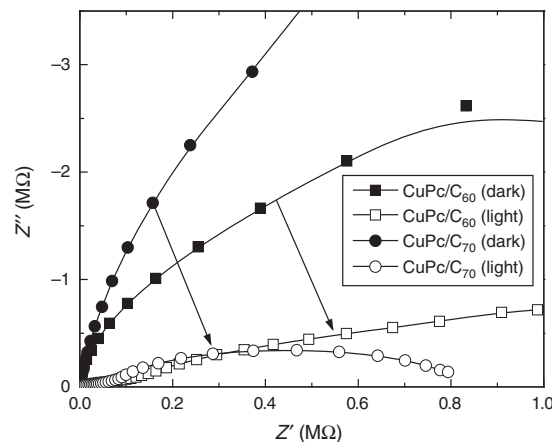


**Fig. 4.** Real versus imaginary components of complex impedance of CuPc/C<sub>60</sub> and CuPc/C<sub>70</sub> devices under dark and  $100$  mW/cm<sup>2</sup> illumination. DC bias was  $-1$  V. Arrows represent the change due to illumination.

### 3.2. Impedance Spectroscopy

We have carried out impedance spectroscopy of the devices under dark and varied illumination conditions. Such measurements isolate the effects of resistive and dielectric components of the photodetectors. Figure 4 represents variation of real ( $Z'$ ) and imaginary ( $Z''$ ) components of complex impedance (Cole-Cole plot) of the CuPc/C<sub>60</sub> and CuPc/C<sub>70</sub> devices with the frequency of ac test voltage as an independent parameter. Each of the Cole-Cole plots showed a semicircle or signs of it. The semicircles in Figure 4 suggest that the devices could be modeled to a parallel combination of a resistor and a capacitor ( $C_p$ - $R_p$ ). Such a  $C_p$ - $R_p$  combination represents bulk of the device. For both CuPc/C<sub>60</sub> and CuPc/C<sub>70</sub> cases, the radius of the semicircular Cole-Cole plots, which represents bulk resistance of the device, decreased with increase in illumination intensity.

A decrease in  $R_p$  of the devices under illumination occurs due to flow of current in the external circuit. Here, carrier injection from either of the electrodes did not become enhanced; photogenerated carriers yielded higher current at the same applied voltage (with respect to that in the dark) implying an effective decrease in bulk resistance ( $R_p$ ) under illumination. In addition, the plots under illumination near the origin showed a sign of a smaller semicircle, which represents another  $C_p$ - $R_p$  combination in series with the bulk  $C_p$ - $R_p$ . The carriers generated due to dissociation of photogenerated excitons may have concentrated at the donor/acceptor interface to result in two equivalent  $C_p$ - $R_p$  combinations in series.

A decrease in the bulk resistance under illumination can best be visualized in Figure 5(a), where  $R_p$  of the devices have been plotted as a function of the test frequency. The plots show that for the whole range of frequency, the  $R_p$  for both the devices decreased under illumination.

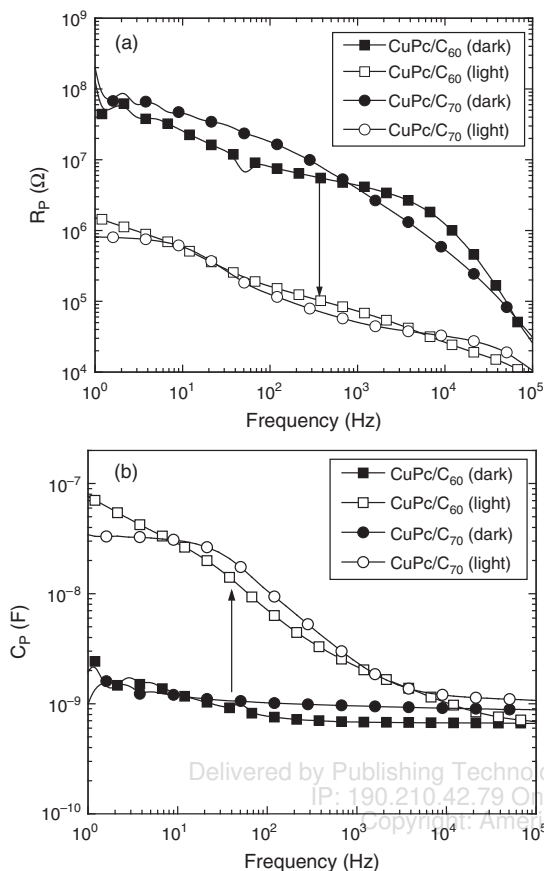


**Fig. 5.** (a) Bulk resistance ( $R_p$ ) and (b) bulk capacitance ( $C_p$ ) of the CuPc/C<sub>60</sub> and CuPc/C<sub>70</sub> devices as a function of test frequency under dark and 100 mW/cm<sup>2</sup> illumination. DC bias was  $-1$  V. Arrows represent the change in the respective cases due to illumination.

The ratio of the resistances was mostly frequency independent. This implies that the ionic conduction did not contribute to the photocurrent in the devices. The capacitance of the devices, which represents dielectric constant of the active material, on the other hand, has showed an increase due to illumination. Figure 5(b) shows that for both the devices, dielectric constant increased for the whole range of frequency—the increase being more in the low frequency region. An increase in the dielectric constant means that more charges can now be stored at the parallel plates of the capacitor. This shows that charge accumulation must have occurred at the donor/acceptor interface. A charge accumulation within the device (at the interface), which can be considered as oriented electrical dipoles, in turn results in an increase in the capacitance of the devices or dielectric constant of the active layers. The results hence show that in a photodetector, photocurrent can be considered to be associated with a decrease in bulk resistance and an increase in dielectric constant of the active material. While the decrease in the bulk resistor

has been due to flow of photocurrent without any increase in carrier injection from the electrodes, the latter (increase in dielectric constant) has been due to the dissociated carriers acting as electrical dipoles at the donor/acceptor interface.

#### 4. CONCLUSIONS

To summarize, we have fabricated photodetectors based on CuPc and fullerenes and characterized their resistive and dielectric properties. Under reverse bias, dark current was low and photocurrent was observed in both CuPc/C<sub>60</sub> and CuPc/C<sub>70</sub> devices. At low illumination range, photocurrent of the devices increased with light intensity with a slope of unity. At the higher range, the slope was 2, which could be due to increased carrier-mobility at a higher carrier concentration. From impedance spectroscopy of the photodetectors under dark and illumination conditions, we modeled the devices to their electrical analogue. We also separated out the changes in resistive and dielectric components of the devices due to illumination. The results show that the photocurrent in such devices was associated with a decrease in bulk resistance and an increase in dielectric constant.

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