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Photoinduced Electron Transfer In Binary Blends of Conjugated Polymers

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Abstract

We report observation of photoinduced electron transfer between two π -conjugated polymers in binary mixtures. Picosecond transient absorption and fluorescence spectroscopies of mixtures of *n*-type (*electron accepting*) poly(benzimidazobenzophenanthroline ladder) (BBL) and *p*-type (*electron donating*) poly(*p*-phenylene benzobisthiazole) (PBZT) or poly(*p*-(2-hydroxy)-phenylene benzobisoxazole)(HPBO) 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.

Photoinduced electron transfer processes of π -conjugated polymers are currently of wide interest¹⁻⁴ 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 C₆₀ or acceptor small molecules have been reported¹⁻³. We have reported exciplex formation and PET between several *n*-type (*electron accepting*) π -conjugated rigid-rod polymers and donor triarylamine molecules⁴. The inherent molecular incompatibility⁵ and poor mutual solubility of π -conjugated polymers and C₆₀ or small molecules have heretofore limited the scope of studies of PET in conjugated polymers¹⁻⁴. Here, we report the study and observation of intermolecular photoinduced electron transfer in compatible 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 C₆₀ which has an EA value of ~3eV⁸. Two *p*-type polymers, relative to BBL, were investigated: poly(*p*-phenylene benzobisthiazole) (PBZT) and poly(*p*-(2-hydroxy)-phenylene benzoxazole) (HPBO). The reported⁹ 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. Our synthesis and characterization of BBL, PBZT, and HPBO have been described^{7,9,10}, following general literature methods¹¹. 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/GaCl₃ (or AlCl₃) 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^{9,10}. The blend films were homogeneous and showed excellent optical transparency and mechanical strength.

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 ($\lambda_{\text{max}} = 405$ and 431 nm). There was thus no evidence of ground state charge transfer or strong interactions between the conjugated polymer pairs.

Transient absorption spectra¹² 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. Transient absorption spectra at 50 ps delay are shown in Figure 2 for two PBZT/BBL blends (33 and 65 mol%) along with those of the pure components. Dramatically enhanced photoinduced bleaching in the 430-480 nm region is 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 decreased with decreasing concentration of BBL in the blend. Figure 3 shows

the relative enhancement of photoinduced bleaching at ~ 470 nm and 50 ps delay as a function of the blend composition. Photobleaching of PBZT/BBL blends at 470 nm, compared to pure PBZT, is 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 feasible¹³. Although there is little known about the spectral properties of PBZT⁺ or HPBO⁺, the known UV-Vis spectra of electrochemically⁶ and chemically¹⁴ produced BBL⁻ showed strong *new* absorption bands at ~ 400 - 480 nm and in the infrared compared to the neutral BBL. Previously reported ultrafast (~ 100 fs) 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 100fs¹⁵. We propose that those 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. The possibility that enhanced photobleaching is due to the decreased π - π^* oscillator strength of PBZT⁺ was ruled out because our prior ps transient absorption studies of PBZT/small molecule electron transfer systems did not reveal such effects^{4c}.

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 4, 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 4 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 very little further quenching. Photoluminescence quenching as a result of photoinduced electron transfer has previously been observed in conducting polymer/ C_{60} systems^{1,2}.

Intermolecular photoinduced electron transfer in molecular mixtures of two conjugated polymers has novel features which suggest that such mixtures are supramolecular materials. As illustrated in Scheme 1, electron transfer creates *radical ion pairs* on adjacent chains. Photogenerated or chemically/electrochemically generated radical ions (polarons) or diions (bipolarons) in conjugated polymers are well known to delocalize along the chain and give rise to the many interesting electronic, photoelectronic, optical, and nonlinear properties of the materials¹⁶. Photogenerated *radical ion pairs (polaron pairs) or diion pairs (bipolaron pairs)* delocalized in adjacent linear chains in binary mixtures of conjugated polymers represent entirely novel excited-state species (excitations) that can be expected to exhibit novel effects and properties not found in the pure components. For example, the charge transport characteristics of both radical cation and radical anion in a binary conjugated polymer mixture are expected to contribute to its photoconductivity; only one charge carrier type contributes to conductivity or photoconductivity of pure conjugated polymers^{4c}. As another example, we have recently observed that mixtures of PBZT

and BBL exhibit enhanced third-order nonlinear optical response compared to the components¹⁵.

In summary, photoinduced electron transfer between two π -conjugated polymers has been observed in 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^{16,17}. Others have also recently reported on photoinduced electron transfer phenomena in phase-separated binary blends of π -conjugated polymers^{18,19}.

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12. 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 H₂O/D₂O (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.
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Figure Captions

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. Selected transient absorption spectra of the PBZT/BBL system at 50 ps after photoexcitation by a 532 nm laser light. The differential optical density ($\Delta OD \times 10^{-3}$) was normalized relative to the 532 nm absorbance of each sample.

Figure 3. Normalized differential optical density (ΔOD) of PBZT/BBL blends relative to that of pure PBZT at ~ 470 nm and 50 ps. The line is to guide the eyes only.

Figure 4. 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% BBL (d) blends photoexcited at 420 nm.

Scheme 1

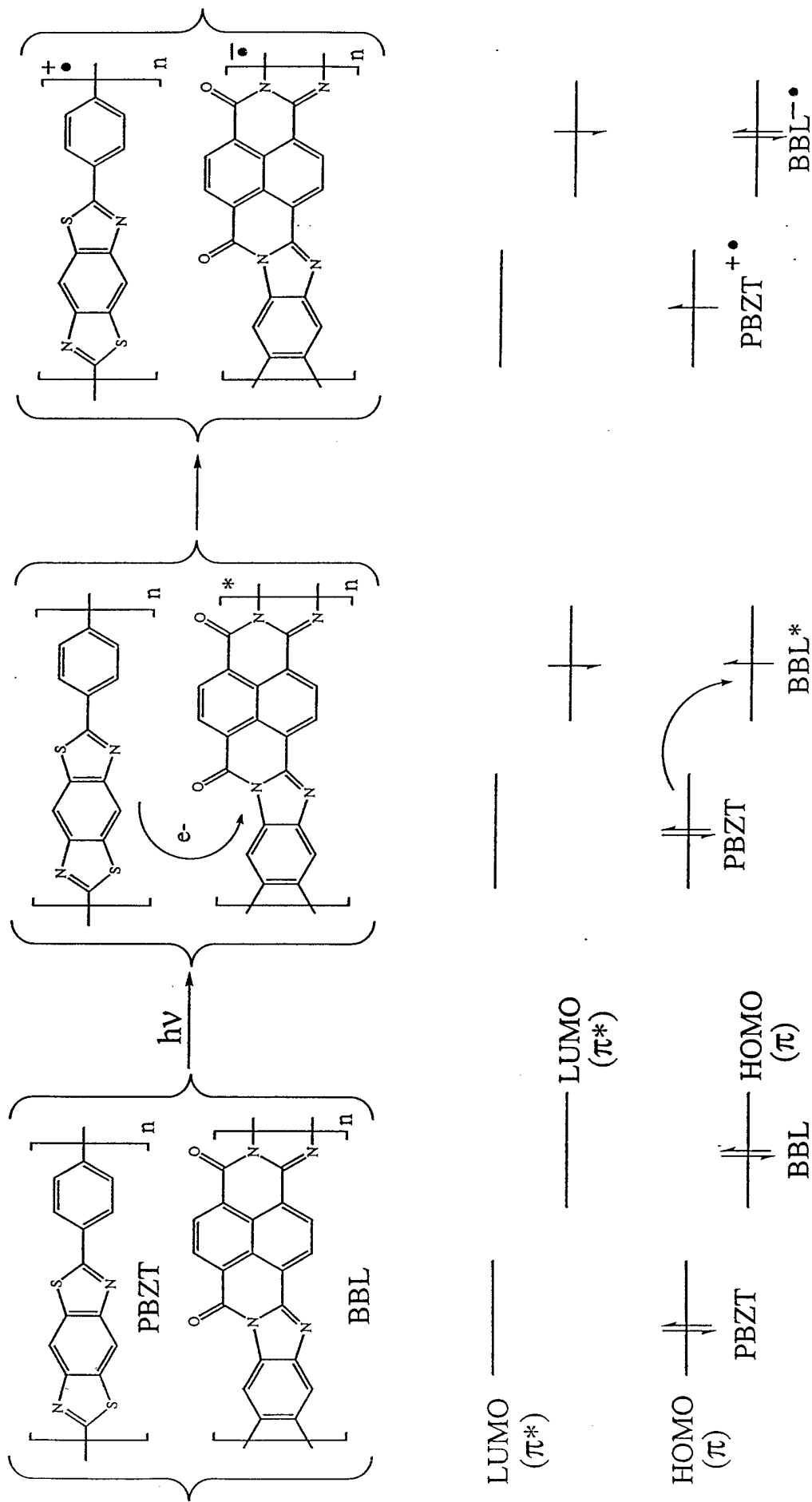
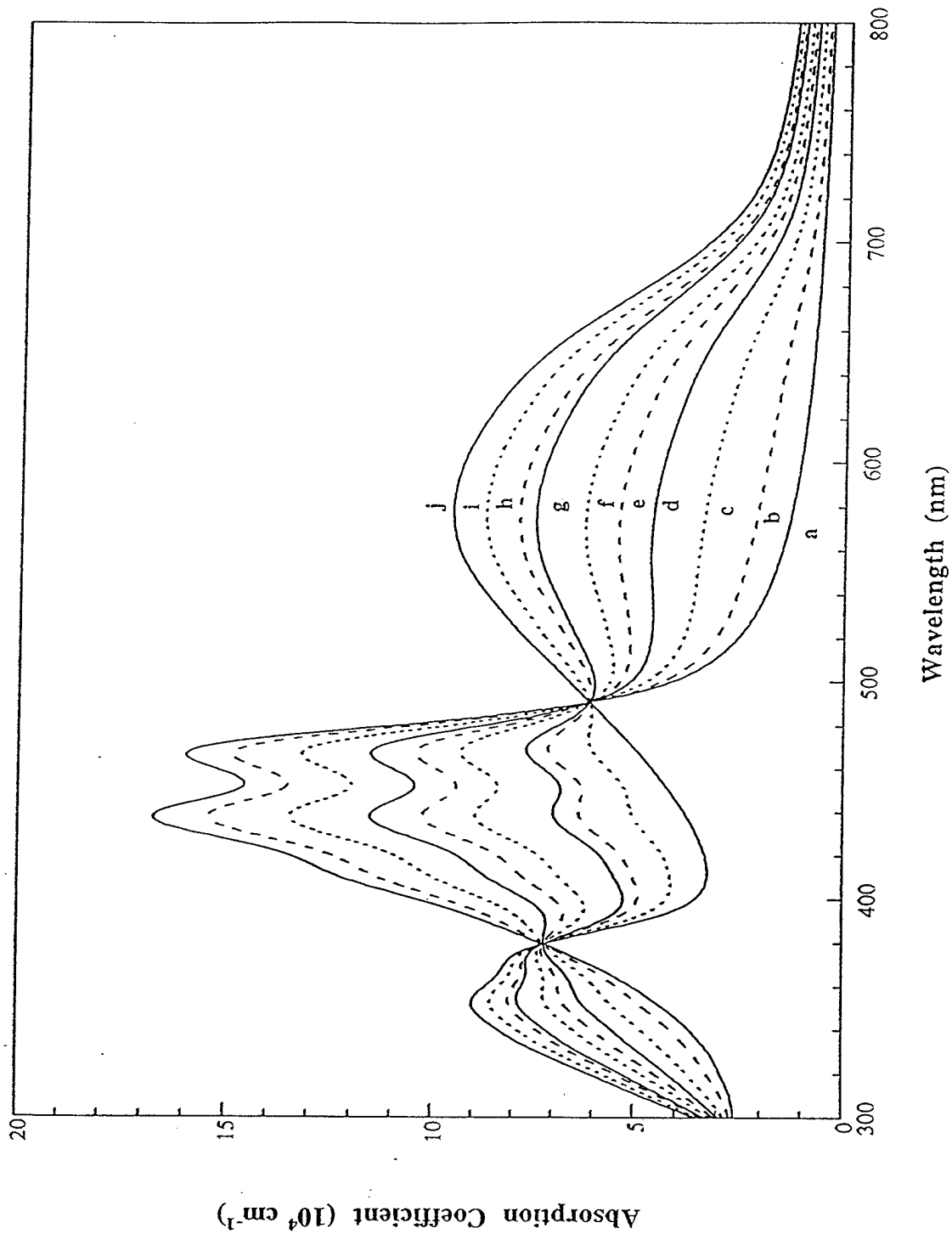


Fig. ~~AA~~ 1



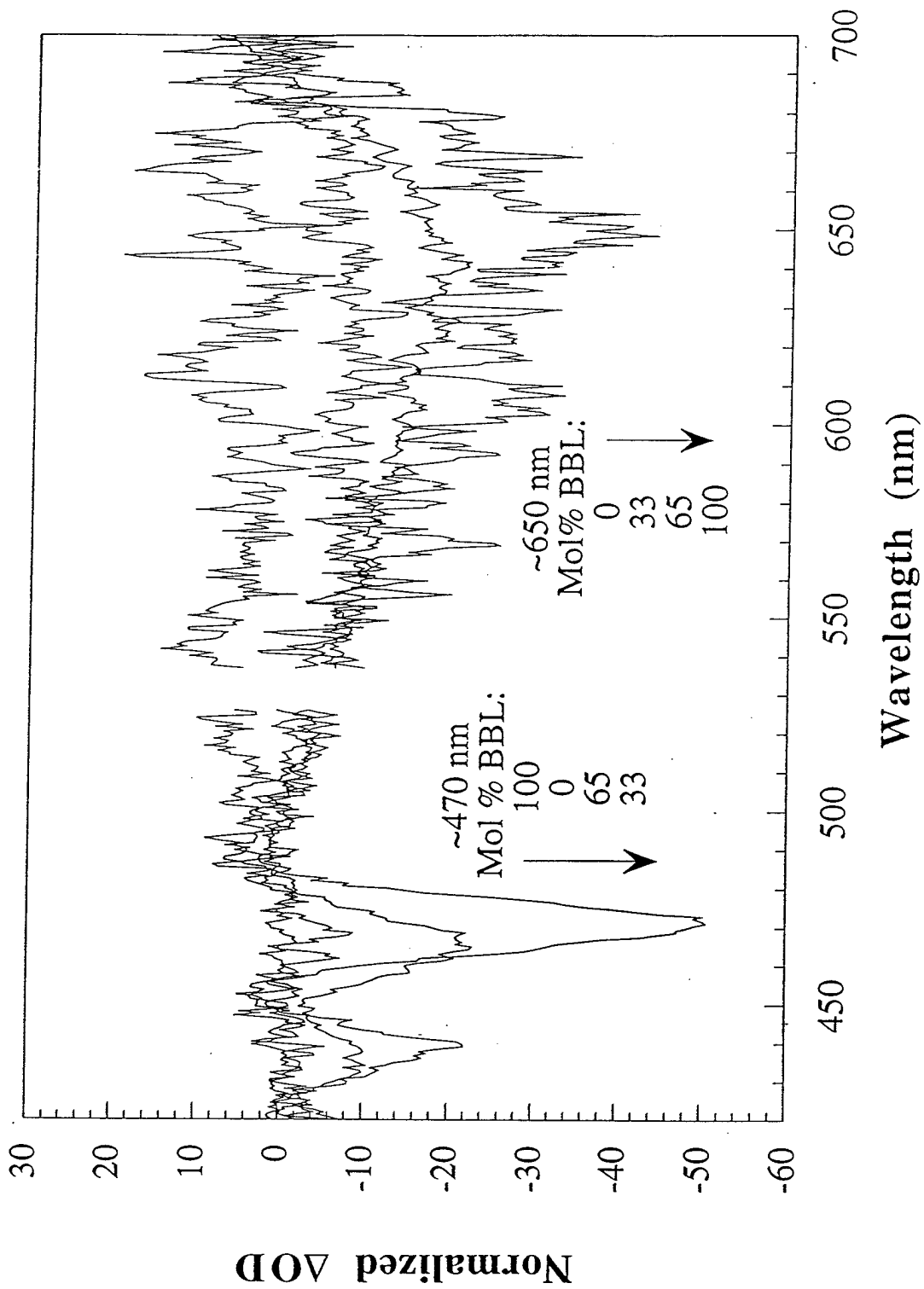


Fig. 2

Fig. (2)

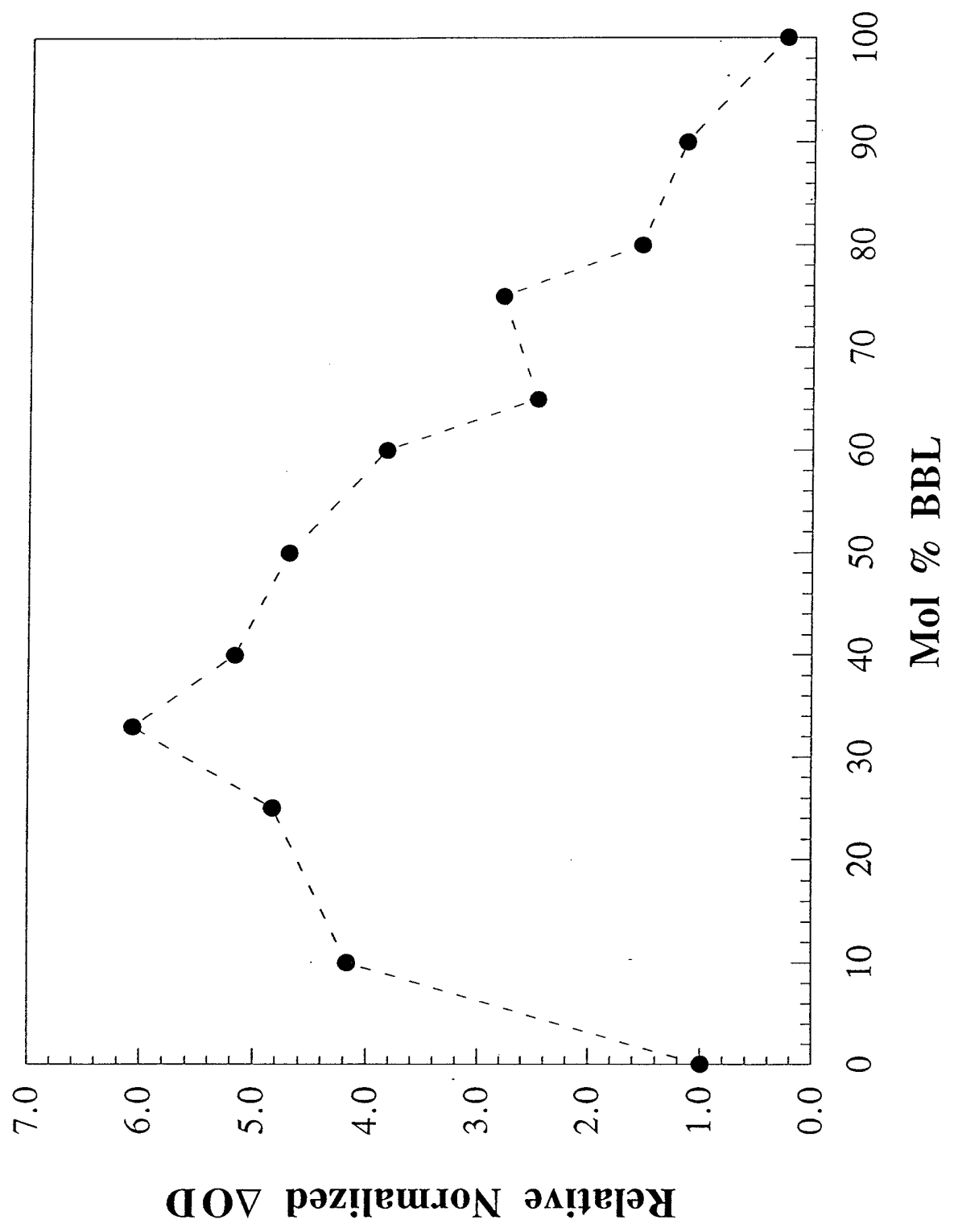


Fig. ~~7~~ 4

