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Z. R. Hong, C. S. Lee, S. T. Lee, W. L. Li, and Y. Shiota

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Bifunctional photovoltaic and electroluminescent devices using a starburst amine as an electron donor and hole-transporting material

Z. R. Hong

Center of Super-Diamond and Advanced Films (COSDAF) and Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, People's Republic of China and Changchun Institute of Optics, Fine Mechanics and Physics, 1-Yan An Street, Changchun, 130021, People's Republic of China

C. S. Lee and S. T. Lee^{a)}

COSDAF and Department of Physics and Materials Science, City University of Hong Kong, Hong Kong SAR, People's Republic of China

W. L. Li

Changchun Institute of Optics, Fine Mechanics and Physics, 1-Yan An Street, Changchun 130021, People's Republic of China

Y. Shirota

Department of Applied Chemistry, Faculty of Engineering, Osaka University, Yamadaoka, Suita, Osaka, 565, Japan

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Photovoltaic (PV) devices, using 4,4',4''-tris(2-methylphenylphenylamino)triphenylamine (m-MTDATA) as an electron donor and tris-(8-hydroxyquinoline) aluminum (Alq) as an electron acceptor, were fabricated. The relationship between photocurrent generation, exciplex formation, and device structure was explored. PV performance was significantly enhanced by inserting a thin mixed layer (5 nm) of m-MTDATA and Alq between the two organic layers of the original m-MTDATA/Alq bilayer device. Both the bilayer and trilayer devices showed PV and electroluminescent (EL) properties, suggesting their potential use as multifunction devices. It was also shown that strong EL emission from exciplex might be used as an indicator of efficient exciton dissociation during the reverse PV process. © 2002 American Institute of Physics.

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Organic electroluminescent (EL) and photovoltaic (PV) devices with heterojunctions have attracted much attention since the reports by Tang *et al.*^{1,2} Both types of devices have numerous advantages, such as light weight, low cost, and easy fabrication, over their inorganic counterparts. The recombination of an electron and hole to form exciton (or the reverse process, i.e., exciton dissociation) at the organic heterojunction is a critical process for the operation of these devices. Therefore, it is important to understand the relationship between exciton actions and organic interface for designing devices with better performance and for understanding details of a mechanism.

The contact of two molecules often led to nonintrinsic broadband luminescence (usually move to the longer wavelength side). This is due to the emission from an exciplex formed between the two materials.³ Exciplex emission has been the subject of recent studies.⁴⁻⁷

In the field of organic PVs, interpenetrating or blending of materials, such as polymers and C60, provides an efficient transient charge transfer between a donor and acceptor, and a percolation path for oriented carrier transport followed by charge collection.^{8,9} Doped organic crystal has also been reported to be a promising pathway for highly efficient photon-electron conversion.¹⁰ Therefore, increasing the

donor-acceptor contact area and providing transport paths for holes and electrons are important for obtaining efficient PV cells. Although thermal coevaporation of low molecular-weight organic materials provides contact on a molecular level, so far, most PV devices reported were prepared by spin coating instead of thermal evaporation.

On the other hand, in order to convert incident photoenergy efficiently into photocurrent, photoluminescence must be suppressed. As a matter of fact, the transient charge transfer in the PV process takes place between two molecules or sites, which strongly interact with each other. In this sense, it is a kind of exciplex formation, showing no luminescence or serious luminescent quenching. On the contrary, it is well known that luminescence can be suppressed by the formation of exciplex. The formation and dynamics of an exciplex are quite complicated and very sensitive to the environmental factors, such as solvents and the surrounding field.^{11,12} This sensitivity not only provides an effective probe for fundamental study but also gives flexibility for controlling these kinds of excited states for practical use. Further insight of an exciplex is available in the review by Bhattacharyya and Chowdhury.¹³

Here we report the relationship between the PV, EL properties, and exciplex formation in the same organic devices, and the effects of device structure on the PV and EL performance. 4,4',4''-tris(2-methylphenylphenylamino)triphenylamine (m-MTDATA), which is known to form an ex-

^{a)}Author to whom correspondence should be addressed; electronic mail: apannale@cityu.edu.hk

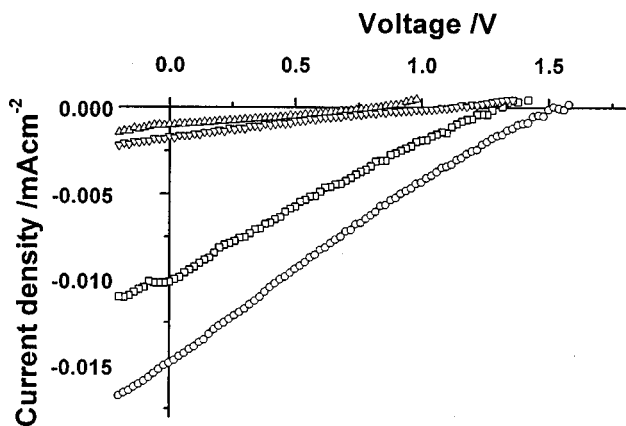


FIG. 1. I - V curves of PV devices under 1.27 mW/cm^2 UV light irradiance, m-MTDATA/Alq (square), m-MTDATA/m-MTDATA:Alq/Alq (circle), NPB/Alq (up triangle), and NPB/NPB:Alq/Alq (down triangle).

ciplex with tris-(8-hydroxyquinoline) aluminum (Alq),^{4,14} was chosen as the electron donor and hole-transporting material, and Alq as the electron acceptor and transport material. For comparison, N,N'-diphenyl-N,N'-bis(1-naphyl)-(1,1'-biphenyl) (NPB) was also used. Our results indicated that strong EL emission from an exciplex might indicate efficient exciton dissociation during the PV process in the same devices.

m-MTDATA was synthesized according to the reported method.¹⁵ Other materials were commercially available and used in this study without further purification. Indium tin oxide (ITO) coated glass substrate, with a sheet resistance of $100 \Omega/\square$, was cleaned by detergent sonication deionized water rinse and UV ozone treatment. All the organic layers and a Mg:Ag (200 nm, 10:1) alloy cathode were sequentially deposited onto the ITO substrates by thermal evaporation at a pressure of 2×10^{-6} Torr without breaking the vacuum. Deposition of all layers was monitored by quartz oscillators and controlled at a rate of 0.2–0.4 nm/s for the organic layers and 1.0 nm/s for the cathode. All the current–voltage (I - V) curves of PV devices in the light state were obtained under an irradiance of 1.27 mW/cm^2 from a Handy UV-240 rechargeable 365 nm UV light source. All measurements were carried out in ambient air at room temperature.

Devices fabricated in the present study have the following configurations:

- m-MTDATA bilayer device: ITO/m-MTDATA(50 nm)/Alq(60 nm)/Mg:Ag;
- m-MTDATA trilayer device: ITO/m-MTDATA(50 nm)/m-MTDATA:Alq(5 nm)/Alq(60 nm)/Mg:Ag;
- NPB bilayer device: ITO/NPB (50 nm)/Alq(60 nm)/Mg:Ag; and
- NPB trilayer device: ITO/NPB(50 nm)/NPB:Alq(5 nm)/Alq(60 nm)/Mg:Ag.

In the mixing layer, the weight ratio of two compounds was 1:1.

The PV response of the four devices fabricated in this work is shown in Fig. 1. It can be seen that the m-MTDATA devices have much better performance than the corresponding NPB devices, and the trilayer devices perform better than the corresponding bilayer ones.

Under UV illumination, the m-MTDATA bilayer device

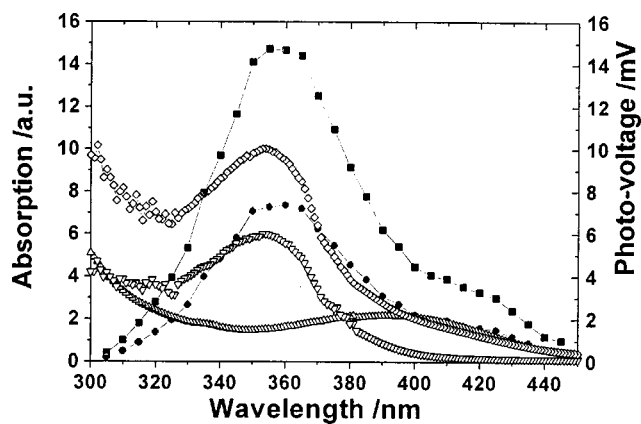


FIG. 2. PV dependence on excited wavelength of m-MTDATA/Alq (solid circle) and m-MTDATA/m-MTDATA:Alq/Alq (solid square), and absorption spectra of Alq film (up triangle), m-MTDATA film (down triangle) and combined m-MTDATA/Alq film (diamond).

showed an open-circuit voltage (V_{oc}) as high as 1.30 V and a short-circuit current (I_{sc}) of 0.0098 mA/cm^2 , which corresponds to a quantum efficiency of 2.6%. The maximum power conversion efficiency is 0.24%. To obtain better contact of the two compounds, a mixed layer was inserted between the original two layers. Similar to the blending method used in devices based on an organic molecule⁵ and polymer,^{6,16} by adding a 5 nm m-MTDATA:Alq mixed layer, the quantum efficiency at I_{sc} and the maximum power conversion efficiency were increased considerably to 3.8% and 0.40%, respectively. It is clear that the bilayer structure limits the contact of Alq and m-MTDATA molecules significantly, although the energy level structure is suitable for exciton dissociation.

When the m-MTDATA bilayer and trilayer devices were illuminated by monochromatic light (obtained from a Perkin-Elmer LS50 fluorescence spectrophotometer) of different wavelengths at a constant power density of $35 \mu\text{W/cm}^2$, the photovoltage–wavelength curves were obtained (Fig. 2). Absorption spectra of thin films of Alq and m-MTDATA and combined Alq/m-MTDATA were also shown for comparison. No detectable change was observed by the insertion of the mixing layer. It is clear that the absorption of both m-MTDATA and Alq was responsible for the photoinduced carrier generation. The bilayer and trilayer devices had the similar PV response, indicating a similar mechanism in the two devices, although the trilayer device exhibited higher photovoltage. Filled factors for bilayer and trilayer devices (0.21–0.23) are almost same, independent on the devices structure, indicating that the generation mechanism of photoinduced carriers probably depended on the inside field and not changed by inserting the mixing layer.

While the molecular structure of m-MTDATA and NPB are rather similar, and hole mobility of NPB is better than that of m-MTDATA,^{17,18} the PV performance of the m-MTDATA and the NPB devices differed considerably. It can be seen from Fig. 1 that the I_{sc} of the NPB-based devices is almost one order smaller than that of the m-MTDATA-based devices in spite of superior hole mobility of NPB. It is

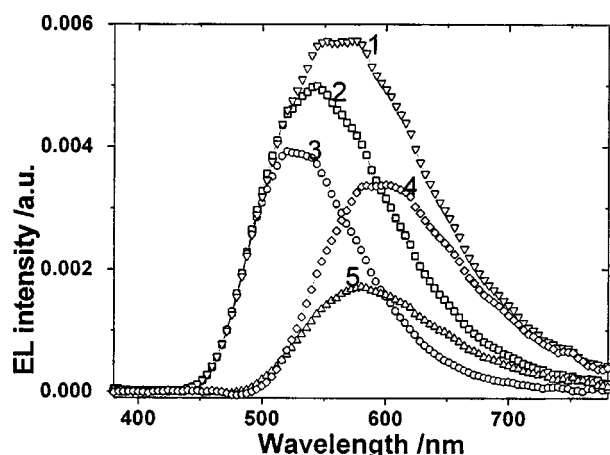


FIG. 3. EL emission from devices, m-MTDATA/m-MTDATA:Alq/Alq (1, down triangle), m-MTDATA/Alq (2, square), NPB/Alq (3, circle), exciplex emission from m-MTDATA/m-MTDATA:Alq/Alq (4, diamond), and m-MTDATA/Alq (5, up triangle).

also interesting that EL spectra of the m-MTDATA and the NPB devices differ significantly as shown in Fig. 3. The bilayer and trilayer NPB devices exhibited the same intrinsic Alq luminescence peak at about 525 nm (curve 3 in Fig. 3), while the m-MTDATA devices show EL peaks broadened toward a longer wavelength. The EL spectra of the m-MTDATA devices could be deconvoluted into the intrinsic Alq peak and another one at a longer wavelength. The deconvoluted longer wavelength components for the trilayer and bilayer m-MTDATA devices are shown as curves 4 and 5 in Fig. 3, respectively, were due to exciplex formation between m-MTDATA and Alq.⁴ The exciplex peak in the trilayer device is stronger than that in the bilayer devices, consistent with a previous study.⁵ This can be understood as the mixed m-MTDATA:Alq layer in the trilayer device provides more direct contacts between the two types of molecules.

Furthermore, comparing curves 4 and 5 in Fig. 3 shows the peak in the trilayer device was shifted by 20 nm to the longer wavelength compared to the bilayer device. This can be attributed to the different average distance between electron donors and acceptors molecules/ions.¹⁹ The present results suggest that the mixing layer has effectively improved donor-acceptor contact and reduced the average distance between the electron donors and acceptors. The formation of an exciplex and exciplex emission is enhanced, and the emission peak is redshifted.⁵

Considering the energy levels,⁴ electron injection from Alq to m-MTDATA, and hole injection from m-MTDATA to Alq are difficult due to the large energy barriers at the Alq/m-MTDATA interface. Thus charge carriers injected from the respective electrode tend to accumulate at the organic/organic interface under low drive voltages and generate the Alq⁻ and m-MTDATA⁺ species. When the spatial distance between the two species was small enough, the ion pairs will be bound by Coulomb force. In this case, the formation of the exciplex is caused by carrier injection. Therefore, electron transition from Alq⁻ to m-MTDATA⁺ either gives rise

to the nonintrinsic emission from an exciplex or leads to other nonradiative processes. Exciplex is usually less efficient emissive center and thus is harmful for EL emission.^{4,14} The situation in the trilayer device was almost the same except that the average donor-acceptor distance was even smaller. This, therefore, causes redshift in the exciplex emission. Both the EL and PV processes in the present m-MTDATA devices involve exciplex formation. It is considered that exciplex formation and emission in EL and PL studies could be criteria for selection of PV materials. Although similar materials²⁰ and devices with both EL and PV functions²¹ have been reported, the present devices have much better performance, including high EL brightness (>400 cd/m² within 10 V).

In summary, PV devices sensitive to near-UV light were obtained. The relationship between the exciplex emission and PV effect of devices based on a starburst amine was established. A relatively strong PV effect was observed from the EL devices which showed exciplex emission. The introduction of a mixing layer enhanced both the PV performance and the exciplex emission. Our results showed that increasing the contact between electron donors and acceptors was an efficient way to improve the PV performance of organic molecular devices. It is considered that strong exciplex emission in an EL device is a good indicator of efficient charge transfer at the organic interface, which is a basic requirement for good PV performance.

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