

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231650772>

Phototransistors of a Rigid Rod Conjugated Polymer

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY C · NOVEMBER 2008

Impact Factor: 4.77 · DOI: 10.1021/jp806120q

CITATIONS

36

READS

40

6 AUTHORS, INCLUDING:



Huanli Dong

Chinese Academy of Sciences

108 PUBLICATIONS 2,612 CITATIONS

SEE PROFILE



Hongxiang li

Chengdu University Of Traditional Chinese ...

104 PUBLICATIONS 2,592 CITATIONS

SEE PROFILE



Keiichi Torimitsu

Tohoku University

138 PUBLICATIONS 2,502 CITATIONS

SEE PROFILE

Phototransistors of a Rigid Rod Conjugated Polymer

Huanli Dong,^{†,‡} Hongxiang Li,^{*,†} Erjing Wang,^{†,‡} Hiroshi Nakashima,[§] Keiichi Torimitsu,[§] and Wenping Hu^{*,†}

Beijing National Laboratory for Molecular Sciences, Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, Graduate School of Chinese Academy of Sciences, Beijing 100039, China, and NTT Basic Research Laboratories, NTT Corporation, 3-1 Morinosato Wakamiya, Atsugi, Kanagawa 243-0198, Japan

Received: July 9, 2008; Revised Manuscript Received: October 20, 2008

Phototransistors of a rigid-rod conjugated polymer, a derivative of poly(*para*-phenylene ethynylene)s with thioacetyl end groups (TA-PPE), were investigated. The phototransistors exhibited high photo-response properties with responsivity at 36 mA/W and switch ratio up to 3.3×10^3 , indicating the potential applications of the phototransistors in optoelectronic devices. Moreover, the photoresponse mechanism of the transistors was examined. Two effects—photoconductive and photovoltaic effects—were both observed in the same transistors depending on the gate bias. With gate bias the polymer phototransistors were dominated by photovoltaic effect, while without gate bias the devices were decided by photoconductive effect.

Introduction

A phototransistor, as the key component of optoelectronic integration, not only realizes the combination of light detection and signal amplification in a single device, but also attractively exhibits high sensitivity and low noise compared to their counterparts, e.g., photodiode.¹ Since the first phototransistor was proposed in 1951, there has been tremendous progress in the development of phototransistors.² Polymer devices can be fabricated by easy solution process and have good compatibility with plastic substrates,³ which are promising for low-cost and large-area optoelectronic integrated circuits. However, few reports have addressed phototransistors of polymers.^{3c,4}

Poly(*para*-phenylene ethynylene)s (PPEs), a kind of electroluminescent materials for organic light-emitting diodes,⁵ did not receive much attention in the early boost of semiconductor polymer research because their highest occupied molecular orbital levels were low and difficult for holes injection, which may be effectively modulated with appropriated substitutions or end-functionalized groups, such as thio-functionalized end groups.^{5,6} Moreover, PPEs show not only ideal conductivity, but also high thermal, oxidative, and photostability, which makes them attractive for solid-state optoelectronic devices.⁷ It is regretful that only a few references have addressed the applications of PPEs in organic field-effect transistors (OFETs),^{4b,7c} not to mention the combination of the outstanding photophysical and electronic properties of PPEs together in a single device, such as phototransistors.^{4b} Recently, we have synthesized a derivative of PPEs with thioacetyl end-functionalized groups⁸ (Figure 1, we call TA-PPE). Here, we would like to examine the phototransistor properties of the rigid-rod conjugated polymer.

Experimental Methods

Top-contact phototransistors were fabricated on the basis of Si/SiO₂ substrates (the back low resistance Si as gate, SiO₂ (500

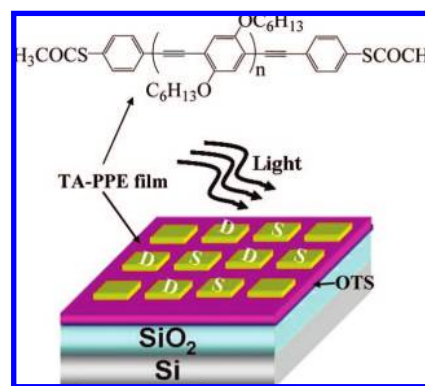


Figure 1. Molecular structure of TA-PPE ($n \approx 100$) (top) and the schematic structure of a TA-PPE phototransistor (bottom).

nm) with a capacitance of 7.5 nF/cm² as gate insulator). White light was irradiated on the devices from the semiconductor side, as shown in Figure 1 (bottom). Prior to the deposition of TA-PPE film, the substrate of Si/SiO₂ was sequentially cleaned with pure water, hot concentrated sulfuric acid–hydrogen peroxide solution (concentrated sulfuric acid/hydrogen peroxide water = 2:1), pure water, pure ethanol, and pure acetone, successively. The Si/SiO₂ substrates were then treated with trichloro(octadecyl)silane (OTS) by a normal vapor deposition method as described elsewhere. TA-PPE films (50–60 nm) were spin-coated on the OTS-modified Si/SiO₂ substrate from chlorobenzene solution (10 mg/mL) at room temperature. Electrodes of Au (25 nm) were vacuum-deposited on TA-PPE films with channel length and width at 0.02 mm and 0.15 mm, respectively. The UV–vis absorption spectra were obtained on a Jasco V-570 UV-vis spectrometer. Surface morphologies of the TA-PPE films were characterized by an atomic force microscope (AFM, Nanoscopy IIIa). Current–voltage (I – V) characteristics were performed by a Keithley 4200 SCS with a Micromanipulator 6150 probe station in a clean and shielded box at room temperature in air.

* Corresponding author. E-mail address: huwp@iccas.ac.cn.

[†] Chinese Academy of Sciences.

[‡] Graduate School of Chinese Academy of Sciences.

[§] NTT Corporation.

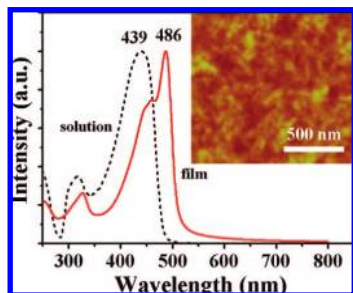


Figure 2. UV-vis absorption spectra of TA-PPE molecules in solution (dashed line) and film (solid line) (inset shows the AFM morphology of the spin-coated TA-PPE thin film).

Results and Discussion

Comparing the UV-vis absorption spectra of the spin-coated TA-PPE thin films to that in solution (as shown in Figure 2), the obvious difference is the new narrow red-shifted band (about 47 nm) with a distinct shoulder, indicating the strong π -aggregation interactions in the solid state.^{5c,9} The band gap of TA-PPE molecules was estimated at about 2.40 eV from the long wavelength edge, indicating that TA-PPE molecules could be easily excited by visible light. Additionally, the AFM topographic image of TA-PPE film showed continuous surface morphology with small rodlike crystallites, and unobvious change was observed until 150 °C, which indicated the facility for the fabrication of devices with high performance (the temperature dependence of AFM images of TA-PPE films is shown in the Supporting Information).

Typical photoresponse characteristics of the transistors are shown in Figure 3. Figure 3a displays the output characteristics of the devices in dark and under illumination (0.37 mW/cm²) at different gate voltages. A clear increase of drain current was observed under illumination, indicating that the light illumination played an important role to tune the properties of the transistors. This conclusion was further confirmed by the results of Figure 3b. It was obvious that the incident light could be used to substitute the V_G as an independent variable to adjust the output characteristics of the transistors, i.e., the light could be used as an additional terminal (the fourth terminal) to optically control the device operation. The responsivity (R), an important parameter of phototransistors, can be defined as follows:^{4c}

$$R = \frac{I_{ph}}{P_{opt}} = \frac{(I_{DS,illum} - I_{DS,dark})S^{-1}}{P_{inc}} \quad (1)$$

where I_{ph} is the source-drain photocurrent, P_{opt} is the incident light power, P_{inc} is the power of the incident light per unit area, $I_{DS,dark}$ and $I_{DS,illum}$ are the drain-source current in dark and under illumination, respectively, and S is the effective device area. It was attractive that the R value of the phototransistors could reach 36 mA/W at $V_G = 0$ V. This value should be further improved by using a monochromatic light source with photon energy corresponding to the maximum absorption of the polymer.¹⁰ The high responsivity of the transistors resulted in the large on/off ratio of the optoelectronic devices. The maximum on/off ratio of the phototransistor reached 3.3×10^3 at $V_G = 0$ V (Figure 3c), indicating the potential applications of the transistors in optoelectronic devices such as optoisolators, highly sensitive optical switches and retro sensors, and so forth.^{2d} The temperature dependence of the phototransistors (Figure S2, Supporting Information) suggested the I_{DS} currents (both in darkness and under illumination) decreased with temperature increasing, which is probably assigned to the mobility decreasing at high

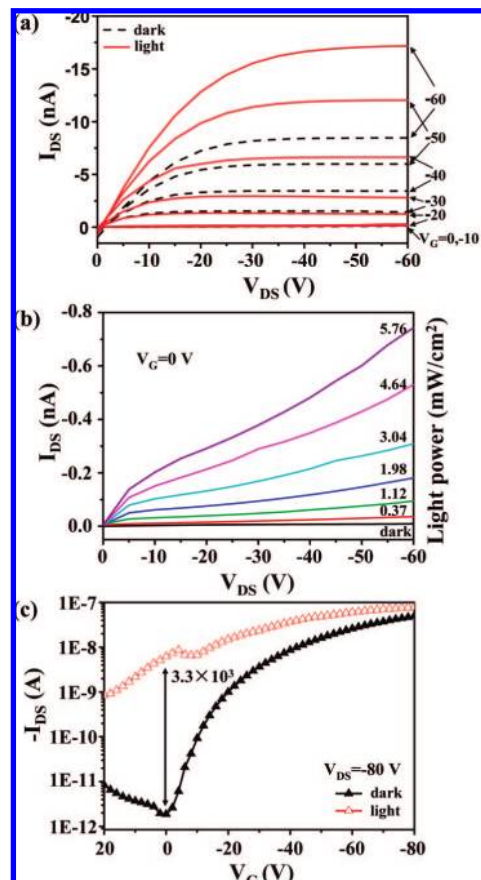


Figure 3. (a) The output characteristics of an exemplary TA-PPE phototransistor at different V_G with light irradiation (light density: 0.37 mW/cm²); (b) the output characteristics of the transistors using light irradiation to substitute V_G (light intensity changed from 0 to 5.76 mW/cm² with a fixed $V_G = 0$ V); and (c) transfer characteristics of the phototransistors in darkness (closed triangles) and under illumination (hollow triangles, light intensity: 5.76 mW/cm²) at $V_{DS} = -80$ V.

temperature because the enhanced chain vibration may have blocked the carrier transport.

As mentioned previously, TA-PPE nanojunctions (gap width around 40 nm) exhibited photoswitch characteristics too.^{7c} However, the highest switch ratio of the nanojunctions was below 1000, even under 52 mW white light irradiation. Here, the maximum on/off ratio of the phototransistor (electrodes gap width around 20 μ m) reached 3.3×10^3 under 5.76 mW white light irradiation (near 1/10 intensity of the nanojunctions). It was obvious that the maximum on/off ratio of the phototransistors was much higher than that of nanojunctions (two end devices). One reason was probably that the gate-applied bias of the transistors provided an efficient route for the dissociation of the photogenerated excitons, and was beneficial for the formation of the conducting channel of the transistors. This deduction was confirmed by the results as shown in Figure 4. When the gate voltage at $V_G = 0$ V ($V_{DS} = -10$ V), with the cycles of photoirradiation increasing (1, 2, 3, 4, 5...), the switch-on current (drain current) increased gradually (Figure 4a). However, when $V_G = -10$ V ($V_{DS} = -10$ V), such cycles dependence of drain current were not obvious (Figure 4b). It was highly possible that, under the gate bias, the dissociated electrons from the photogenerated excitons were attracted to the polymer/insulator interface to form the conductive channel between the source and drain electrodes, which provided an efficient way for the dissociation of excitons into free electrons and holes and increased the charge density in the conductive channel.

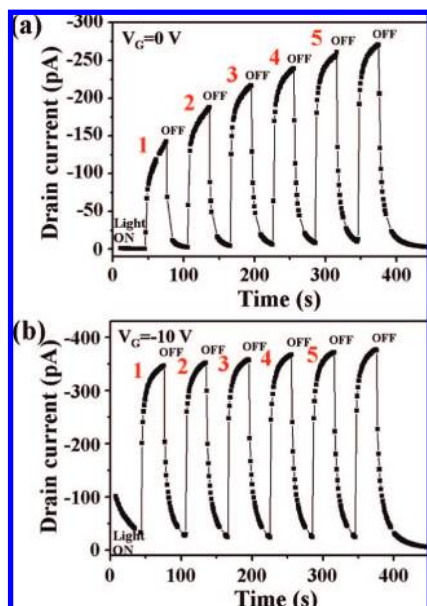


Figure 4. Photo-switch properties of TA-PPE phototransistors with an applied gate bias of (a) 0 V and (b) -10 V at $V_{DS} = -10$ V (white-light intensity, 5.76 mW/cm^2).

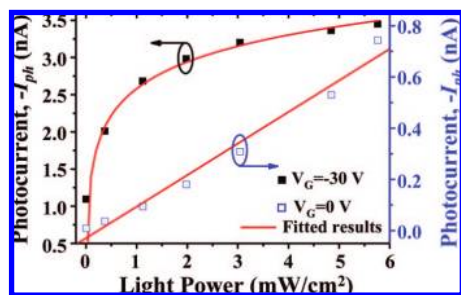


Figure 5. Photocurrent as a function of incident light power under turn-on ($V_G = -30$ V) and turn-off ($V_G = 0$ V) conditions at $V_{DS} = -60$ V. Symbols are measured data, and red solid lines indicate the fitted results using reported equations.

Actually, under photoillumination, two different effects, i.e., photoconductive and photovoltaic effects, possibly occur in the polymer layer. The photovoltaic effect depends on the light absorbance, excitons dissociation, electrons and hole diffusion, and electrode collections. Additionally, the photoconductive effect depends on the huge increase of the carrier density in the polymer films ($\sigma = nq\mu$, where σ is the conductivity, n is the number of carriers, q is the electronic charge, and μ is the mobility of TA-PPE). Keeping the drain-source voltage constant ($V_{DS} = -60$ V), the photocurrents of the transistors were found depending on the power of the incident light at different gate bias ($V_G = 0$ and -30 V). The results were shown in Figure 5. It was believed that, in phototransistors at on-state, the photovoltaic effect was dominant because a photovoltage would be induced by the large number of accumulated trapped electrons under the source, which could be described (at $V_G > V_{th}$) as¹¹

$$I_{ph,pv} = G_M \Delta V_{th} = \frac{AkT}{q} \ln \left(1 + \frac{\eta q \lambda P_{opt}}{I_{pd} hc} \right) \quad (2)$$

where η is the quantum efficiency, q is the elementary charge, P_{opt} is the incident optical power, I_{pd} is the dark current for electrons, hc/λ is the photon energy, G_M is the transconductance,

ΔV_{th} is the threshold voltage shift, k is the Boltzmann constant, T is the absolute temperature, and A is the fitting parameter. While at off-state, the photoconductive effect of the transistors would be more significant as given by ref 12.

$$I_{ph,pc} = (q\mu nE)WD = BP_{opt} \quad (3)$$

where μ is the charge carrier mobility, n is the carrier density, E is the electrical field in the channel, W is the gate width, D is the thickness of the active layer, P_{opt} is the incident optical power, and B is the fitting parameter. The experimental and fitted results of the transistors at different gate voltage were shown in Figure 5. It was clear that the photocurrents at $V_G = -30$ V fitted well with eq 2, while those at $V_G = 0$ V fitted well with eq 3, indicating that the polymer phototransistors with gate bias were dominated by photovoltaic effect, while those without gate bias were decided by photoconductive effect.

Conclusion

In conclusion, here we successfully fabricated polymer phototransistors based on rigid-rod conjugated TA-PPE molecules. The TA-PPE phototransistors exhibited excellent photoresponse properties with a maximum on/off ratio of 3.3×10^3 and responsivity of 36 mA/W , indicating potential applications of the transistors in optoelectronic devices. Two effects—photoconductive and photovoltaic effects—were both observed in the same transistors, depending on the gate bias. With gate bias, the polymer phototransistors were dominated by photovoltaic effect, while, without gate bias, they were decided by photoconductive effect.

Acknowledgment. The authors acknowledged financial support from the National Natural Science Foundation of China (60736004, 60771031, 20721061, 50725311), the Ministry of Science and Technology of China (2006CB806200, 2006CB-932100), and the Chinese Academy of Sciences.

Supporting Information Available: AFM images of TA-PPE films before and after annealing at different temperatures and the corresponding phototransistor performance prepared from annealed TA-PPE films. This material is available free of charge via the Internet at <http://pubs.acs.org>.

References and Notes

- (1) (a) Campbell, J. C. In *Semiconductors and Semimetals*; Tsang, W. T., Ed.; Academic: New York, 1985; Vol 22D. (b) Seeds, A. J.; de Salles, A. A. *IEEE Trans. Microwave Theory Tech.* **1990**, *38*, 577. (c) Romero, M. A.; Martinez, M. A. G.; Herczfeld, P. R. *IEEE Trans. Microwave Theory Tech.* **1996**, *44*, 2279. (d) Saragi, T. P. I.; Pudzich, R.; Fuhrmann, T.; Salbeck, J. *J. Appl. Phys. Lett.* **2004**, *84*, 2334.
- (2) (a) Kang, H. S.; Choi, C. S.; Choi, W. Y.; Kim, D. H.; Seo, K. S. *Appl. Phys. Lett.* **2004**, *84*, 3780. (b) Noh, Y. Y.; Kim, D. Y.; Yoshida, Y.; Yase, K.; Jung, B. J.; Lim, E.; Shim, H. K. *Appl. Phys. Lett.* **2005**, *86*, 043501. (c) Noh, Y. Y.; Kim, D. Y.; Yase, K. *J. Appl. Phys.* **2005**, *98*, 074505. (d) Tang, Q.; Li, L.; Song, Y.; Liu, Y.; Li, H.; Xu, W.; Liu, Y.; Hu, W.; Zhu, D. *Adv. Mater.* **2007**, *19*, 2624. (e) Saragi, T. P. I.; Londenberg, J.; Salbeck, J. *J. Appl. Phys.* **2007**, *102*, 046104.
- (3) (a) Bao, Z. In *Semiconductive Polymers*; Hsieh, B.; Wei, Y.; Galvin, M. E., Eds.; American Chemical Society: Washington, D.C., 1999. (b) Meixner, R. M.; Göbel, H.; Yildirim, F. A.; Bauhofer, W.; Krautschnider, W. *Appl. Phys. Lett.* **2006**, *89*, 092110. (c) Marjanović, N.; Singh, Th. B.; Dennler, G.; Gunes, S.; Neugebauer, H.; Sariciftci, N. S.; Schwödiouer, R.; Bauer, S. *Org. Electron.* **2006**, *7*, 188.
- (4) (a) Narayan, K. S.; Kumar, N. *Appl. Phys. Lett.* **2001**, *79*, 1891. (b) Xu, Y.; Berger, P. R.; Wilson, J. N.; Bunz, U. H. F. *Appl. Phys. Lett.* **2004**, *85*, 4219. (c) Hamilton, M. C.; Martin, S.; Kanicki, J. *IEEE Trans. Electron Dev.* **2004**, *51*, 877. (d) Deen, M.; Kazemeini, M. H. *Proc. IEEE* **2005**, *93*, 7.
- (5) (a) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605. (b) Schmitz, C.; Posch, P.; Thelakkat, M.; Schmidt, H. W.; Montali, A.; Feldman, K.; Smith,

P.; Weder, C. *Adv. Funct. Mater.* **2001**, *11*, 41. (c) Pschirer, N. G.; Miteva, T.; Evans, U.; Roberts, R. S.; Marshall, A. R.; Neher, D.; Myrick, M. L.; Bunz, U. H. F. *Chem. Mater.* **2001**, *13*, 2691. (d) Montali, A.; Smith, P.; Weder, C. *Synth. Met.* **1998**, *97*, 123. (e) Wilson, J. N.; Windscheif, P. M.; Evans, U.; Myrick, M. L.; Bunz, U. H. F. *Macromolecules* **2002**, *35*, 8681.

(6) (a) Robey, S. W.; Ciszek, J. W.; Tour, J. M. *J. Phys. Chem. C* **2007**, *111*, 17206. (b) Zangmeister, C. D.; Picraux, L. B.; van Zee, R. D.; Yao, Y.; Tour, J. M. *Chem. Phys. Lett.* **2007**, *442*, 390. (c) Zangmeister, C. D.; Robey, S. W.; van Zee, R. D.; Yao, Y.; Tour, J. M. *J. Phys. Chem. B* **2004**, *108*, 16187. (d) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537. (e) Tour, J. M. *Acc. Chem. Res.* **2000**, *33*, 791.

(7) (a) Hu, W.; Nakashima, H.; Furukawa, K.; Kashimura, Y.; Ajito, K.; Han, C.; Torimitsu, K. *Phys. Rev. B* **2004**, *69*, 165207. (b) Hu, W.; Nakashima, H.; Furukawa, K.; Kashimura, Y.; Ajito, K.; Torimitsu, K. *Appl. Phys. Lett.* **2004**, *85*, 115. (c) Hu, W.; Nakashima, H.; Furukawa, K.; Kashimura, Y.; Ajito, K.; Liu, Y.; Zhu, D.; Torimitsu, K. *J. Am. Chem. Soc.* **2005**, *127*, 2804. (d) Hu, W.; Jiang, J.; Nakashima, H.; Luo,

Y.; Kashimura, Y.; Chen, K.; Shuai, Z.; Furukawa, K.; Lu, W.; Liu, Y.; Zhu, D.; Torimitsu, K. *Phys. Rev. Lett.* **2006**, *96*, 027801.

(8) (a) Nakashima, H.; Furukawa, K.; Kashimura, Y.; Torimitsu, K. *Polym. Prepr. (Am. Chem. Soc. Div. Polym. Chem.)* **2003**, *44*, 482. (b) Nakashima, H.; Furukawa, K.; Ajito, K.; Kashimura, Y.; Torimitsu, K. *Langmuir* **2005**, *21*, 511.

(9) (a) Miteva, T.; Palmer, L.; Kloppenburg, L.; Neher, D.; Bunz, U. H. F. *Macromolecules* **2000**, *33*, 652. (b) Kim, J.; Swager, T. M. *Nature* **2001**, *411*, 1030.

(10) (a) Martin, S.; Hamilton, M. C.; Kanicki, J. *Proc. IDRC* **2003**, 14. (b) Hamilton, M. C.; Kanicki, J. *IEEE J. Sel. Top. Quantum Electron.* **2004**, *10*, 840.

(11) Takanashi, Y.; Takahata, K.; Muramoto, Y. *IEEE Trans. Electron Dev.* **1999**, *46*, 2271.

(12) Sze, S. M. In *Physics of Semiconductor Devices*; Wiley: New York, 1981; p 744.

JP806120Q