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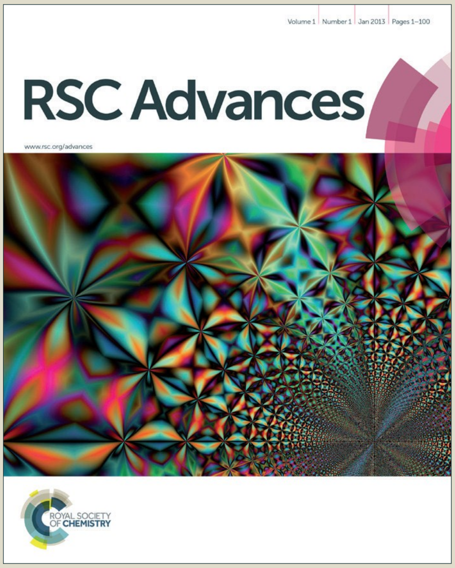

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A simple and cost effective experimental method for verifying singlet fission in pentacene/C_{60} solar cells

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Abstract

In solar cells, a maximum external quantum efficiency of 100% can be attained if the photocurrent is originated from dissociation of singlet excitons. However, a higher efficiency can be attained through singlet fission (SF), where multiple charge carrier pairs are generated from a single photon, thus increasing the number of excitons and hence the photocurrent generation. The verification of SF is normally a heavy work and costly. In this study, SF is verified in pentacene by simply measuring the external quantum efficiency (EQE) of a device with a very thick pentacene (Indium tin oxide/poly (3,4-ethylenedioxythiophene):poly (4-styrenesulphonate) (PEDOT:PSS) (40 nm)/pentacene (600 nm)/fullerene (40 nm)/tris-8-hydroxy-quinolinato aluminum (8nm)/Al). A measured EQE of 6.16% at 695 nm is achieved, which is much larger than the maximum calculated EQE (3.45%). The calculation was based on the assumption that all singlet excitons (if SF were not happened) that reached the pentacene-C_{60} interface contribute to the photocurrent. To narrow this discrepancy, only the singlet fission to double the number of excitons can be supposed since the longer singlet diffusion length of 140 nm is not practical in pentacene. Thus, SF in pentacene and the dissociation of triplet excitons at the pentacene-C_{60} interface are verified.

1. Introduction

Organic Photovoltaic (OPV) materials have demonstrated great potential for solar cell fabrication, due to their low-cost, light weight, flexibility, and simple roll-to-roll production.[1-3] In recent years, the reported power conversion efficiency (PCE) of small-molecule solar cells has exceed 7%,[4,5] which has been attained through solution-processing fabrication, and is still lower than that of polymer solar cells. One promising method for improving the PCE of organic solar cells is to increase the short circuit current (J_{sc}) by converting each high energy photon into multiple electron-hole pairs.[6-8] In organic semiconductors, this process is known as singlet fission (SF). SF is a process in which a delocalized singlet exciton (spin 0) generated through optical excitation splits into a pair of triplet excitons (spin 1).[8-10] To make SF an efficient phenomenon, the speed of fluorescent de-excitation, direct singlet exciton dissociation or intersystem crossing must be slower or at least comparable to that of singlet fission.[10] By using SF together with tandem structure, the efficiency limit of organic solar cells can be boosted from the Shockley-Queisser limit of 33% to 44%.[7,11,12]

The best understood fission material to date is pentacene. A few methods have been used to prove the existence of SF in pentacene-based devices. The first approach, which is the most direct, has been based on achieving external quantum efficiency (EQE) exceeding 100%, which is larger than the maximum attainable EQE when the photocurrent is originated from singlet excitons. Indeed a peak EQE of (109±1)% at 670 nm has been reported recently, firmly confirming the existence of SF in pentacene.[10] However, this SF verification method is very difficult to realize practically and only a few studies have successfully demonstrated an EQE exceeding 100%.[10,13,14] Another approach based on measuring the photocurrent difference with and without a magnetic field has been reported for SF verification by Daniel N. Congreve et al.[10] This technique based on the fact that the triplet excitons would be affected by an external magnetic field, thus the photocurrent due to triplet excitons (arising from singlet fission) would be modulated by an external magnetic field.[10,13] To get accurate characterization results, a variable wide-range magnetic field generator is typically needed in conjunction with a low temperature control equipment. This arrangement is quite expensive and hence unavailable in many research labs. Also, the limitation of this approach is that it cannot discriminate the origin of the generated triplet excitons i.e. whether they originate from singlet fission or intersystem crossing. A third approach for SF verification based on measuring the lifetime difference between singlet and triplet excitons has recently been reported.[12,15-17] Transient absorption spectroscopy was used to detect the number of triplet/singlet excitons versus time. The reduction of singlet excitons followed by the increase of triplet excitons was attributed to the SF process in pentacene/C_{60} devices.[12,15] Since the SF process is very fast, a femtosecond laser (or at least a picosecond laser) is typically required for accurate transient absorption spectroscopy. Though the above-mentioned three approaches for SF verification are fairly satisfactory, they are also heavy work and costly. In this study, SF in pentacene is verified by a very simple and cost effective method based on just measuring the EQE of a pentacene-based heterojunction device. The measured EQE of a typical solar cell device employing a 600 nm-thick pentacene layer is much larger than the EQE calculated with the assumption that all singlet excitons reached the pentacene-C_{60} interface contribute to the measured photocurrent. This assumption sets the upper EQE limit from the singlet exciton contribution. The experimental EQE is much larger than the calculated EQE when the largest reported singlet diffusion length of 80 nm[18-20] is used. To narrow this discrepancy, only the singlet fission to double the number of excitons can be supposed since the longer singlet diffusion length of 140 nm is not practical in pentacene. Thus, SF in pentacene and then dissociation of triplet excitons at the pentacene-C_{60} interface can be verified by a very simple and cost effective method.

2. Experiments

A thick layer of pentacene blended with an acceptor can exacerbate exciton-charge annihilation because excitons and charges are kept closed. [14,21] So, a planar heterojunction device, composed of 600 nm pentacene as a donor and 40 nm C_{60} as an acceptor, was fabricated, as illustrated in Fig. 1. Experiments with the thickness of pentence from 50 nm to 600 nm were also conducted. Above 350 nm, all the experiments came to the same conclusion as we presented in this manuscript with 600 nm pentacene. A very thick pentacene layer was especially chosen in this study to: (1) ensure that all light is absorbed before reaching the exciton dissociation interface of pentacene-C_{60}; (2) distinguish the singlet excitons from triplet excitons based on the large difference of diffusion length between them; (3) ease the optical model of device. Poly (3,4-

ethylenedioxy-thiophene):poly (4-styrenesulphonate) (PEDOT:PSS) and tris-8-hydroxy-quinolinato aluminum (Alq3) were used as anode and cathode buffer layers, respectively, to improve the device performance and stability.[13,22] The device was fabricated on pre-cleaned indium tin oxide (ITO) glass substrate. The thickness of PEDOT:PSS film was 40 nm. Pentacene, C_{60}, Alq3 and Al were deposited by thermal evaporation at rates 0.5, 0.2, 0.05 and 1.5 Å/s, respectively, in high vacuum ($<3.5\times10^{-8}$ Torr) chamber. The active area of the device was 9 mm^2, defined by the cross area of ITO and the top Al electrode bar.

3. Results and discussions

Fig. 2a shows the measured current-voltage (I-V) curve under 100 mW/cm^2 AM1.5G simulated sunlight. It is clear from Fig. 2a that for the developed heterojunction device have the short circuit current density, J_{sc}, of 1.74 mA/cm^2, the open circuit voltage of 0.36 V, and the fill factor of 47%. Fig. 2b shows the EQE spectrum, which displays a maximum EQE of 6.16% at 695 nm. By integrating the EQE over the AM1.5G spectrum, a calculated J_{sc} of 1.70 mA/cm^2 is obtained, which is in agreement with the measured one (1.74 mA/cm^2). An antibatic EQE behavior is seen in Fig. 2b, i.e. The maximum EQE is at the wavelength corresponding to the minimum absorption of pentacene.[23,24] Since the spin of photon is zero, only singlet excitons can be produced upon light absorption. If SF did not take place in pentacene, only singlet excitons reached the pentacene-C_{60} interface and direct ionization of excitons would have contributed to the measured photocurrent and hence the EQE. The upper limit photocurrent contribution from singlet excitons can be calculated if we assume that all singlet excitons that reached the pentacence-C_{60} interface contributed to the photocurrent with 100% efficiency. To determine the number of singlet excitons that can reach the pentacene-C_{60} interface, a transfer matrix calculation[25-28] was made to figure out the distribution of singlet excitons, $f_1(x)$, as shown in Fig. 3a. In brief, by supposing the continuity of the tangential component of the electric field at each interface, a 2×2 matrices can be used to calculate the optical electric filed distribution. By using the complex index of refraction for each layer, the number of absorbed photons, $f_1(x)$, can be obtained simultaneously. The refractive index of pentacene used in this work was measured by an ellipsometry. It has been reported that the refractive index of a pentacene layer changes with its thickness.[29] Our measured results are consistent with the reported one.[29] By multiplying $f_1(x)$ with the diffusion probability of exciton, $f_2(x)$, which is shown in Fig. 3a, the upper limit photocurrent (EQE) originated from the singlet excitons can be estimated as:[30]

$$\mathrm{I} = \int_{0}^{600} (f_1(x)\mathrm{e}^{-\frac{600-x}{\mathrm{L}}})dx + \int_{600}^{640} (f_1(x)\mathrm{e}^{-\frac{x-600}{\mathrm{L}}})dx \qquad (1)$$

$f_2(x)$ is calculated as follow:[19]

$$f_2(x) = \mathrm{e}^{-\frac{600-x}{\mathrm{L}}} \qquad (0 \le x \le 600)$$
$$f_2(x) = \mathrm{e}^{-\frac{x-600}{\mathrm{L}}} \qquad (600 < x \le 640) \qquad (2)$$

Where L is the diffusion length of excitons. By using the diffusion lengths of 80 nm and 40 nm for pentacene and C_{60}, respectively,[18-20,27] (which are the maximum reported for singlet excitons), then the maximum calculated EQE is found to be 3.45% at 695 nm.

To estimate the contribution from the direct ionization of pentacene, we fabricated a device (ITO/PEDOT:PSS (40 nm)/pentacene (600 nm)/Alq_3 (8 nm)/Al) with a single pentacene layer. The EQE at 695 nm was found to be 0.10%, which is negligible. Therefore, the device can attain a maximum EQE of 3.55%, only if the contribution of singlet exciton dissociation at the pentacene-C_{60} interface and the direct ionization of singlet exciton are taken into account. Compared with the measured EQE value extracted from Fig. 2b, the above-calculated maximum EQE at 695 nm is much smaller. To get an EQE of 6.16% at 695 nm, more excitons must be allowed to diffuse to the pentacene-C_{60} interface, i.e. the singlet exciton diffusion length in equations (1) and (2) should be as large as 140 nm or singlet fission happens to double the number of excitons. This large exciton diffusion length of 140 nm can not apply to singlet excitons in pentacene.[18-20] Thus only the SF is left to explain the big difference between calculation and experiment. The energies for singlet, triplet, and higher triplet excitons of pentacene are 1.83, 0.86, and 2.3 eV, respectively.[15,31] SF in pentacene is slightly exoergic, unidirectional, and very fast (~80 fs), competing with vibrational relaxation and easily outcompeting prompt fluorescence.[10,12,31] Indeed, by supposing that singlet excitons are converted through SF into triplet excitons immediately after their generation and put the L=80 nm (triplet diffusion length) into the calculation, the experimental EQE curve can be roughly reproduced, as shown in the inset of Fig. 2b. The reported triplet diffusion length is $L_{film}\approx(40-80)$ nm in evaporated films and even larger in single crystals.[32] As shown in Fig. 4 for our 600 nm-thick pentacene film, the XRD of 600 nm thick pentacene film indicates the coexistence of the thin-film (001′, 002′) and bulk (001, 002) phases.[19,33] So assuming a diffusion length as large as 80 nm for triplet excitons in our device is practical. Another thick device with 500 nm thick pentacene showed the similar results. The measured (9.95%) EQE at wavelength of 690 nm was also much larger than the calculated (6.13%) by using the largest singlet diffusion length of 80 nm in the calculation.

4. Conclusions

To sum up, we have developed a solar cell device employing a pentacene-C_{60} interface and calculated a maximum EQE at 695 nm of 3.55% based on the assumption that all singlet excitons reaching the pentacene-C_{60} interface contribute to the measured photocurrent. We have found that the calculated EQE value is much smaller than the experimental value (6.16%). To get an EQE of 6.16% at 695 nm, more excitons must be allowed to diffuse to the pentacene-C_{60} interface, i.e. either singlet exciton diffusion length as large as 140 nm or the existence of singlet fission should be assumed. This large diffusion length of 140 nm can not apply to singlet excitons in pentacene. Thus, our experiments have provided a simple and cost effective method to verify the SF in pentacene and the dissociation of triplet exciton in pentacene-C_{60} solar cells.

Acknowledgements

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Figure captions:

Fig. 1. Schematic energy level and structure diagram of the pentacene/C_{60} device studied in this work.

Fig. 2. (a) I-V curve of the fabricated device under one sun illumination. (b) The measured EQE of the heterojunction device and the measured extinction coefficient of 600 nm pentacene. The EQE at 695 nm can be read out as 6.16%. Inset shows the measured and calculated EQE spectra supposing the existence of singlet fission (L=80 nm for triplets and the number of excitons is doubled).

Fig. 3. (a) The distribution ($f_1(x)$), full line) and the diffusion probability ($f_2(x)$, dotted line) of singlet excitons. (b)Probability distribution of singlet excitons that can reach the pentacene-C_{60} interface ($f_1(x)f_2(x)$). X is the distance away from the PEDOT:PSS-pentacene interface. (c) The refractive index of device.

Fig. 4. XRD of the pentacene film, indicating the coexistence of the thin film (00L′) and bulk phases (00L). The bulk phase includes the single-crystal and vapor-deposition phases.

Figure 1.

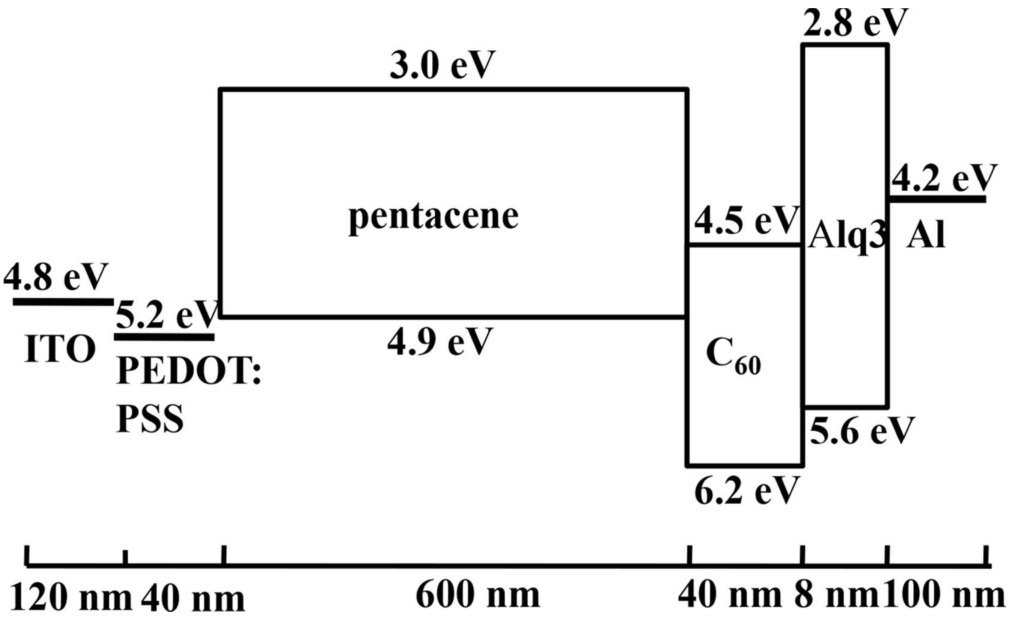
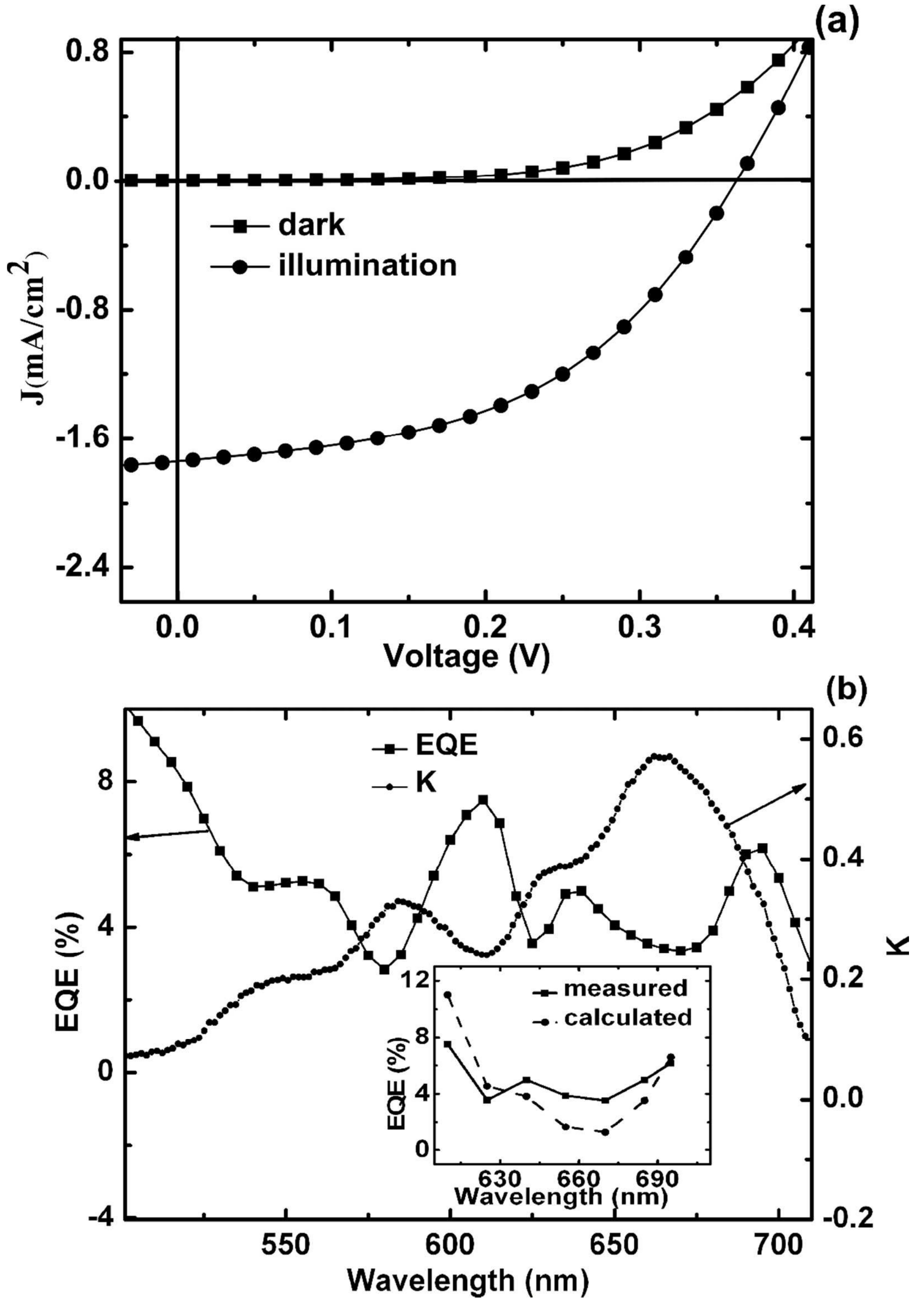

2.8 eV
3.0 eV
4.2 eV
pentacene
4.5 eV
Alq3
Al
4.8 eV
5.2 eV
ITO
PEDOT:
PSS
4.9 eV
C_{60}
5.6 eV
6.2 eV
120 nm
40 nm
600 nm
40 nm
8 nm
100 nm

Figure 2.


(a)
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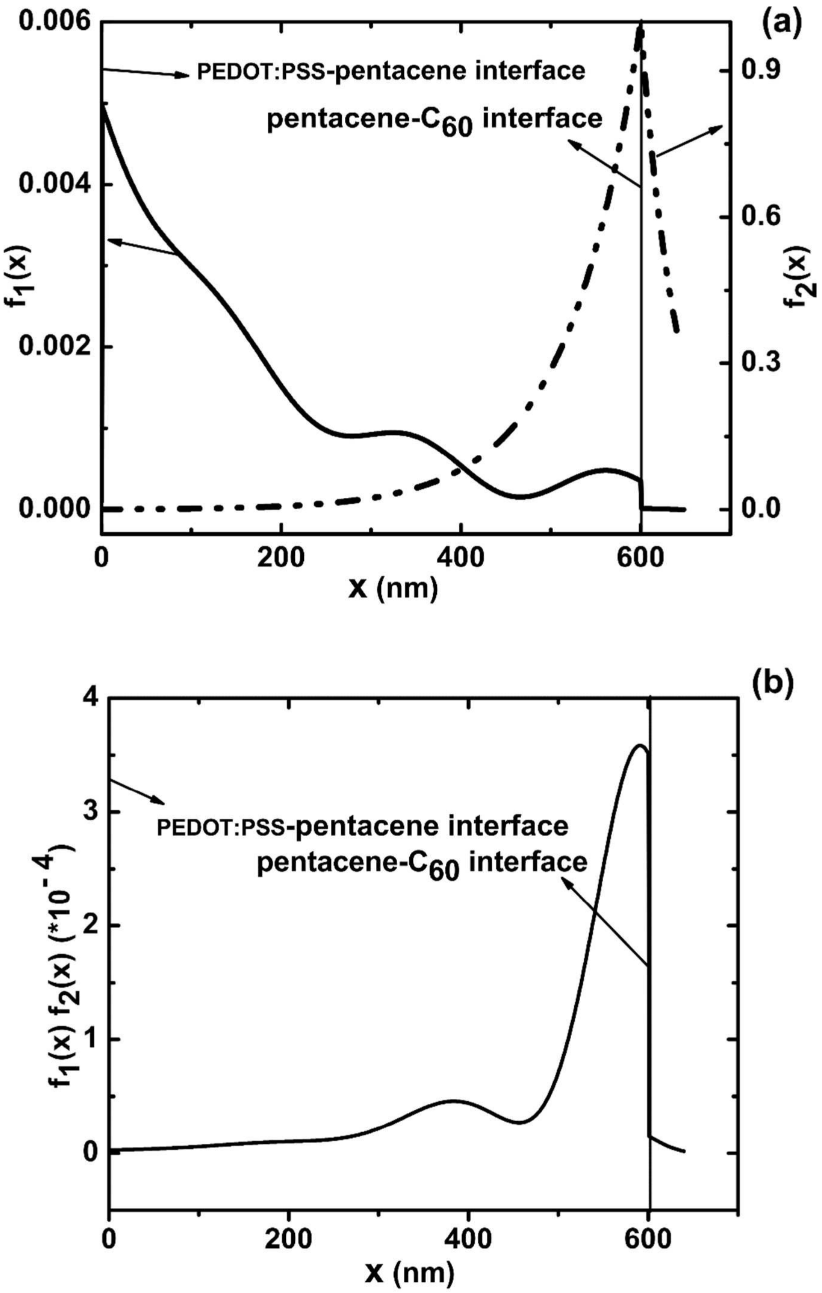
0.0
-0.8
-1.6
-2.4
0.0
0.1
0.2
0.3
0.4
Voltage (V)
dark
illumination
(b)
EQE (%)
8
4
0
-4
K
0.6
0.4
0.2
0.0
-0.2
550
600
650
700
Wavelength (nm)
EQE
K
measured
calculated
EQE (%)
12
8
4
0
630
660
690
Wavelength (nm)

Figure 3.



Refractive Index (λ=695 nm) **(C)**

$n_{glass}=1.5076$

$n_{ITO}=1.6546 + i*0.0085$

$n_{PEDOT:PSS}=1.5041 + i*0.0073$

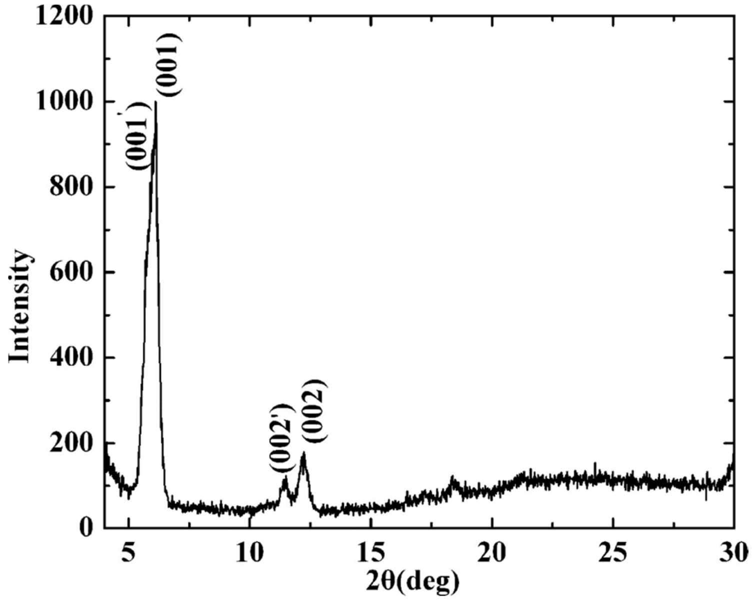
$n_{Alq3}=1.6478 + i*0.0071$

$n_{C60}=2.1054 + i*0.0108$

$n_{Pentacene}=1.6137 + i*0.3252$

$n_{Al}=1.7898 + i*8.27$

Figure 4.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1000
800
600
400
200
0
Intensity
(001′)
(001)
(002′)
(002)
5
10
15
20
25
30
2θ(deg)