REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY *(Leave blank)*	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	Sept. 9, 1996	Technical Report # 13

4. TITLE AND SUBTITLE

Photoinduced Electron Transfer in Binary Blends of Conjugated Polymers

5. FUNDING NUMBERS

N00014-94-1-0540

Kenneth J. Wynne
R & T Code: 3132111

6. AUTHOR(S)

S. A. Jenekhe and L. R. de Paor

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Department of Chemical Engineering
University of Rochester
206 Gavett Hall
Rochester, NY 14627

8. PERFORMING ORGANIZATION REPORT NUMBER

13

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

Office of Naval Research
800 North Quincy Street
Arlington, VA 22217-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

Published in *PolymerPreprints* **37(1)**, 94-95 (1996).

12a. DISTRIBUTION/AVAILABILITY STATEMENT

Reproduction in whole or in part is permitted for any purpose of the United States Government.
This document has been approved for public release and sale; its distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT *(Maximum 200 words)*

We report the first observation of photoinduced electron transfer between two π-conjugated polymers in binary systems. Picosecond transient absorption and fluorescent spectroscopies of mixtures *of n-type (electron accepting)* poly(benzimidazobenzophenanthroline ladder) (BBL) and *p-type (electron donating)* poly(p-phenylene benzobisthiazole) (PBZT) evidence intermolecular electron transfer when BBL is selectively photoexcited. The results suggest that blends of π-conjugated polymers are supramolecular materials which have novel features such *as delocalized radical ion pairs or diion pairs*, novel properties, and implications for organic p-n junction devices, photodiodes, photovoltaic cells, photoreceptors, and molecular electronic devices. Observation of photoinduced electron transfer between the components of the binary blends also implies molecular level miscibility of the blends.

14. SUBJECT TERMS

photoinduced electron transfer; supramolecular materials; polymer blends; conjugated polymers

15. NUMBER OF PAGES 2

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	Unlimited

OFFICE OF NAVAL RESEARCH

GRANT N00014-94-1-0540

R&T Code 3132111

Kenneth J. Wynne

Technical Report No. 13

Photoinduced Electron Transfer in Binary Blends of Conjugated Polymers

by

Samson A. Jenekhe and Liam R. de Paor

Published

in

Polymer Preprints

University of Rochester
Department of Chemical Engineering
Rochester, NY

September 9, 1996

TECHNICAL REPORT DISTRIBUTION LIST - GENERAL

Office of Naval Research (1)*
Chemistry and Physics Division
Ballston Tower 1, Room 503
800 North Quincy Street
Arlington, Virginia 22217-5660

Defense Technical Information Center (2)
Building 5, Cameron Station
Alexandria, VA 22314

Dr. James S. Murday (1)
Chemistry Division, Code 6100
Naval Research Laboratory
Washington, D.C. 20375-5000

Dr. Kelvin Higa (1)
Chemistry Division, Code 385
Naval Air Weapons Center
Weapons Division
China Lake, CA 93555-6001

Dr. Peter Seligman (1)
Naval Command, Control and Ocean Surveillance Center
RDT&E Division
San Diego, CA 92152-5000

Dr. Richard W. Drisko (1)
Naval Civil Engineering Laboratory
Code L52
Port Hueneme, CA 93043

Dr. Harold H. Singerman (1)
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

Dr. Eugene C. Fischer (1)
Code 2840
Naval Surface Warfare Center
Carderock Division Detachment
Annapolis, MD 21402-1198

* Number of copies to forward

Photoinduced Electron Transfer In Binary Blends of Conjugated Polymers

Samson A. Jenekhe* and Liam R. de Paor
Department of Chemical Engineering
and
Center for Photoinduced Charge Transfer
University of Rochester, Rochester, New York 14627-0166

Introduction

Photoinduced electron transfer processes of π-conjugated polymers are currently of wide interest[1-4] in view of their importance to the fundamental understanding of the electronic structure and properties of the materials and applications such as photodiodes, photovoltaic cells, electrophotographic photoreceptors, and molecular electronic devices. Photoinduced electron transfer (PET) between *p-type (electron donating)* π-conjugated polymers such as poly(arylene vinylenes) or poly(3-alkylthiophenes) and C_{60} or acceptor small molecules have been reported[1-3]. We have reported exciplex formation and PET between several *n-type (electron accepting)* π-conjugated rigid-rod polymers and donor triarylamine molecules[4]. The inherent molecular incompatibility[5] and poor mutual solubility of π-conjugated polymers and C_{60} or small molecules have heretofore limited the scope of studies of PET in conjugated polymers[1-4]. Here, we report the study and first observation of intermolecular photoinduced electron transfer in miscible binary blends of n-type/p-type π-conjugated polymers.

The n-type conjugated polymer investigated is poly(benzimidazobenzophenanthroline ladder) (BBL) whose electronic, optical, and redox properties have been widely reported[6,7]. From the literature[6,7] and our recently measured values of redox potentials of BBL, we estimate its solid state electron affinity (EA) and ionization potential (IP) to be ~4.0-4.4eV and 5.9-6.2eV, respectively. The lower EA and IP values are for the neutral polymer and the higher values are for its protonated form. Thus, BBL is an excellent electron acceptor and can be compared to C_{60} which has an EA value of ~3eV[8]. Several p-type polymers, relative to BBL, were investigated and are exemplified by poly(p-phenylene benzobisthiazole) (PBZT) and poly(p-(2-hydroxy)-phenylene benzobisoxazole) (HPBO). The reported[9] solid state EA and IP values of PBZT are 2.7 and 5.5eV, respectively. The EA and IP values for HPBO are estimated to be 2.4 and 5.6eV, respectively. The structures of BBL and PBZT are shown in Scheme 1. A detailed version of this paper has been submitted for publication[10].

Experimental Section

Our synthesis and characterization of BBL, PBZT, and related polymers have been described[7,9,11]. The BBL, PBZT, and HPBO samples had intrinsic viscosities of ~9.8 or 20 dL/g, 32 dL/g , and 12 dL/g, respectively, indicating that they are high molecular weight materials[7,9]. The two series of binary blends (BBL/PBZT and BBL/HPBO) were prepared by mixing the two components in nitromethane/$GaCl_3$ (or $AlCl_3$) solutions. Thin films of blends were obtained from the solutions by casting or spin coating onto silica or glass substrates following methods described for the pure components[9,11]. The blend films were homogeneous and showed excellent optical transparency and mechanical strength.

The transient absorption system consisted of a Continuum PY61 Series Nd:YAG laser utilizing Kodak QS 5 as the saturable absorber to produce laser light pulses of ~25 ps FWHM. These output pulses were then amplified and the second and third harmonics generated (532 nm and 355 nm respectively). Dichroic beamsplitters in conjunction with colored glass filters were used to isolate the fundamental (1064 nm) and desired harmonic. The fundamental was directed along a variable optical delay and then focused into a 10 cm quartz cell filled with H_2O/D_2O (50:50) to generate a white light continuum probe pulse. The excitation and probe pulses (*ca.* 2 mm diameter) were passed approximately coaxially through the sample. The probe pulse was directed to a Spex 270 M monochromator through a Princeton Instruments fiber optic adapter and dispersed onto a Princeton Instruments dual diode array detector (DPDA 512). This allowed ~350 nm width of the visible spectrum to be collected in a single experiment. A ST-121 detector controller/interface was incorporated into a 386/25 MHz PC to control the arrays and for data storage, manipulation and output.

Results and Discussion

Optical absorption spectra of the blend thin films in the 190-3200 nm region were simple compositional averages of those of the pure components. Only the BBL absorption peaks at 351 and ~575 nm and the PBZT absorption peaks at 438 and 468 nm were observed in the PBZT/BBL blends (Figure 1). Similarly, HPBO/BBL blend spectra had only peaks due to BBL and those due to HPBO (λ_{max} = 405 and 431 nm). There was thus no evidence of ground state charge transfer or strong interactions between the conjugated polymer pairs.

Transient absorption spectra [10] of blend thin films in the 420-730 nm region were obtained at various time delays (50 ps to 82 ns) following photoexcitation at 532 nm. Dramatically enhanced photoinduced bleaching in the 430-480 nm region was observed in the blends compared to the pure PBZT which has a small bleaching and the pure BBL which has no photobleaching in this region. Photobleaching in the ~550-700 nm region was not enhanced but it decreased with decreasing concentration of BBL in the blend. The relative enhancement of photoinduced bleaching at ~470 nm and 50 ps delay as a function of the blend composition was obtained for comparison. Photobleaching of PBZT/BBL blends at 470 nm, compared to pure PBZT, was found to be enhanced by up to factors of 4-6 in the 10-50 mol % BBL concentration region. Similar transient absorption results were obtained in the HPBO/BBL blends.

We propose that the observed enhanced photobleaching in the blends is a consequence of photoinduced electron transfer from PBZT (or HPBO) in the ground state to the photoexcited BBL as illustrated in Scheme 1. The relative highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels in Scheme 1 are based on the IP and EA values. These HOMO/LUMO levels of the two blend pairs suggest that PET is thermodynamically feasible[12]. Although there is little known about the spectral properties of $PBZT^+$ or $HPBO^+$, the known UV-Vis spectra of electrochemically[6] and chemically[13] produced BBL show strong *new* absorption bands at ~400-480 nm and in the infrared compared to the neutral BBL. Previously reported ultrafast (~100fs) transient absorption spectroscopy on the same PBZT/BBL blends indicated that there was enhanced photoinduced absorption at near infrared wavelengths (>690 nm) as a result of *unknown* excited-state species formed on the order of 100fs[14]. We propose that this previously unidentified excited-state species created in less than 1 ps are BBL^- and $PBZT^+$ resulting from PET. At the time delays of 50 ps or later, following photoexcitation in the present experiments, the strong 430-480 nm absorption of BBL^-, already formed by PET between the blend components, leads to the enhanced photobleaching at ~430-480 nm in the transient absorption spectra of blends.

Additional evidence of PET in the binary blends is the large quenching of the photoluminescence of PBZT or HPBO in mixtures with BBL. As shown in the inset of Figure 2, the blends have two emission bands centered at ~540 nm and ~715 nm due respectively to PBZT and BBL components. Relative photoluminescence quantum efficiencies of the blends, compared to the pure components, were estimated from the integration of each emission spectrum. The quenching of the luminescence of PBZT when mixed with BBL is shown in Figure 2 as a function of the blend composition. It is interesting that the maximum luminescence quenching had occurred by 40% mol BBL after which there is saturation. Similar quenching of photoluminescence as a result of photoinduced electron transfer has previously been observed in conducting polymer/C_{60} systems[1,2].

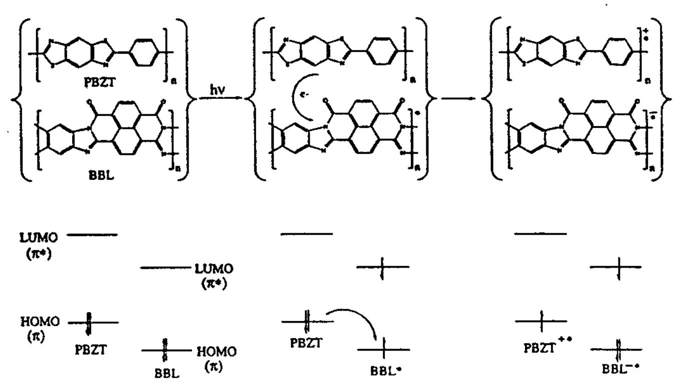
In summary, photoinduced electron transfer between two π-conjugated polymers has been observed in miscible binary blends. Consequences of the excited-state intermolecular electron transfer in these blends include enhanced picosecond photoinduced bleaching observed in transient absorption experiments, large fluorescence quenching, and generation of radical ion pairs delocalized on adjacent chains. These results suggest that mixtures of π-conjugated polymers are *supramolecular materials* which have novel properties and implications for molecular p-n junctions, photovoltaic cells, and molecular electronic devices.

Acknowledgement. This research was supported by the National Science Foundation (Grant CTS-9311741), the Office of Naval Research, and the Center for Photoinduced Charge Transfer (Grant CHE-9120001).

References.

1. (a) Sariciftci, N.S.; Smilowitz, L.; Heeger, A.J.; Wudl, F. *Science* **1992**, *258*, 1474-1476. (b) Sariciftci, N.S.; Braun, D.; Zhang, C.; Srdanov, V.I.; Heeger, A.J.; Stucky, G.; Wudl, F. *Appl. Phys. Lett.* **1993**, *62*, 585-587. (c) Kraabel, B.; Lee, C.H.; McBranch, D.; Moses, D.; Sariciftci, N.S.; Heeger, A.J. *Chem. Phys. Lett.* **1993**, *213*, 389-394. (d) Lee, K.; Janssen, R.A.J.; Sariciftici, N.S.; Heeger, A.J. *Phys. Rev. B* **1994**, *49*, 5781-5784.
2. (a) Yoshino, K.; Yin, X.H.; Morita, S.; Kawai, T.; Zakhidov, A.A. *Chem. Express* **1992**, *7*, 817-820. (b) Morita, S.; Zakhidov, A.A.; Yoshino, K. *Solid State Commun.* **1992**, *82*, 249-252. (c) Morita, S.; Zakhidov, A.A.; Yoshino, K. *Jpn. J. Appl. Phys.* **1993**, *32*, L873-L874.
3. Antoniadis, H.; Hsieh, B.R.; Abkowitz, M.A.; Jenekhe, S.A.; Stolka, M. *Mol. Cryst. Liq. Cryst.* **1994**, *256*, 381-390.
4. (a) Jenekhe, S.A.; Osaheni, J.A. *Science* **1994**, *265*, 765-768. (b) Osaheni, J.A.; Jenekhe, S.A. *Macromolecules* **1994**, *27*, 739-741. (c) Osaheni, J.A.; Jenekhe, S.A.; Perlstein, J. *J. Phys. Chem.* **1994**, *98*, 12727-12736. (d) Jenekhe, S.A. *Adv. Mater.* **1995**, *7*, 309-311.
5. Flory, P.J. *Macromolecules* **1978**, *11*, 1138-1141.
6. Wilbourn, K.; Murray, R.W. *Macromolecules* **1988**, *21*, 89-96; and references therein.
7. Jenekhe, S.A. *Polym. Mater. Sci. Eng. (ACS Div.)* **1989**, *60*, 419-423.
8. Curl, R.F.; Smalley, R.E. *Science* **1988**, *242*, 1017-1022.
9. (a) Osaheni, J.A.; Jenekhe, S.A. *Chem. Mater.* **1995**, *7*, 672-682. (b) *ibid* **1992**, *4*, 1282-1290, and references therein.
10. Jenekhe, S.A.; de Paor, L.R.; Chen, X.L.; Tarkka, R.M. *Chem. Mater.*, submitted.
11. Jenekhe, S.A.; Johnson, P.O. *Macromolecules* **1990**, *23*, 4419-4429.
12. Kavarnos, G.J.; Turro, N.J. *Chem. Rev.* **1986**, *86*, 401-449.
13. Chen, X.L.; Jenekhe, S.A.; Unpublished results.
14. Jenekhe, S.A.; de Paor, L.R.; Fischer, G.L.; Boyd, R.W.; Weng, X.; Fauchet, P.M.; Manuscript submitted for publication.
15. Brédas, J.L.; Chance, R.R.; Eds. *Conjugated Polymeric Materials: Opportunities in Electronics, Optoelectronics, and Molecular Electronics;* Kluwer Academic Publishers: Dordrecht, Holland, 1990.

Scheme 1



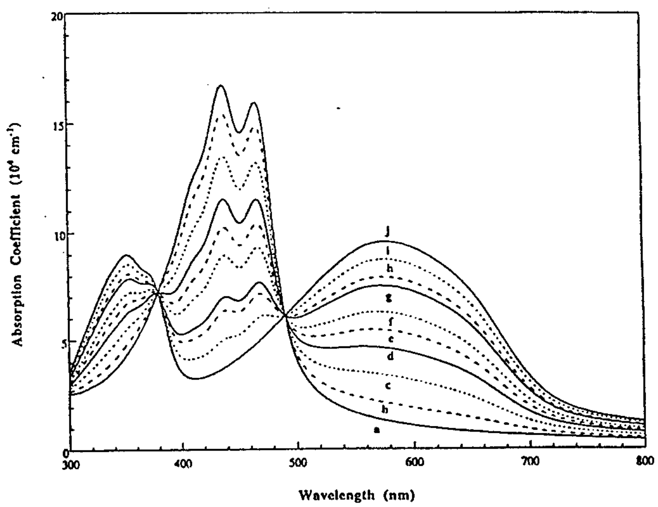


Figure 1. Thin-film optical absorption spectra of PBZT/BBL blends showing the evolution of linear optical properties with composition in mol% BBL: a = 0; b = 10; c = 25; d = 40; e = 50; f = 60; g = 75; h = 80; i = 90; j = 100.

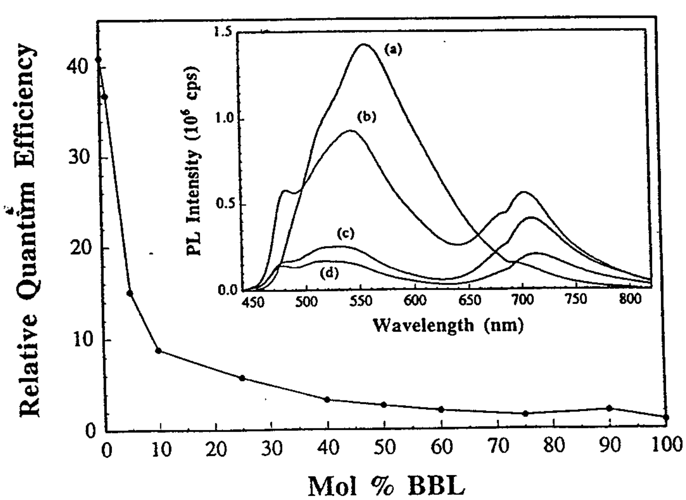


Figure 2. Relative photoluminescence efficiency of ~60 nm PBZT/BBL blends photoexcited at 420 nm compared to the pure components. Inset: PL spectra of PBZT (a), 1% (b), 5% (c), and 10% blends photoexcited at 420 nm.