Effect of UV-Ozone Exposure on PCBM

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Abstract—The effect of ultraviolet (UV)-light ozone exposure on phenyl-C61-butyric acid methyl ester ($PC_{61}BM$) is studied using solid-state modification of the material. In this study, solution processed PCBM films that have been deposited and dried over glass were exposed to UV ozone at ambient temperature and pressure from 0 to 120 min. Core-level and valence-band photoelectron spectroscopy studies indicate that the UV-ozone-induced oxidation results in C-O-C bonds in PCBM and a change in the highest occupied molecular orbital level, respectively. The modification of PCBM with C-O-C binding was observed from 5 to 60 min, but further exposure, typically beyond 120 min, was found to degrade the material. A solubility study also showed an exposure time-dependant solubility change of the material, in solvents like toluene and acetone, where it indicates the change in the chemistry of the material that can be related to the C-O-C binding of the material by the exposure. The method is an easily implementable approach for flexibility on choice of solvents for PCBM, and it has implications on the processing and stability of the material.

Index Terms—Oxidation and solubility, phenyl-C61-butyric acid methyl ester (PCBM), ultraviolet (UV)-ozone.

I. INTRODUCTION

PHENYL-C61-butyric acid methyl ester ($PC_{61}BM$) is a material of interest for emerging next-generation organic solar cells. The material is a modification of fullerene (C_{60}), which was first discovered in 1985 and is one of the most novel materials for the 21st century as its pure and modified form has wide application in organic electronic and photovoltaic (OPV) devices [1]–[4]. The small molecule-based PCBM is used as electron acceptor material mainly with poly(3-hexylthiophene) (P3HT), electron donor material in organic solar cells. The preference of the material as electron acceptor is mainly due to the high electron affinity of the material. While there are varieties of n-type organic and inorganic acceptor materials, e.g., ZnO

and TiO_2, PCBM with a matching electron donor has by far enhanced OPVs efficiency significantly [5]. Besides, as compared with its inorganic semiconductor rivals, the material, together with a matching polymer donor material, seems to be a potential candidate for flexible, light-weight, and easily processable OPVs. The PCBM-based materials have also found their way in other novel devices like organic field-effect transistor [6], [7], sensors [8], and the like. While the material has such impressive and diverse application, little is known about the stability and/or oxidation of the material when exposed to different conditions such as moisture, light, temperature, and the like; however, there are some studies on the effect of different exposures of the material, while mixed with P3HT in OPVs [2], [3], [5]. As a result, a distinct stability or chemical modification study of the PCBM or C_{60} based material upon exposure appears to be an important area for investigation. Of the few studies on stability or oxidation of the material by different exposures, Shibao *et al*. reported that exposure of PCBM to green laser light with wavelength 532 nm under vacuum increased the mobility of the material significantly [7]. Li *et al*. have also studied the photosensitivity of azafullerene ($C_{59}N$), as compared with fullerenes (e.g., C_{60}) [9]. However, their study was not directly on PCBM; they indicated that the conductance $C_{59}N$ showed much higher photoresponse sensitivity than in fullerene due to the difference in photoinduced charge transfer mechanism between the two materials, i.e., the degree of photoinduced stability of C_{60} is different from other C_{60} base modified materials. On the other hand, significant efforts have also been made in the development of cross linkable and stable C_{60} based polymers with the desirable property of the material [1], [10]. Drees *et al*. have also showed the chemical polymerization of a C_{60} derivative called phenyl-C_{61}-buryric acid glycidol ester, where they improved the morphological stability in bulk hetrojunction C_{60} based OPV [11]. However, to date, the effect of the ultraviolet (UV)-light ozone (both UV light and ozone gas in combination) exposure of PCBM at ambient temperature and pressure, from scientific point of view and technological perspective, is not well understood.

In this study, the effect of UV-ozone exposure on the oxidation of PCBM and the impact of the exposure time on the degree of oxidation of the material are studied. In addition, the separate effects of UV-ozone versus ozone gas alone on the oxidation of the PCBM are considered individually. Additionally, the change in the solubility of the material upon exposure is studied, which could have technological implications in relation to the choice of solvents and processing of the material. The experimental part of this study will be described in Section II. Next, in Section III, the results for the material with and without the exposure are presented and discussed in relation to the change in the chemistry of the material and solubility using

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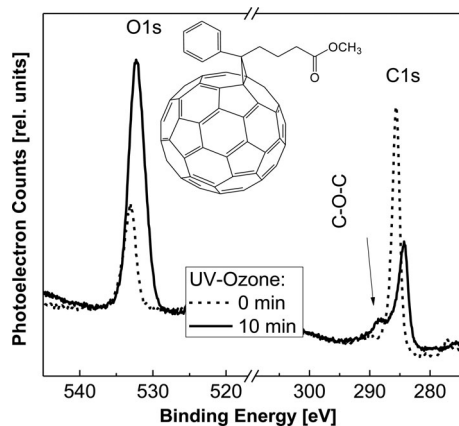
Fig. 1. XPS spectra of PCBM without and with 10 min of UV-ozone exposure at ambient condition. The inset shows a molecular structure of the PCBM.

Fig. 2. Valence-band spectra photoelectron spectroscopy measurements of PCBM without and with 10 min of UV-ozone exposure at ambient condition.

photoelectron spectroscopy and different organic solvents, respectively. Finally, the conclusion of this study is presented in Section IV.

II. Experimental Details

The study of oxidation of PCBM by UV-ozone exposure is studied over a thin film of the material under ambient temperature and pressure. Before depositing the material, the glass substrates were cleaned by detergent, acetone, and isopropanol using ultrasonic bath, followed by dry cleaning of UV-ozone exposure for 20 min. Consequently, a solution of PCBM, of 0.6%wt. in dichloromethane (DCM) solvent, was stirred for 90 min, and then, the solution was filtered and spin-coated at 2000 r/min for 15 s. Finally, the deposited film was annealed at 150 °C for 30 min. The dry samples were exposed to UV ozone (Novascan, PSD Pro Series) for 0, 5, 10, 15, 30, 60, and 120 min at ambient temperature and pressure. A chemical analysis of the material with and without exposure was then performed by photoelectron spectroscopy measurements. Similarly, the solubility of the material with and without the exposure was also studied by exposing the film to the UV ozone through a metal mask, followed by dip coating it to solvents like toluene and acetone for a given time. Expecting a different outcome regarding oxidation for UV ozone and ozone gas alone, the PCBM films were exposed to both types of exposures. While the UV ozone is an exposure over the entire film, the exposure with ozone gas alone is carried out by simply blocking the incident UV light from the sample, while the ozone gas is allowed to diffuse throughout the exposure chamber, i.e., the metal shadow mask is made at a distance of ∼1 cm from the film so that ozone can reach the film without UV light reaching.

III. Result and Discussion

A. Oxidation of Phenyl-C61-Butyric Acid Methyl Ester

The effect of UV-ozone exposure on the oxidation of PCBM is studied in comparison with PCBM films that are not exposed. Fig. 1 presents the core-level X-ray photoelectron spectroscopy
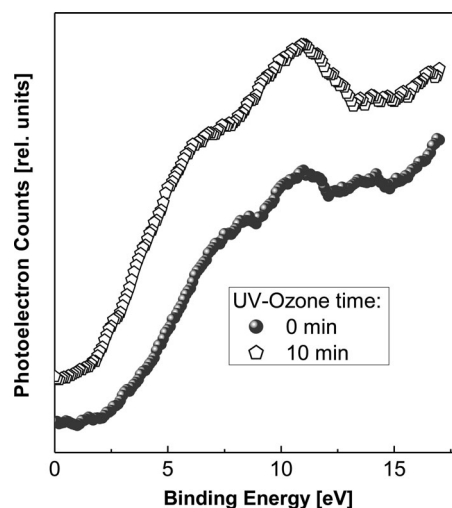
(XPS) measurements of PCBM films with and without 10 min of UV-ozone exposure. As seen from Fig. 1, it is evident that the C1s signal (i.e., counts) is much higher than the O1s signal in the case of unexposed PCBM. However, in the case of exposed PCBM, the effect is reversed, i.e., the exposure results in much higher count of O1s as compared with that of C1s signal. This indicates that the UV-ozone exposure results in increasing the amount of oxygen segregated into the film. More importantly, the C-O-C bond is also evident for the sample exposed to UV ozone, while the unexposed sample does not show signal of the bond. The two peaks 285 and 286.5 eV, for the exposed case, are due to C-C and C-O-C bonds [12], respectively. Here, it is important to note the possible presence of C-O bond at 533.7 eV, C=O bond at 532.5 eV, and O-C=O bond at 531.9 eV in either of the two cases. An earlier XPS study of pristine PCBM showed that the O1s features a small signal and almost invisible count, while C1s has a massive count. Thus, the increased oxidation, or O1s, in our case seems to originate from thermal oxidation, and the more enhanced oxidation after the exposure seems to indicate further oxidation caused by the UV ozone or ozone treatments. Thus, oxidation of the material without C-O-C binding seems to occur for the PCBM without even UV-ozone exposure, where it is solution processed and dried at ambient conditions, i.e., it seems to be thermal-induced oxidation in the presence of air. The other important aspect that is observed from this study is the already existing oxidation, without the exposure, enhancement by the UV-ozone exposure, i.e., O1s as seen in Fig. 1. This seems to indicate that the activated oxygen or ozone by the UV ozone does not only induce C-O-C based oxidation but enhances other forms of oxidation of the material significantly as well. Here, one may raise an important question whether the C-O-C bond is between the molecules or within the molecules. If the molecules are bonded (i.e., C-O-C bond is formed) between molecules, the diffusion coefficient of the bonded molecules should increase due to molecular mass increasing [13]. However, if the C-O-C bond is within the molecule, a change in diffusion coefficient is not expected. For this, we performed nuclear magnetic
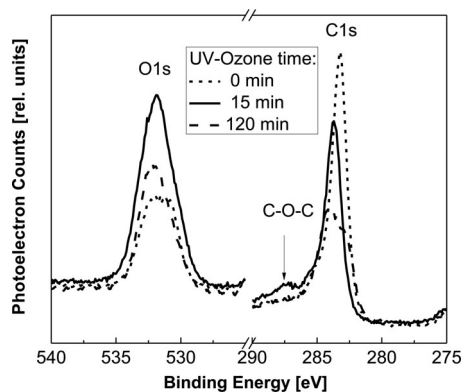
Fig. 3.   XPS spectra of PCBM for 0, 15, and 120 min of UV-ozone exposure at ambient condition.

Fig. 4.   XPS spectra of PCBM without, with 15-min UV-ozone, and 15-min ozone treatments.

resonance (NMR) 2-D diffusion-ordered spectroscopy (DOSY) experiments of the unexposed PCBM and compared with the UV-ozone exposed case: 15 min. The DOSY experiment showed that the diffusion coefficient of the unexposed case, characterized in solution form, is about 6.5×10^{-10} m^2/s, where it is comparable with the diffusion coefficient of the exposed case having C-O-C bond. However, here, the change in the chemistry of the material by the exposure was evident from the NMR, as the exposed case has additional chemical shifts peaks different from the unexposed one. On the other hand, the valence band of the two cases, with and without 10 min of exposure, was also characterized as shown in Fig. 2. As observed, the exposure results in a change in valence-band structure of the exposed PCBM with a reduction in the highest occupied molecular orbital (HOMO) level of the material, as compared with the unexposed case. The result indicates that the UV-ozone oxidation resulted in a change of the electronic properties of the material. Such a change in the HOMO level by oxidation of a material was also evident for pentacene, as studied by Griffith *et al.* [14]. The effect is also comparable with an oxidation of the material and change in the HOMO level of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) by the UV-ozone exposure, as studied earlier [15], [16].

To get more insight on the effect of the UV-ozone exposure on the PCBM, the exposure time was adjusted from 10 min to five additional cases—5, 15, 30, 60, and 120 min of UV ozone, all of which were compared with the unexposed PCBM. For the first four of the five cases (5, 15, 30, and 60 min), the effect regarding oxidation was comparable with that of the 10-min case; the C-O-C bond (286.5 eV) peak was observed for each case. Here, it is important to note that the 60-min exposure of the material shows a reduced signal of C-O-C bond with shouldering instead of having peck. Unexpectedly, when the exposure time was increased massively to 120 min, the result was different. Fig. 3 presents XPS spectra of PCBM for 120 min of UV-ozone exposure, as compared with the unexposed and exposed case with the C-O-C bond, which is shown from a 15-min UV-ozone sample as typical. As shown in Fig. 3, the 120-min exposure results in the absence of C-O-C signal and a reduced signal of even the C-C bond or C1s signal as compared with the unexposed sample case. Now, based on the time of exposure, the modification or
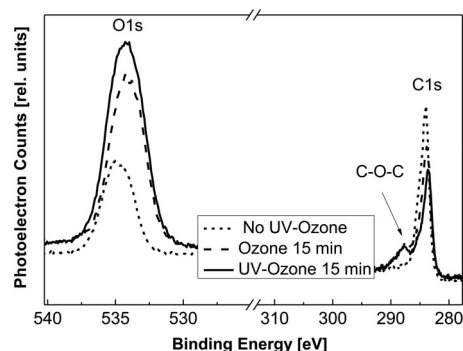
oxidation process at ambient temperature and pressure seems to have three stages: the first oxidation without the C-O-C bond, the second oxidation accompanied by the C-O-C bond, and the third having oxidation signal without the C-O-C bond. Based on the signals from XPS study, the 60-min exposure of the PCBM seems to reach the transition from the second to third regime. Fig. 3 presents the three typical regimes. Based on our study, the first regime is observed without exposure, while the second exists even at 5 min but below 60 min, and the third regime at higher time of exposure, e.g., exposure at 120 min. Here, it is worthwhile to note that the signal for the third regime is different from either of the two cases, i.e., either the unexposed or the exposures of the resulting C-O-C bond for the time range 5–60 min. Such a change, including absence of the C-O-C bond, seems to indicate that degradation of the PCBM by the further exposure as the application of UV-ozone after a limited time is capable of breaking molecular bonds and creating CO, CO_2, and/or other oxygen–carbon complexes [17].

In the next study, we have investigated the contribution of UV in the oxidation of the material, where it is the key question in relation to the possibility of the oxidation only using ozone without the UV-light exposure of the material. To address these fundamental issues, three cases were considered: sample without exposure, with 15 min of UV-ozone exposure, and with 15 min of only ozone exposure. Fig. 4 presents photoelectron spectroscopy measurements of the three cases. As can be seen, in Fig. 4, the sample exposed to only ozone does also shows the C-O-C bond, while the UV-ozone case for 15 min does show superior O1s than the ozone-only case or significant signal change when compared with the sample that is not exposed. The unexpected presence of the C-O-C bond for the 15 min of ozone, like that of the UV-ozone case, indicates that the oxidation of PCBM comes through the presence of either only ozone or UV-ozone. However, here, it is important to note that the ozone is formed by UV light and ambient air or oxygen and moisture.

Our study has also included the optical properties of the PCBM before and after the exposures. The optical properties study using UV-visible spectrometer showed that there is no significant change in the absorption of the PCBM by the exposure for either those showing C-O-C type oxidation or the overexposed case without the C-O-C bond at 120 min. Since there is a change in the HOMO level of the PCBM by the
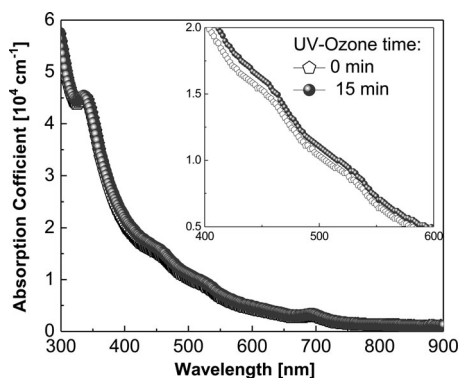
Fig. 5. Absorption coefficient of PCBM, without and with 15-min UV-ozone exposure, as a function of wavelength and zoomed view between 400 and 600 nm (inset).

exposure, it was expected to have a change in the optical properties of the material. The chemical modification of the material without a significant effect on the optical properties might indicate a structural change. Such an effect, that is, a change in the chemical or HOMO level of a material without a significant change in the optical properties, was also witnessed by UV-ozone exposure of PEDOT:PSS [15], [16]. A study of the material by Nagata *et al.* also reported the UV-ozone-induced oxidation and HOMO level change of PEDOT:PSS with a change in the structural or chain orientation, while there is no significant change in the optical absorption of the material [16]. Thus, it is not an unexpected phenomenon in PCBM. Considering the insignificant change on the absorption coefficient of the material both before and after the exposure, it is expected that there will not be significant change in the bandgap and, as a result, on the lowest unoccupied molecular orbital level as well [18]. The optical properties of the material were also additionally studied using UV-visible absorption spectroscopy measurements, which is used to extract the absorption coefficient as a function of wavelength. The absorption coefficient as a function of a wavelength is given by [19], [20]

$$\alpha = \left(\frac{2.303}{t} \right) \log \left(\frac{I_o}{I} \right) = 2.303(A/t) \qquad (1)$$

where I_o and I are incident and transmitted intensity, respectively, and A and t are absorbance (in a.u) and film thickness. Fig. 5 presents the absorption coefficient, using (1), of the PCBM without and with 15-min exposure that is spin-coated on a glass substrate and dried. As seen from the graph, it is evident that the change in absorption coefficient of the material by the exposure is insignificant. Such an insignificant change in the optical properties of the material, while being flexible on the choice of solvents, might be an important aspect for potential devices with improved stability.

In addition to the optical property of the material, with and without the exposure, the electrical property of the material is an important issue. Of the electrical property, the dielectric constant of the material is the determinant for the overall electrical property parameters of the material and charge separation or formation in OPVs. The dielectric property of the material,

before and after the exposure, was studied using ellipsometry measurements. In the study, the average dielectric constant of the unexposed PCBM at different wavelengths is 3.97, where it is comparable with previous studies [21]. On the other hand, the UV-ozone-exposed PCBM, for 15 min, showed a dielectric constant of 4.19. Unexpectedly, the dielectric constant for sample exposed to ozone only, for the same time of exposure, is 3.71. Although not significant, such a difference in the electrical property, for ozone versus UV-ozone exposure, was also evident from former studies using PEDOT:PSS [16]. Here, one may not expect such a small difference while the material has undergone a significant chemical modification, but the results support the earlier studies, which reported that modification of C-60 based molecules does not result in a drastic change in the dielectric constant [22]. Here, the retaining of such a relatively high dielectric constant of the PCBM, while it is chemically modified, is important for charge carrier formation in blend OPVs with donor polymers like P3HT or poly(2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene [22], [23].

B. Solubility of Phenyl-C61-Butyric Acid Methyl Ester

If the chemistry of materials and processing is the same, it is expected that their solubility is the same for a given solvent. However, when there is a modification of the material, particularly oxidation, solubility, or at least degree of solubility, of the material can change for some type of solvents. As an example, Najafi *et al.* have demonstrated that solubility of single-walled carbon nanotubes (SWCNTs) can be changed by UV-ozone exposure [24]. In their study, they found that the solubility of SWCNTs depends on the time of exposure. Similarly, here, solubility testing is used as a supplement to photoelectron spectroscopy measurements (see Section III-A). One common solvent for fullerene or fullerene-based small molecules is toluene. In this study, three cases of PCBM were considered: 1) without UV-ozone treatment; 2) with the treatment having the C-O-C bond; and 3) with extended treatment of ozone only exposure. Thus, the typical treatment times used were 0, 15, and 120 min for the three (1, 2, and 3) cases considered, respectively. The effect of the treatment without and with 15 min was made by dip coating the film in toluene solvent for 2–5 min. It was evident that the organic solvent relatively selectively removed the unexposed region quickly than the exposed part. The effect of the exposure on the solubility of the material for the solution is observed in Fig. 6. Thus, for the PCBM exposed to 15 min versus 0 min, the UV-ozone-induced oxidation changes the material from a relatively soluble to less soluble in toluene. Such a difference in solubility of the material after oxidation or C-O-C formation of PCBM seems originate from the change in polarity of the material after the exposure effect, as studied in Section III-A. It is known that UV-ozone or ozone-induced oxidation increases the polarity of the material. As a result, the material before oxidation needs less polar solvent to be dissolved, while it needs relatively high polar solvent to be dissolved after oxidation or C-O-C formation. Thus, the relatively selective removal of the unexposed PCBM by toluene comes from the difference in the chemistry or oxidation of the material. This seems to
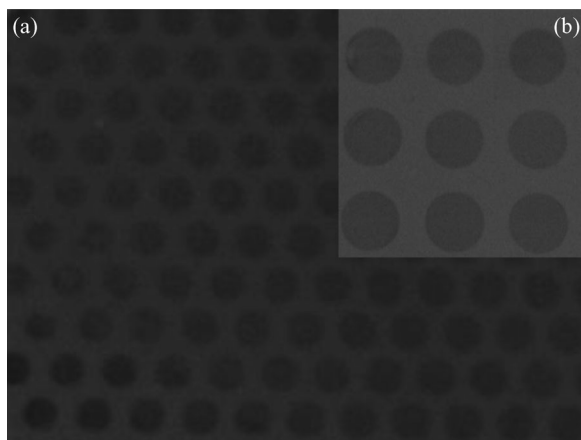
Fig. 6. Optical micrograph etched (bright) and unexposed (dark) PCBM film after UV-ozone exposure, over a mask, and dip coated in toluene solvent. The test metal mask used has holes (dark regions) of radius (a) ∼700 μm and (b) 1700 μm.

indicate that solvents with a relatively high polarity are good solvents for exposed cases, while the less polar cases are solvents for the unexposed PCBM, i.e., choice of solvents can vary before and after oxidation.

A similar solubility study of PCBM in the solvents was also made on the effect of ozone exposure without the UV-light exposure on the material. Our result indicated that the PCBM exposed to 15 min of only ozone showed a significant difference from the nonexposed material. Comparing the unexposed versus exposed, the 15-min exposed PCBM is less soluble in toluene, as compared with the unexposed. Thus, the trend in the solubility is comparable with that of the 15-min UV-ozone exposed case, where it supports the XPS study made in Section III-A. Extended ozone exposure time, e.g., 120 min, was also considered in this study. However, the extended ozone exposure case revealed that the solubility is comparable as the optimized UV-ozone exposure, e.g., 15-min UV-ozone exposure case. The PCBM exposed to 120-min ozone alone is also less soluble in toluene and relatively more soluble in acetone. However, the 120-min ozone-exposed PCBM is relatively less soluble when compared with the unexposed. Such solubility changes give further understanding of the oxidation mechanism and offers the possibility of an easily implementable oxidation method via a solid-state modification, as opposed to electrochemical oxidation methods used in C_{60} [25]. From this study, it is clear that the oxidation can be processed in the exposure of UV-ozone or ozone gas alone, where the ozone is, in turn, created by UV exposure of oxygen and/or moisture.

IV. CONCLUSION

The UV-ozone exposure of PCBM resulted in oxidation of the material, including C-O-C formation. The exposure results in a change of the electronic properties (i.e., HOMO level) of the material without a significant change in the optical absorption property. Besides, the method does not alter the high dielectric constant, where it is an important material requirement in the OPVs device design. The oxidation of the material, through the C-O-C bond, occurred for exposures in the range of 5–60 min, but further exposure resulted in degradation with the absence of the C-O-C bond. The C-O-C based oxidation can also be processed using only ozone without the UV-light exposure over the surface of the material. The oxidation process also results in a change of the solubility chemistry of the material in relation to the increase in the polarity of the material by the oxidation. The method is an easily implementable approach and has a potential application for the choice of solvents and stability of PCBM that has implications on the processing and stability of the devices using the material.

REFERENCES

[1] N. Martín, F. Giacalone, and M. Prato, *Fullerene Polymers: Synthesis, Properties and Applications*. Weinheim, Germany: Wiley-VCH, 2009, pp. 1–11.

[2] N. Martín and F. Giacalone, *Fullerenes: Principles and Applications*. Weinheim, Germany: Wiley-VCH, 2007, pp. 191–259.

[3] J. Shinar, Z. V. Vardeny, and Z. H. Kafafi, *Optical and Electronic Properties of Fullerenes and Fullerene-Based Materials*. New York: Marcel Dekker, 1999, ch. 11.

[4] J. Peet, J. Y. Kim, N. E. Coates, W. L. Ma, D. Moses, A. J. Heeger, and G. C. Bazan, "Efficiency enhancement in low-bandgap polymer solar cells by processing with alkane dithiols," *Nature Mater.*, vol. 6, pp. 497–500, May 2007.

[5] H.-Y. Chen, J. Hou, S. Zhang, Y. Liang, G. Yang, Y. Yang, L. Yu, Y. Wu, and G. Li, "Polymer solar cells with enhanced open-circuit voltage and efficiency," *Nature Photon.*, vol. 3, pp. 649–653, Nov. 2009.

[6] M. Shibao, T. Morita, W. Takashima, and K. Kaneto, "Ambipolar transport in field-effect transistors based on composite films of poly(3-hexylthiophene) and fullerene derivative," *Jpn. J. Appl. Phys.*, vol. 46, pp. L123–L125, Feb. 2007.

[7] M. Shibao, T. Morita, W. Takashima, and K. Kaneto, "Light illumination effects in ambipolar FETs based on poly(3-hexylthiophene) and fullerene derivative composite films," *Thin Solid Films*, vol. 516, pp. 2607–2610, Mar. 2008.

[8] G. Yu, J. Wang, J. McElvain, and A. J. Heeger, "Large-area, full-color image sensors made with semiconducting polymers," *Adv. Mater.*, vol. 17, pp. 1431–1434, Dec. 1998.

[9] Y. Li, T. Kaneko, and R. Hatakeyama, "Electrical transport properties of fullerene peapods interacting with light," *Nanotechnol.*, vol. 19, pp. 415201-1–415201-7, Sep. 2008.

[10] F. Cataldo and O. Ori, "Ozone reaction with C_{60} fullerene. A study on the antiozonant activity of C_{60} fullerene in dienic rubber," *Polym. Degradation Stability*, vol. 48, pp. 291–296, Feb. 1995.

[11] M. Drees, H. Hoppe, C. Winder, H. Neugebauer, N. S. Sariciftci, W. Schwinger, F. Schäffler, C. Topf, M. Scharber, Z. Zhu, and R. Gaudiana, "Stabilization of the nanomorphology of polymer–fullerene 'bulk heterojunction' blends using a novel polymerizable fullerene derivative," *J. Mater. Chem.*, vol. 15, pp. 5158–5163, Apr./Oct. 2005.

[12] C. Daniel, K. E. Sohn, T. E. Mates, E. J. Kramer, J. O. Rädler, E. Sackmann, B. Nickel, J. O. Rädler, E. Sackmann, B. Nickel, and L. Andruzzi, "Structural characterization of an elevated lipid bi-layer obtained by stepwise functionalization of a self-assembled alkenyl silane film," *Biointerphases*, vol. 2, pp. 109–118, Oct. 2007.

[13] J. R. Lakowicz, *Principles of Fluorescence Spectroscopy*. New York: Academic, 2007, p. 806.

[14] O. L. Griffith, J. E. Anthony, A. G. Jones, and D. L. Lichtenberger, "Electronic properties of pentacene versus triisopropylsilylethynyl-substituted pentacene: Environment-dependent effects of the silyl substituent," *J. Amer. Chem. Soc.*, vol. 132, pp. 580–586, Aug. 2010.

[15] A. Benor, S. Takizawa, C. P. Bolivar, and P. Anzenbacher, Jr., "Energy barrier, charge carrier balance, and performance improvement in organic light-emitting diodes," *Appl. Phys. Lett.*, vol. 96, pp. 243310-1–244310-3, Jun. 2010.

[16] T. Nagata, S. Oh, T. Chikyow, and Y. Wakayama, "Effect of UV–ozone treatment on electrical properties of PEDOT:PSS film," *Org. Electron.*, vol. 12, pp. 279–284, Feb. 2011.

[17] J. R. Vig, "UV/ozone cleaning of surfaces," *J. Vac. Sci. Technol. A*, vol. 3, pp. 1027–1034, May 1985.

[18] D. Fan, P. J. Thomas, and P. O'Brien, "Deposition of CdS and ZnS thin films at the water–toluene interface," *J. Mater. Chem.*, vol. 17, pp. 1381–1386, Dec. 2007.

[19] M. Fox, *Optical Properties of Solids*. New York: Oxford Univ. Press, 2001.

[20] Y. Ramadin, M. Al-Haj Abdallah, M. Ahmad, A. Zihlif, and S. K. J. Al-Ani, "Optical properties of epoxy-glass microballoons composite," *Opt. Mater.*, vol. 5, pp. 69–73, 1996.

[21] V. D. Mihailetchi, J. K. J. van Duren, P. W. M. Blom, J. C. Hummelen, R. A. J. Janssen, J. M. Kroon, M. T. Rispens, W. J. H. Verhees, and M. M. Wienk, "Electron transport in a methanofullerene," *Adv. Funct. Mater.*, vol. 13, pp. 43–46, Jan. 2003.

[22] C. J. Brabec, V. Dyakonov, and U. Scherf, *Organic Photovoltaics: Materials, Device Physics, and Manufacturing Technologies*. Weinheim, Germany: Wiley-VCH, 2008.

[23] B. Yang, J. Cox, Y. Yuan, F. Guo, and J. Huang, "Increased efficiency of low band gap polymer solar cells at elevated temperature and its origins," *Appl. Phys. Lett.*, vol. 99, pp. 133302-1–133302-3, Sep. 2011.

[24] E. Najafi, J.-Y. Kim, S. H. Han, and K. Shin, "UV-ozone treatment of multi-walled carbon nanotubes for enhanced organic solvent dispersion," *Colloids Surfaces A, Physicochem. Eng. Aspects*, vol. 284–285, pp. 373–378, Jan. 2006.

[25] K. Winkler, A. L. Balch, and W. Kutner, "Electrochemically formed fullerene-based polymeric films," *J. Solid State Electrochem.*, vol. 10, pp. 761–784, Jul. 2006.

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