Solar cells based on the poly(N-vinylcarbazole):porphyrin: tris(8-hydroxyquinolinato) aluminium blend system*

Zhang Tian-Hui(张天慧)[a)b)], Zhao Su-Ling (赵谡玲)[a)†], Piao Ling-Yu(朴玲钰)[b)‡], Xu Zheng(徐 征)[a)], Ju Si-Ting(鞠思婷)[b)], Liu Xiao-Dong(刘晓东)[a)], Kong Chao(孔 超)[a)], and Xu Xu-Rong(徐叙瑢)[a)]

[a)] *Key Laboratory of Luminescence and Optical Information, Ministry of Education, Institute of Optoelectronics Technology, Beijing Jiaotong University, Beijing* 100044, *China*

[b)] *National Center of Nanoscience and Technology, Beijing* 100190, *China*

(Received 30 July 2010; revised manuscript received 17 October 2010)

Organic solar cells based on poly(N-vinylcarbazole) (PVK): porphyrin: tris (8-hydroxyquinolinato) aluminium (Alq3) blend p-n junction systems have been fabricated in this work. The roles of the different components in the blend system and of the amount of porphyrin have been investigated. The 5, 10, 15, 20–tetraphenylporphyrin (TPP) and 5, 10, 15, 20-tetra(o-chloro)phenylporphyrinato-copper (CuTClPP) are used in the solar cells. The results show that TPP is better than CuTClPP in enhancing the performance of PVK:Alq3 solar cells. When the weight ratio of PVK:TPP:Alq3 is 1:1.5:1, the best performance of solar cell is obtained. The open circuit voltage (V_{oc}) is 0.87 V, and the short circuit current (J_{sc}) is 17.5 μA·cm^{-2}. In the ternary bulk hereojunction system, the device may be regarded as a cascade of three devices of PVK:TPP, TPP:Alq3 and PVK:Alq3. PVK, TPP and Alq3 can improve the hole mobility, light absorption intensity and electron mobility of the ternary bulk hereojunction system, respectively.

Keywords: organic solar cell, porphyrin, ternary blend system

PACS: 84.60.Jt, 88.40.–j, 88.40.jr, 78.56.–a **DOI:** 10.1088/1674-1056/20/3/038401

1. Introduction

Polymer and organic solar cells have attracted wide interest due to their potential properties of light weight, flexibility, low cost and serving as coatings for large areas.[1] A considerable amount of research has been carried out on polymer and organic materials in the past three decades. Many polymer and organic solar cells with novel structures have been fabricated to improve the power conversion efficiency, such as organic–inorganic heterostructures, organic small molecular-polymer heterojunctions[2,3] and using dyes as light-harvesting materials.[4] Porphyrin has an extended p-conjugation system leading to a wide range of wavelengths for light absorption.[5] It has high stability, typical organic p-type semiconductor behaviour[6] and has been considered as a potential light harvester for photovoltaic applications.

Kim *et al.*[7] fabricated a plastic solar cell device by using poly (*N*-vinylcarbazole) (PVK) with metalloporphyrin dye-dispersion The structure of the device was in the form of ITO/PVK (porphyrin) /Alq3/Al. 5, 10, 15, 20tetra (*o*-nitro)phenylporphyrinato-zinc (ZnTNPP) was used as dye. The parameters of the cell were as follows: open circuit voltage (V_{oc}) = 0.605 V, short circuit current (J_{sc}) = 0.677 μA·cm^{-2} filling factor (FF)=0.312 and power conversion efficiency (η)=0.0326%. However, little research has been done on studying the effects of the type and the amount of porphyrin added to solar cells based on PVK:Alq3. At the same time, porphyrin can lead to a wide range of wavelength for light absorption and can be used as a light harvester. So in this work, we chose the hole transport material PVK,[7] the electron transport material Alq3,[8] and the light-harvesting material porphyrin to fabricate a solar cell. Then the properties of these solar cells with different kinds and amounts of porphyrin are investigated. At the same time, the roles of the different components in the blend system are discussed in detail.

*Project supported by the National Natural Science Foundation of China (Grant Nos. 60978060 and 50602008), the Beijing Municipal Science & Technology Commission (Grant No. Z090803044009001), and the Excellent Doctor's Science and Technology Innovation Foundation of Beijing Jiaotong University of China (Grant No. 141107522).

†Corresponding author. E-mail: slzhao@bjtu.edu.cn

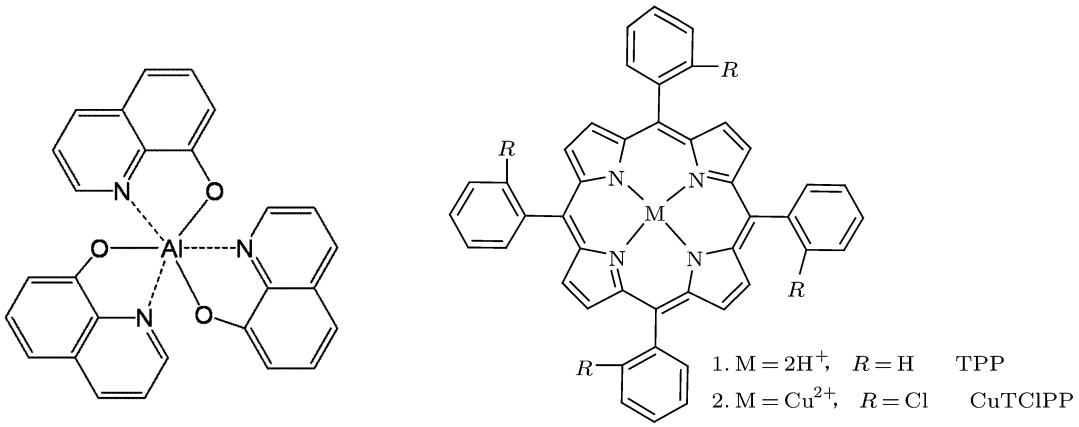
‡E-mail: piaoly@nanoctr.cn

© 2011 Chinese Physical Society and IOP Publishing Ltd

2. Experiments

2.1. Materials

The 5, 10, 15, 20-tetraphenylporphyrin (TPP) was prepared by the direct condensation of pyrrole with benzaldehyde according to a documented procedure.[9] The 5, 10, 15, 20- tetra(o-chloro) phenylporphyrinato-copper (CuTClPP) were synthesized by the one-pot method:[10] pyrrole, o-chlorobenzaldehyde and cupric salt were reacted directly. These two compounds were purified by column chromatography on silica gel. They were also confirmed by element analysis using a THERMOQUEST Flash EA1112, Fourier transform infrared spectrometer (SPECTRUM ONE), and Shimadzu UV-3101 PC spectrometer. The Alq3 and PVK used in this work were purchased from Sigma-Aldrich. Other chemicals used were not further purified. The molecular structures of the porphyrins (TPP (Fig. 1(b1)), CuTClPP (Fig. 1(b2))) and Alq3 are illustrated in Fig. 1.



(a) Alq3 (b) porphyrins

Fig. 1. Molecular structures of Alq3 and porphyrins.

2.2. Device manufacture

The photovoltaic devices studied were prepared as follows: Indium tin oxide (ITO) coated glass substrate (ITO thickness of 25 nm with a sheet resistance of 60 Ω/square) was pre-cleaned with acetone, ethanol and de-ionized water for 20 min consecutively and then dried with dry nitrogen. UV-ozone treatment was performed using an ultraviolet light source with a wavelength of 245 nm at 20 mm distance from the substrate under an oxygen flow in order to raise the work function of ITO.[11] Solution of the active layers was prepared in chloroform with a particular weight ratio. The mixed solution was passed through a 0.22 μm filter and then spin coated at 2000 rpm (revolutions per minute) on an ITO glass substrate. Finally, an Al electrode was deposited on the organic film by thermal evaporation at 5×10^{-4} Pa to serve as the device cathode. The photoactive area of the devices was 0.1 cm^2 as limited by a shadow mask.

2.3. Device testing

A 150 W xenon lamp was used as a broad band light source. The current density–voltage (J–V) characteristics of the devices were measured with a Keithley 2410 source measure unit. Films for UV–Vis absorption and photoluminescence (PL) measurements were prepared by spin coating onto cleaned quartz slides and were detected with a Shimadzu UV-3101 PC spectrometer and a system of ACTON 150 CCD spectrometer. All measurements were carried out in an air atmosphere and at room temperature.

3. Results and discussion

The configuration of the device and its energy band structure is depicted schematically in Fig. 2. The Al and ITO were used as electrodes. The Alq3:PVK film or Alq3:porphyrin:PVK film was used as an active layer. The introduction of porphyrin into the PVK:Alq3 system can adjust the energy bands of donor and acceptor.

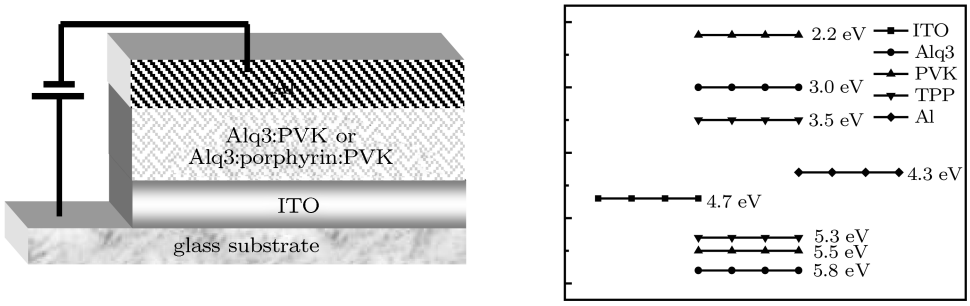


Fig. 2. Schematic illustration of solar cell and its energy band structure.

3.1. Varying the kind of porphyrin

UV–Vis absorption spectra of PVK:Alq3(1:1, mass ratio) film, PVK:TPP:Alq3 (1:0.5:1) film and PVK:CuTClPP:Alq3 (1:0.5:1) film were measured and are shown in Fig. 3. The characteristic absorption bands (from 200 to 400 nm) correspond to the absorptions of PVK[12] and Alq3,[13] and the absorption from 400 to 700 nm is due to the porphyrins.[14] The spectra show clearly that the introduction of TPP or CuTClPP into the active layer leads to the enhancement of the photosensitivity in the range of visible light where PVK and Alq3 absorb weekly. Therefore the absorption spectrum of the whole active layer is broadened.[15] The enhanced light absorption of the active layer is favourable for exciton generation and thereby can lead to a larger photocurrent in theory. The energy gaps of the porphyrins, i.e., TPP and CuTClPP, are E_g (TPP)=1.8 eV, E_g (CuTClPP)=2.0 eV, respectively.[16] The energy gap of TPP is closer to the optimum energy gap of 1.5 eV of solar cell than that of CuTClPP. So the PVK:TPP:Alq3 cell is predicted to have a better performance than the PVK:CuTClPP:Alq3 cell.

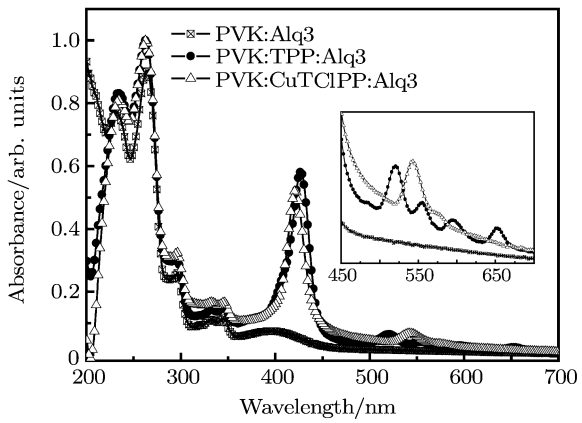


Fig. 3. Absorption spectra of active layers.

In order to confirm whether the introduced porphyrin can lead to a larger photocurrent and whether TPP is better than CuTClPP in improving the cell performance of the PVK : Alq3 system, three kinds of organic solar cells were fabricated. The structures of the devices were in the forms of ITO/PVK:Alq3 (1:1)/Al, ITO/PVK : TPP : Alq3 (1:0.5:1)/Al and ITO/PVK : CuTClPP : Alq3 (1:0.5:1)/Al, respectively. Photovoltaic parameters of these cells such as V_{oc}, J_{sc} and FF were calculated from the analysis of the J–V characteristics (seen in Fig. 4) and are listed in Table 1. It is seen that cell with porphyrin is characterised by higher photocurrent and voltage than the cell without porphyrin. In addition, TPP has better properties than CuTClPP, with the active layer introduced into it. The improved J_{sc} is partly due to the contribution made by porphyrin to extending the light harvesting. Another reason is that when metal porphyrin is formed, metal ion is not in one plane along with porphyrin ring and the decrease of molecular planarity leads to reducing the porphyrin conjugation, consequently the ability of carrier transport was decreased. So the J_{sc} of the device with CuTClPP is lower than that of the device with TPP. The blended p–n junction system with three materials can facilitate the separation of charge from the excitons formed by irradiation. Therefore, the photovoltaic effect of device incorporated with porphyrins is actually improved.

Table 1. Photovoltaic parameters of different solar cells.

device	V_{oc}/V	J_{sc}/μA·cm^{-2}	FF
PVK:Alq3	0.33	0.485	0.275
PVK:CuTClPP:Alq3	0.66	1.37	0.230
PVK:TPP:Alq3	0.77	7.13	0.216

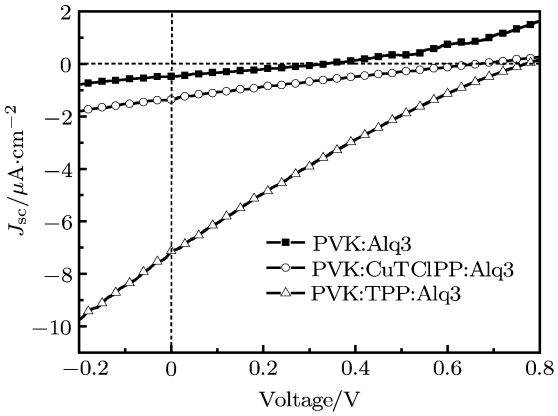


Fig. 4. *J–V* characteristics of different solar cells.

3.2. Varying the weight ratio of porphyrin

The effect of the amount of porphyrin on the solar cell was further investigated. Figure 5 shows the effect of varying the PVK:TPP:Alq3 weight ratio from 1:0.5:1 through to 1:2:1. The photovoltaic parameters of the cells such as V_{oc}, J_{sc} and FF are summarized in Table 2. Variations of FF, J_{sc} and V_{oc} with TPP doping ratio are shown in Fig. 6. It can be observed that the values of V_{oc}, J_{sc}, and FF depend remarkably on the amount of TPP. The values of V_{oc} and J_{sc} increase at first and reach a maximum, then they decrease with further increase in the amount of TPP. The FF value increases monotonically from 0.216 to 0.257. When the ratio of PVK:TPP:Alq3 is 1:1.5:1, the best performance of the solar cell is obtained. The V_{oc} of the cell is 0.87 V and J_{sc} is 17.5 $\mu A\cdot cm^{-2}$. The enhanced performance can be ascribed to the enhancement of light absorption with the increase of TPP concentration in the film. The degradation in performance may be due to aggregation occurring as TPP reaches a certain concentration and the resistance of the film increases. Excitons generated in the film have a lower probability of reaching the dissociation interface where they are converted into charges.[17] Therefore, the performance decreases.

Table 2. Photovoltaic parameters of devices based on PVK:TPP:Alq3 film with different amounts of TPP.

weight ratio	V_{oc}/V	$J_{sc}/\mu A\cdot cm^{-2}$	FF
1:0.5:1	0.77	7.13	0.216
1:1:1	0.82	11.2	0.221
1:1.5:1	0.87	17.5	0.227
1:2:1	0.82	15.1	0.257

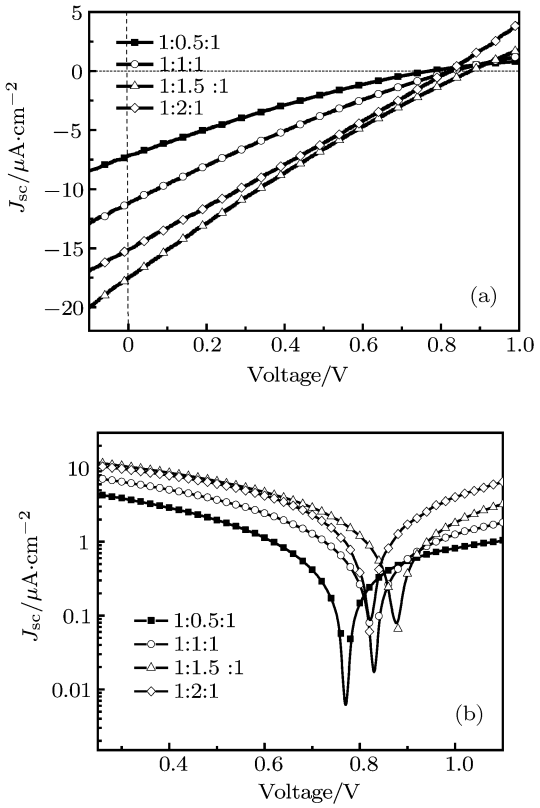


Fig. 5. *J–V* characteristics of devices with different amounts of TPP; below the exponential form of the *J–V* characteristics.

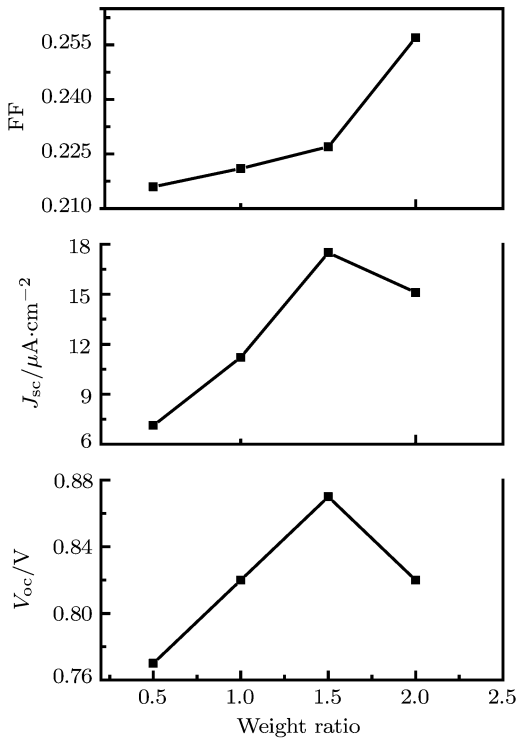


Fig. 6. Variations of FF, J_{sc} and V_{oc} with TPP doping ratio.

3.3. Varying the composition of the active layers

In order to identify the roles of the different components in the active layer, four kinds of cells with the same structure but different active layers were designed and prepared. Then their properties were measured. Table 3 shows the photovoltaic parameters of different cells, such as V_{oc}, J_{sc} and FF. The cell with the best performance is the PVK:TPP:Alq3 system. It is known that porphyrin is a light-harvesting material and a relatively weak electron donor[18] while PVK is a good hole transport material and Alq_3 is a good electron transport material. The device of number D in Table 3 has a better performance than the device of number A because of introducing TPP to enhance the light absorption. The device of number D has a better performance than the device of number B because of introducing PVK to enhance the hole mobility of the active layer. The device of number D has a performance better than the device of number C because of introducing Alq3 to enhance the electron mobility of the active layer. The three chemicals blended into the active layer all impart good performance to the cell device, but none of the three can be omitted. From the absorption spectrum, it is concluded that TPP can broaden the absorption spectrum of the active layer, which favours the exciton generation. In addition, the blended active layer has good electron and hole mobilities thanks to the Alq3 and PVK components, respectively. Therefore, the PVK:TPP:Alq3 cell has good performance compared with the other cells.

Table 3. Photovoltaic parameters of different solar cells.

number	device	weight ratio	V_{oc}/V	$J_{sc}/\mu A\cdot cm^{-2}$	FF
A	PVK:Alq3	1:1	0.33	0.485	0.272
B	TPP:Alq3	1.5:1	0.20	5.01	0.290
C	TPP:PVK	1.5:1	0.23	2.74	0.289
D	PVK:TPP:Alq3	1:1.5:1	0.87	17.5	0.227

In addition, the PL spectra of PVK, Alq3, TPP and any two of them blended into a film were also measured and are plotted in Fig. 7. In Fig. 7(a), the PL spectra of these films were obtained when the films were excited by 340 nm light, corresponding to the absorption of PVK. The exciton emittion of PVK disappeared and the emission peaks of Alq3 and TPP emerged for the cases of PVK:Alq3 (1:1) and PVK:TPP (1:1.5), respectively. This reveals that the energy of PVK exciton was quenched in these two blended films. Emission quenching results from two processes: Förster energy transfer[19] and exciton dissociation.[20] In PVK:Alq3 (1:1), the emission of Alq3 is relatively strong thanks to Förster energy transfer from PVK to Alq3. This means that more excitons of PVK transfer their energy to excite Alq3, but the dissociation of excitons into electrons and holes at the interface of the two materials is relatively weak. On the other hand, for PVK:TPP (1:1.5), even the overlap between the emission of PVK and the absorption of TPP (Fig. 7(b)) is large, Förster energy transfer from PVK to TPP is not superior in this system because the emission of TPP is comparatively weak. Therefore, the main emission quenching of PVK is due to exciton dissociation at the interface of PVK and TPP. Figure 7(c) shows the PL spectra of the pure Alq3 film, the PVK:Alq3 (1:1) film and the TPP:Alq3 (1.5:1) film, which were obtained with excitation at 390 nm corresponding to the absorption of Alq3. It is apparent that the PVK:Alq_3 (1:1) and the pure Alq3 have similar PL spectra in shape, but the former is higher than the latter in PL intensity. This also indicates that the Förster energy transfer occurs from excited PVK to Alq3. For Alq3:TPP (1:1.5). The small overlap between the emission spectrum of Alq3 and the absorption band of TTP (Fig. 7(d)) may causes the Förster energy transfer. But for the case of TPP:Alq3 (1.5:1), the exciton emission of Alq3 was not detected even though the excitation corresponds to the absorption of Alq3. In addition, the emission of TPP is weak. So the main emission quenching of Alq3 is not due to energy transfer from Alq3 to TPP, but due to exciton dissociation at the interface between Alq3 and TPP.

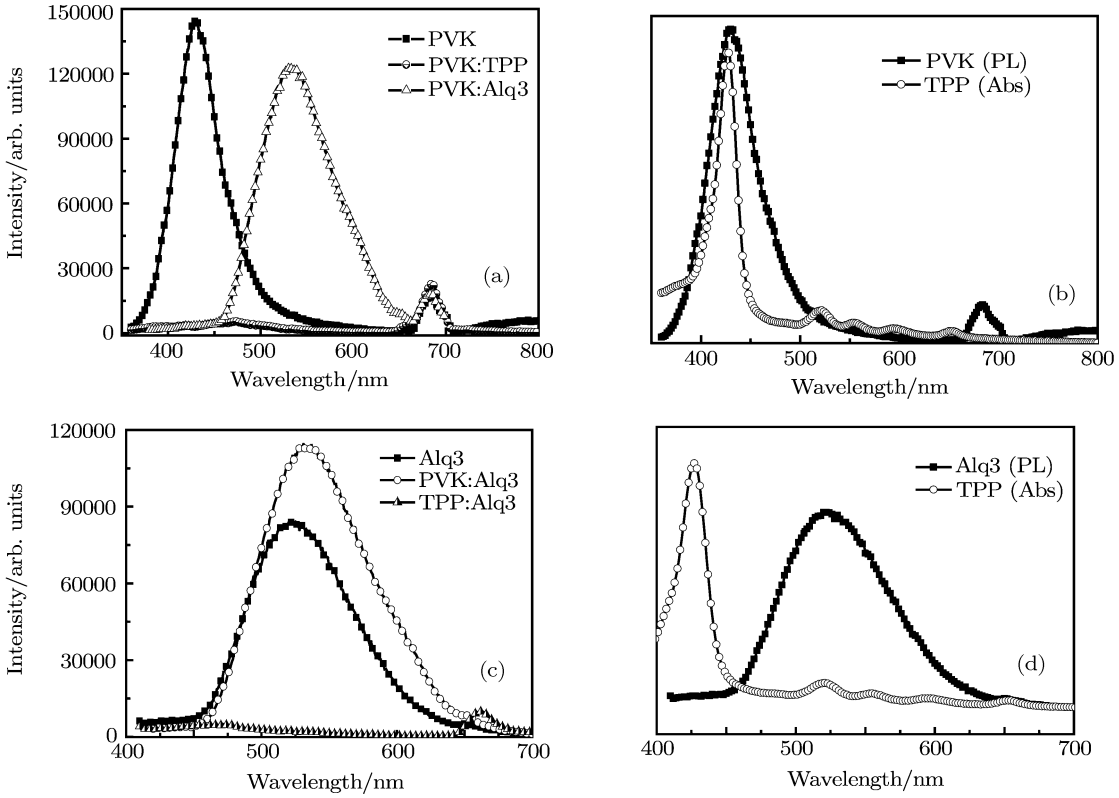


Fig. 7. PL spectra of pure PVK film, PVK:TPP (1:1.5) film and PVK:Alq_3(1:1) film with 340 nm excitation (a), Optical absorption of TPP film and PL spectrum of PVK film (b), PL spectra of pure Alq_3 film, PVK:Alq_3 (1:1) film and TPP:Alq3 (1.5:1) film with 390 nm excitation (c), optical absorption of TPP film and PL spectrum of Alq_3 film (d).

As described above, it is believed that the doped TPP favours exciton dissociation in the PVK:Alq3 system and results in an enhancement of the properties of the cells. As a consequence, the PVK:TPP:Alq3 solar cell system may be regarded as a cascade connection of three sub-cells of PVK:TPP, TPP:Alq3 and PVK:Alq3. PVK, TPP and Alq3 can improve the hole mobility, light absorption intensity and electron mobility of the ternary bulk hereojunction system, respectively.

4. Conclusions

The performances of ternary blend solar cell based on PVK:porphyrin:Alq3 systems are sharply dependent on each of its components: PVK, porphyrin and Alq3. Much more photogeneration is obtained from the ternary bulk hereojunction solar cell. Two kinds of porphyrins are included in the blend systems. TPP is better than CuTClPP in improving the cell performance of the PVK:Alq3 system. TPP can induce more exciton dissociation in the PVK:Alq3 system. When the ratio of PVK:TPP:Alq3 is 1:1.5:1, the best-performance solar cell is obtained. V_{oc} is 0.87 V, and J_{sc} is 17.5 $\mu A \cdot cm^{-2}$. The solar cell of a PVK:TPP:Alq3 system can be regarded as a cascade of three solar cells of PVK:TPP, TPP:Alq3 and PVK:Alq3. PVK, TPP and Alq3 can improve the hole mobility, light absorption intensity and electron mobility of the ternary bulk hereojunction system, respectively.

References

[1] Gunes S, Neugebauer H and Sariciftci N S 2007 *Chem. Rev.* **107** 1324
[2] Gunes S, Fritz K P, Neugebauer H, Sariciftci N S, Kumar S and Scholes G D 2007 *Sol. Energy Mater. Sol. Cells* **91** 420
[3] Zhang C F, Tong S W, Jiang C Y, Kang E T, Chan D S H and Zhu C X 2008 *Appl. Phys. Lett.* **93** 43307
[4] Takahashi K, Takano Y, Yamaguchi T, Nakamura J,

Yokoe C and Murata K 2005 *Synth. Met.* **155** 51
[5] El-Nahass M M, Zeyada H M, Aziz M S and Makhlouf M M 2005 *Thin Solid Films* **492** 290
[6] Miyairi K, Itoh E and Hashimoto Y 2003 *Thin Solid Films* **438** 147
[7] Kim H S, Kim C H, Ha C S and Lee J K 2001 *Synth. Met.* **117** 289
[8] Jin H, Hou Y B, Meng X G, Tang A W and Teng F 2008 *Chin. J. Polym. Sci.* **26** 249
[9] Adler A D, Longo F R, Finarell J D, Goldmach J, Assour J and Korsakof L 1967 *J. Org. Chem.* **32** 476
[10] Li Z F, Wang S W, Wang J X, Wang Y Q and Wang Y X 2003 *J. Inorg. Chem.* **19** 691 (in Chinese)
[11] Hu T, Zhang F J, Xu Z, Zhao S L, Yue X and Yuan G C 2009 *Synth. Met.* **159** 754
[12] Park J H, Park O O, Kim J, Yu J W, Kim J K and Kim Y C 2004 *Curr. Appl. Phys.* **4** 659
[13] Hovsepyan A, Lee H, Sarpyan T, Melikyan H, Yoon Y, Babajanyan A, Friedman B and Lee K 2008 *Ultramicroscopy* **108** 1058
[14] Zheng W Q, Shan N, Yu L X and Wang X Q 2008 *Dyes Pigments* **77** 153
[15] Lai S L, Chan M Y, Fung M K, Lee C S and Lee S T 2007 *Appl. Phys. Lett.* **90** 203510
[16] Takahashi K, Iwanaga T, Yamaguchi T, Komura T and Murata K 2001 *Synth. Met.* **123** 91
[17] Belcher W J, Wagner K I and Dastoor P C 2007 *Sol. Energy Mater. Sol. Cells* **91** 447
[18] Takahashi K, Kuraya N, Yamaguchi T, Komura T and Murata K 2000 *Sol. Energy Mater. Sol. Cells* **61** 403
[19] Dorovskataran V, Vanhoek A, Link T A, Visser A and Hagen W R 1994 *FEBS Lett.* **348** 305
[20] Haugeneder A, Lemmer U and Scherf U 2002 *Chem. Phys. Lett.* **351** 354