JOURNAL OF MATERIALS SCIENCE **39** (2004) 4053 – 4056 LETTERS

High photoconductivity properties of perylene polyimide containing triarylamine unit

HAIJUN NIU
Department of Applied Chemistry, Harbin Institute of Technology 410#, Harbin 150001, People's Republic of China
E-mail: haijunniu@hit.edu.cn

CHENG WANG, XU DUO BAI*
School of Chemistry and Chemical Engineering, Heilongjiang University, Harbin 150080, People's Republic of China
E-mail: xuduobai@hotmail.com

YUDONG HUANG
Department of Applied Chemistry, Harbin Institute of Technology 410#, Harbin 150001, People's Republic of China

Organic photoconductive materials are widely used as photoreceptors in electrophotographic imaging and laser printing. Such organic xerographic photoreceptors are bilayer devices consisting of a charge generation layer (CGL) and a charge transport layer (CTL) in which the functions of photocarrier generation and charge transport are separately carried out and optimized. The current charge photogeneration materials on which photogeneration studies have been focused are small molecules (dyes, pigments, or salts) such as phthalocyannines, perylenes, squaraines, and azo compounds. Among these materials, perylene chromophores, with strong fluorescence and photoconductive properties, find importance as functional dyes and are especially attractive for electric photography, solar cells, color liquid crystal, optical recording systems, light collection systems, and nonlinear optical materials, etc. [1–7], because of their robust mechanical properties, chemical, photochemical and thermal stability, and their ready processability into high quality thin films and coating. But there is phase separation in bilayer devices which would impede conductor transporting.

In this letter we report the results of our investigation of large photoinduced currents in novel monolayers with two functions as photoreceptors and charge transporting layers employing thin films of *N*,*N*′-dialkyl perylene-3,4:9,10-biscarboximide derivatives as the charge photogeneration units and 4,4′-biaminetriphenylamine units as charge transporting groups.

The diamine 1 was chosen for preparation of homopolyimides with dianhydride (Scheme 1) and diamine1 and diamine 2 reacted with 3,4,9,10-perylenetetracarboxylic acid dianhydride and 6FDA to give PPI-2 and PPI-3 (Scheme 2).

The synthesis and characterization of the polymers and preparation of solar cells will be published elsewhere in detail.

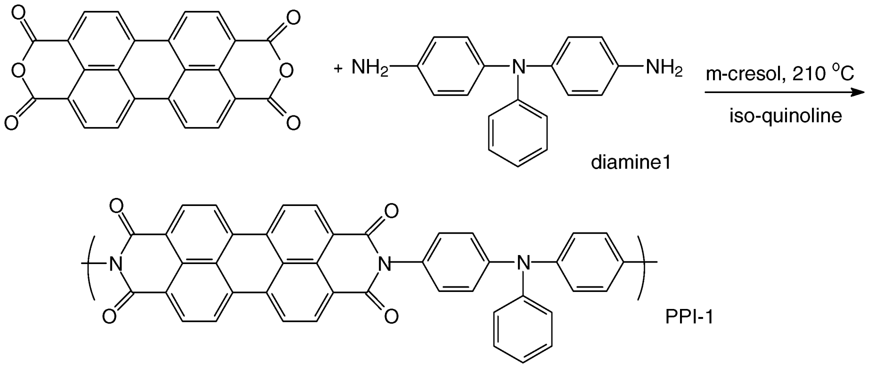
The polymerization was best carried out in m-cresol with a small amount of isoquinoline at 210 °C. Completion of imidization was confirmed by IR spectra (Fig. 1), showing the absence of the anhydride's carbonyl peaks (1650 cm^{-1}) and the presence of the carbonyl peaks for the imide (1771 and 1727 cm^{-1}). In addition, there was a weak peak at 3400 cm^{-1} that can be attributed to terminal groups ($-\mathrm{NH}_2$).

The ^{1}HNMR showed multipeaks in the region of δ-8.7 ppm that could be attributed to protons in the perylenetetracarboxylic ring, and aromatic signals of its benzene ring and perylene ring in the range of 6.6–8.2 ppm. The signals of PPI-3 in 2.49 ppm (2H,s) represented $-\mathrm{CH}_2$-groups in 4,4′-methylenedianiline unit of polymer. Gel permeation chromatography (GPC) showed weights M_n of PPI-1, PPI-2, PPI-3 were 3.4×10^4, 2.0×10^5, and 6.6×10^4 g/mol, respectively, with a polydispersity of 2.0–3.5. M_n of PPI-2 is highest among these three polymers and this may be explained by the reality that it can be more liable to dissolve in m-cresol than the others. In the process of polymerization, it did not precipitate early, favoring growth of M_n. The DSC showed that T_d were above 400 °C and T_g were 334, 302, and 287 °C, respectively. All these results indicated that they have better thermal stability after film formation. Figs 2 and 3 show the UV spectra of PPI-1, PPI-2, and PPI-3. PPI-1 has two UV absorption peaks at about 499 and 539 nm, which are almost identical with those observed in the absorption spectrum of PPI-2 and PPI-3, respectively. It is considered that the electric state of polyimide was maintained even after incorporating the chromophore into the polymer. On the other hand, UV absorption peaks of films of polyimides have blueshifted by 15–20 nm compared with those in m-cresol, because polarity around the chromophore became weaker, and the intermolecular reaction of the polymer became stronger.

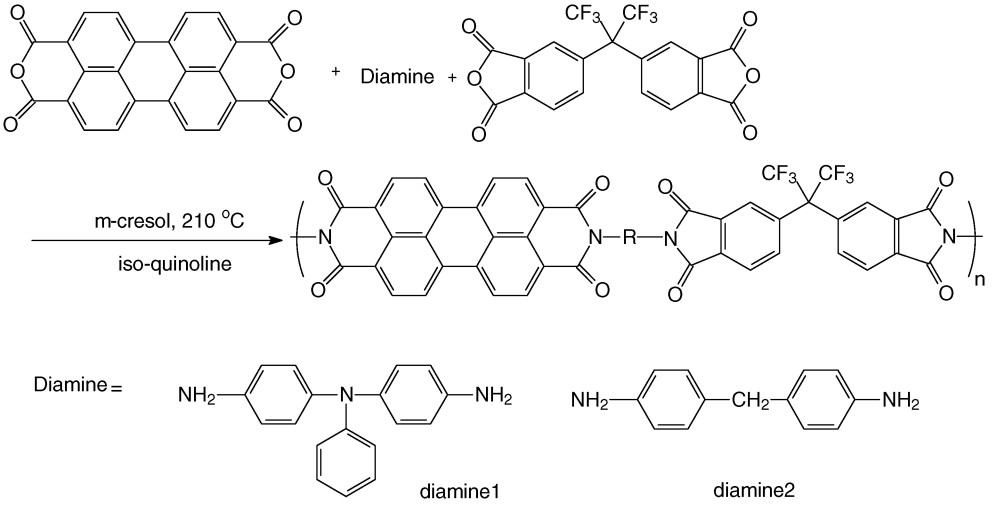
---

*Author to whom all correspondence should be addressed.

0022–2461 © 2004 Kluwer Academic Publishers



Scheme 1 One step solution polymerization of perylenetetracarboxylic dianhydride and diamine1 (PPI-1).



Scheme 2 Synthesis of copolyimides (PPI-2, PPI-3).

Fig. 4 shows the photocurrent spectra of PPI-1, PPI-2, and PPI-3 films versus incidence with different wave length. From the results of these experiments, as expected, the photocurrent density of PPI-1 and PPI-2 containing 4,4′-diaminetriphenylamine units was one order of magnitude higher than that for PPI-3 containing 4,4′-methylenedianiline because electro-rich triarylamine could react with the electron-acceptor perylenetetracarboxylic dianhydride, then complexes came into being which favored separation

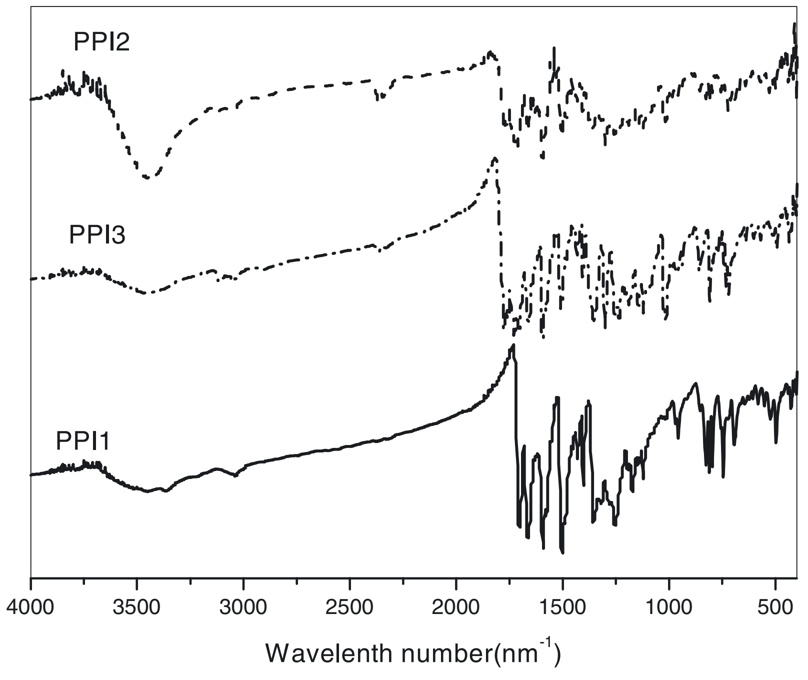


Figure 1 IR spectra of PPIs.

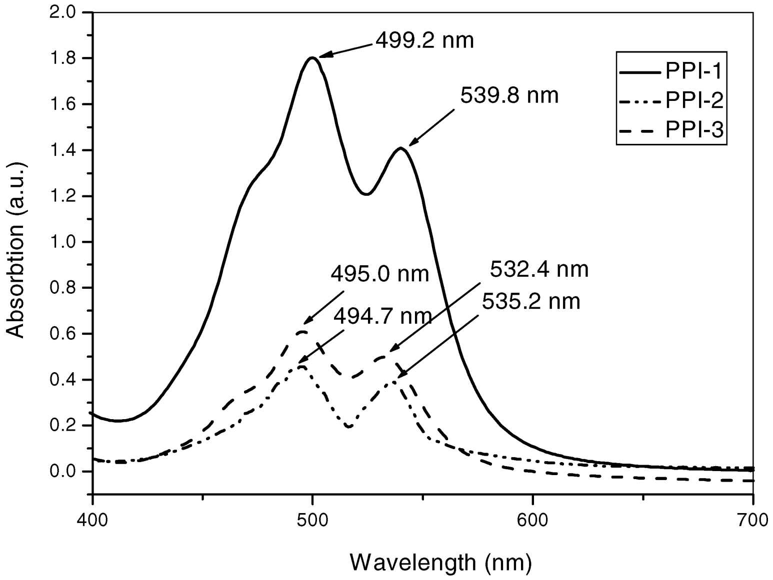


Figure 2 UV-Vis absorption spectra of PPI-1, PPI-2, and PPI-3 solid film (Thickness 15–20 μm).

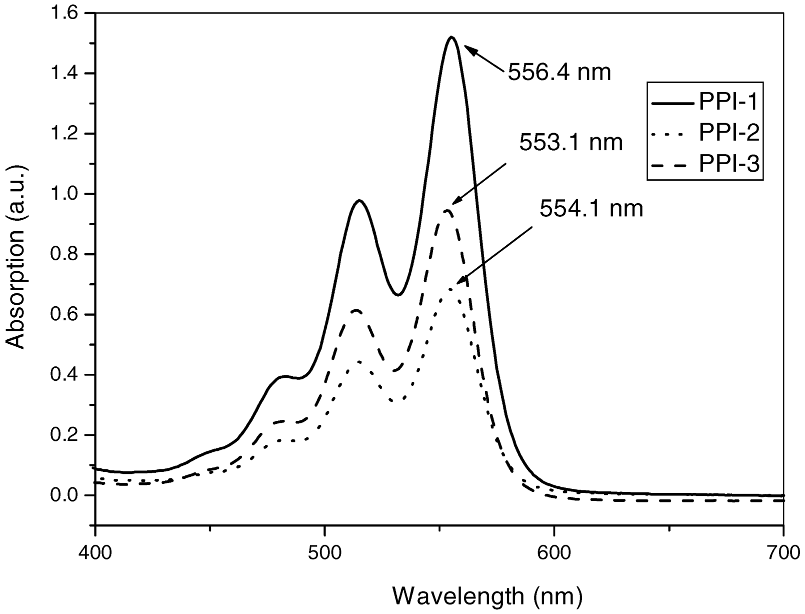


Figure 3 UV-Vis absorption spectra of PPI-1, PPI-2, and PPI-3 in m-cresol.

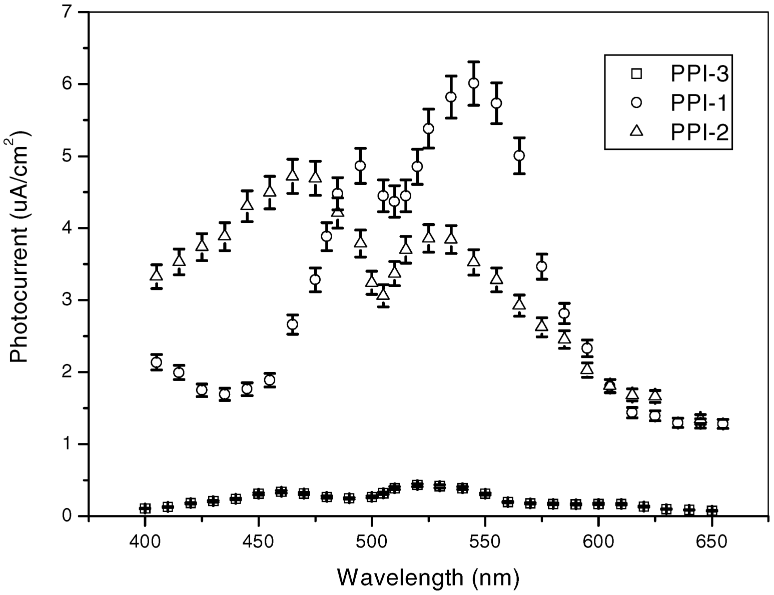


Figure 4 Photocurrent spectra of PPI-1, PPI-2, and PPI-3 as the function of wavelength of incident light.

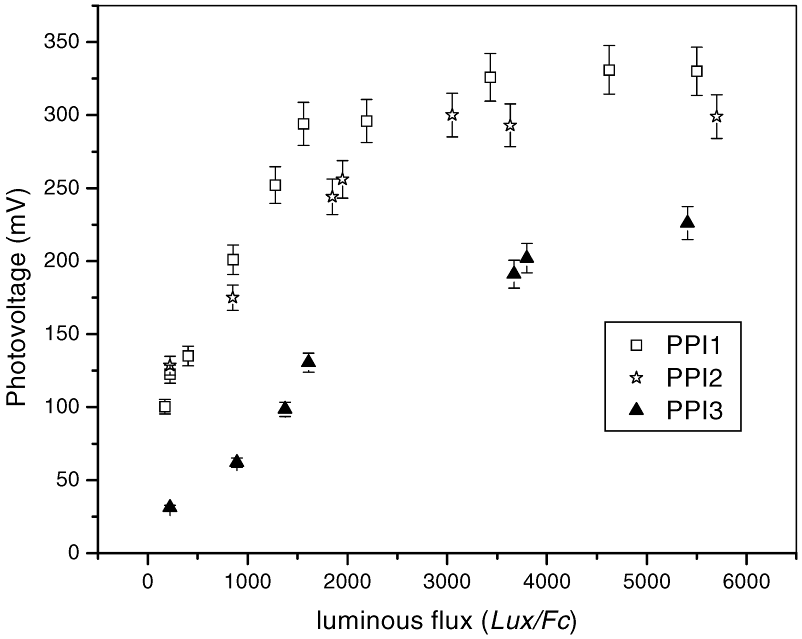


Figure 5 Open-circuit voltage with intensity luminescence.

and transporting of photogenerated charge, contributing to great photocurrent [9]. When 544 nm light irradiated the film the current density was the biggest. The current density versus incidence is similar to the UV absorption of polyimides which indicated the photocharge originated the electron structure.

Fig. 5 presents the open-circuit voltages spectra with the change of intensity of luminescence. The results demonstrate that the voltage becomes a constant when the intensity of luminescence reaches a key point. The voltage of PPI-1 is higher than PPI-2 and PPI-3 by 30–50 mV because there is more extending conjugated π–π^* bond than in PPI-2 and PPI-3.

References

1. M. SCHNEIDER, J. HAGEN, D. HAARER and K. MÜLLEN, *Adv. Mater.* **12** (2000) 351.
2. T. KATSUME, M. HIRAMOTO and M. YOKOYAMA, *Appl. Phys. Lett.* **64** (1994) 2546.
3. K. PETRITSCH, J. J. DITTMER, E. A. MARSEGLIA, R. H. FRIEND, A. LUX, G. G. ROZENBERG, S. C. MORATTI and A. B. HOLMES, *Solar Energy Mater. Solar Cells* **61** (2000) 63.
4. M. P. O'NEIL, M. P. NIEMCZYK, W. A. SVEC, D. GOSZTOLA, G. L. GIII and M. R. WASIELEWSKI, *Science* **257** (1992) 63.
5. W. HUANG, D. YAN and Q. LU, *Chem. J. Chinese Univers.* **23**(10) (2002) 2005.
6. M. THELAKKAT, P. PÖSCH and H. W. SCHMIDT, *Macromolecules* **34** (2001) 7441.
7. W. LU, J. P. GAO, Z. Y. WANG, Y. QI, G. G. SACRIPANTE, J. D. DUFF and P. R. SUNDARARAJAN, *ibid.* **32** (1999) 8880.
8. Y. OISHI, H. TAKADO, M. Y. M. KAKIMOTO and Y. IMAI, *J. Polym. Sci., Part A: Polym. Chem.* **28** (1990) 1763.
9. X. D. BAI, Z. Q. ZHANG, J. K. FENG, G. XIE and J. S. CHEN, *Chem. J. Chinese Univers.* **21** (2000) 1455.

Received 18 November
and accepted 11 December 2003