Synthesis and Characterization of a Novel –D-B-A-B- Block Copolymer System for Light Harvesting Applications

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ABSTRACT

Supra-molecular or nano-structured electro-active polymers are potentially useful for developing variety inexpensive and flexible shaped opto-electronic devices. In the case of organic photovoltaic materials or devices, for instance, photo induced electrons and holes need to be separated and transported in organic acceptor (A) and donor (D) phases respectively. In this paper, preliminary results of synthesis and characterizations of a coupled block copolymers containing a conjugated donor block RO-PPV and a conjugated acceptor block SF-PPV and some of their electronic/optical properties are presented. While the donor block film has a strong PL emission at around 570 nm, and acceptor block film has a strong PL emission at around 590 nm, the PL emissions of final -B-D-B-A- block copolymer films were quenched over 99%. Experimental results demonstrated an effective photo induced electron transfer and charge separation due to the interfaces of donor and acceptor blocks. The system is very promising for variety light harvesting applications, including "plastic" photovoltaic devices.

Keywords: Conjugated block copolymers, donor and acceptor blocks, organic supramolecular and nano structured materials, opto-electronic and photovoltaic devices.

1. INTRODUCTION

Light harvesting is a process where light (or photon) is absorbed by a media and is converted into a certain material state. On earth, photo synthesis in plants are the most common form of light harvesting where sunlight become energetic substances in plants, and that these energies can be transferred to animals via food chains, or can be simply released by burning. The technique of converting solar energy directly into electrical power by means of photovoltaic materials has been widely used in spacecraft power supply systems, and is more and more extended for terrestrial applications to supply autonomous customers (portable apparatus, houses, automatic meteostations, etc.) with electric power.[1] Sunlight is free, it does not use up an irreplaceable resource, and its conversion to electricity is non-polluting (clean energy). To generate appreciable electrical power in space and on the earth, it is necessary to collect sunlight from large areas due to low density of sunlight. In comparison to current commercial inorganic photovoltaic materials, polymeric photovoltaic materials appear having the advantages of versatile fabrication schemes and low cost on large-scale production, therefore exhibiting potential for future large-scale solar industry. For space and any portable applications, lightweight and flexible shape of polymers are other key advantages. While the power conversion efficiency for inorganic photovoltaic cells have reached nearly 30%,[1] it is still less than 7% for the recently developed polymer photovoltaic systems.[2-5] Therefore, development of highly efficient polymeric photovoltaic materials, and to better understand the fundamental mechanisms involved in polymer opto-electronic processes has become a critical research effort.

The π–electron conjugated polymers, and often a specific packing order of these conjugated polymers results in unique multi-dimensional electronic structures.[8-9] Most semi-conducting conjugated polymers appear to have a band

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gap that lies in the range 1.5–3 eV, which makes them ideally suited as light harvesting or opto-electronic devices working in the visible light range.[2-5] Electronic materials derived from conjugated polymers have been studied or developed for diverse items such as sensors, light-emitting diodes, actuators, field effect transistors, corrosion protection agents, battery components, photovoltaic cells, etc.[6-7, 10-12]

As shown in Scheme 1, photo-induced electron transfer and charge separation observed in organic composites of donors (electron-rich or p-type organic species, such as donor derivatized PPV or polythiophenes PThs), and acceptors (electron-deficient or n-type organic species, such as C_{60}, CN-PPV, etc.) provided a potential organic molecular approach to high efficiency light harvesting or opto-electronic conversion.[2-5,10-18] Since the time scale for photo-induced exciton (electron-hole pairs and related species) generation in organic systems is almost instantaneous (e.g., it can follow the time scale of excitation pulses in femto seconds), at least a thousand times faster than the radiative or non-radiative decay of the excitons,[18-19] the quantum efficiency for exciton generation is near unity. Since the donor (D) conjugated polymers can stabilize and transport the positive charge (holes), and acceptor (A) conjugated polymers helps stabilize and transport the negative charge (electrons), a donor-acceptor block copolymer conjugated system has the potential for developing a photovoltaic device, where holes accumulated at donor HOMO can be collected by a low work function electrode, and electrons accumulated at acceptor LUMO is collected by a high work function electrode. The photo-induced charge separation facilitated by the donor and acceptor interfaces thus offer great potential for highly efficient light harvesting and opto-electronic applications. Such polymeric systems have been demonstrated using PThs/CN-PPV bilayers,[3] MEH-PPV/CN-PPV blends,[13-14] MEH-PPV/C_{60} bilayers and blends,[4,11] PThs/C_{60} blends,[15] MEH-PPV/PS-C_{60} di-block copolymers,[17] etc., as active materials.
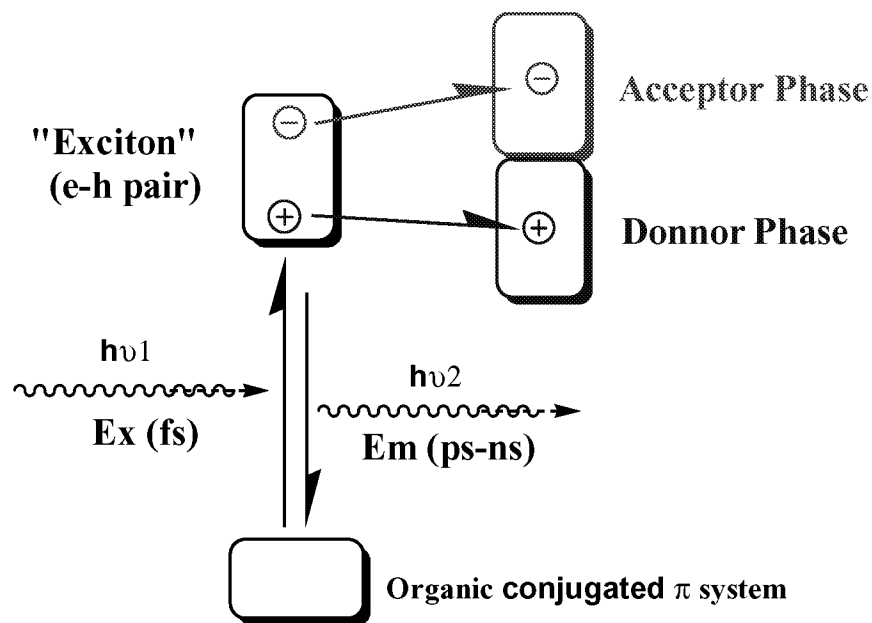
Scheme 1. A Simplified Light Harvesting Scheme in an Organic Conjugated Donor/Acceptor System

Previous studies have suggested that an ideal organic photovoltaic material might be a bi-continuous interpenetrating network of donor-acceptor phase-separated system that possessing large donor and acceptor interfacial areas.[4] In fact it has been shown that much higher (e.g., two orders of magnitude) opto-electronic energy conversion efficiencies were obtained with devices using D/A blends (also called "bulk D/A heterojunction" materials) than devices with D/A bilayers or the pristine donor or acceptor polymers, and this was attributed mainly to the increased interfacial area in D/A blend systems.[10-16] However, it is not easy to obtain a uniform, ordered nano-phase separation simply by blending donor and acceptor polymers. The very low charge carrier collection efficiencies in polymeric blend systems

are believed mostly due to poor phase separation (inhomogeneous too small or too large scale phase separation) that cause poor charge separation at interfaces and poor charge mobility in the materials.

Block copolymer phase separation and behavior has been known for several decades. The incompatibility between the blocks leads to the formation of unique micro- or nano- phase separated and ordered structures affected by chemical composition, size of each block, temperature and other factors.[20-22] Recent study of MEH-PPV/Polystyrene-C_{60} (D-A) di-block copolymers demonstrated a nice honeycomb shaped nano phase separated structures.[17] However, polystyrene itself is a well known insulator due to its non-conjugated backbone, and therefore the charge mobility in this block is not expected to be efficient. In our approach, by coupling both donor and acceptor conjugated blocks via a relatively short non-conjugated bridge unit into a D-B-A-B type block copolymer, the charge separation and transportation can be maximized and yet charge recombination is hindered at the same time. The charge separation is maximized because there are larger and more uniform interfacial areas in the nano-phase separated donor and the acceptor separated phases. Furthermore, the interfacial area can be conveniently controlled via block copolymer segment size control. Every donor block can be built in a convenient reach of an acceptor block within the exciton diffusion range.[2,15] Therefore, one limitation to the efficient charge separation (due to long range exciton diffusion) is reduced.[14] Charge transportation is also facilitated by the conjugated polymer backbones in both donor and acceptor phases. Also, one may tune the chemical structures of each block to induce some unique π–stacked ordered structure. Such oriented and stacked π–systems have been reported to have significantly enhanced charge mobility.[9, 25-26] The charge recombination between the donor and acceptor blocks at the backbone junction is also significantly retarded due to an aliphatic bridge unit. Though a non-conjugated bridge is used, overall charge mobility will not be affected significantly since intra-molecular charge migration and exciton diffusion can also proceed effectively through σ-bonds or through space in a short range.[23-28]

2. MATERIALS AND EXPERIMENTAL

Materials and Equipment

All starting materials, reagents and solvents were purchased from commercial sources and used directly except noted otherwise. NMR data were obtained using a Bruker Avance 300 MHz spectrometer. Elemental analysis was done at Atlantic Microlab. HR-MASS and MALDI data were obtained from Mass Spectrometry facility at Emory University in Georgia. FT-IR Spectra were collected on either a Nicolet Avatar or a Bruker IFS66 FT-IR spectrophotometer. Perkin-Elmer DSC-6/TGA-6 systems were used to characterize the thermal property of the materials. GPC analysis was done using a Viscotek T60A/LR40 Triple-Detector GPC system with mobile phase of THF at ambient temperature (Universal calibration based on polystyrene standards is used). UV-VIS spectra were collected from a Varian Gary-5 spectrophotometer. Luminescence spectra were obtained from an ISA Fluoromax-3 spectrofluorometer. Electrochemical analysis was done on a BAS Epsilon 100 cyclic voltammeter.

Materials Synthesis

Scheme 2 shows the chemical structures of the donor block, the acceptor block, the bridge units, and the synthetic scheme of final -D-B-A-B- blocks. Specifically, the donor block (D) is an alkyloxy derivatized polyphenylenevinylene or RO-PPV, the acceptor block (A) is an alkyl-sulfone derivatized polyphenylenevinylene or SF-PPV. Two bridge units were investigated, first one is a dialdehyde terminated bridge unit 1, and the second is a diamine terminated bridge unit 2. When bridge unit 1 was used, both donor and acceptor blocks were synthesized with terminal phosphate groups. When amine terminated bridge unit 2 was used, both donor and acceptor blocks were synthesized with terminal aldehyde groups. The alkyl derivatives investigated include branched 2-ethyl-hexyl group (C_8H_{17}), the linear ethyl (C_2H_5) and linear decatyl ($C_{10}H_{21}$) groups. The synthesis of 2-ethyl-hexyl derivatized RO-PPV and SF-PPV conjugated blocks has been described previously,[29-30] and properties of the SF-PPV has been reported elsewhere.[31-32] In this paper, preliminary results of the synthesis and properties of –DBAB- blocks via dialdehyde bridge unit 1, and comparison to donor and acceptor blocks is presented.

As shown in Scheme 2, the synthetic strategy for the final –D-B-A-B- block copolymer involves using excess amount of bridge units to couple either donor block or acceptor block to form –B-D-B- or –B-A-B- intermediate first, then couple the intermediate –B-D-B- with equal mole ratio of acceptor (A) block, or couple –B-A-B- with equal mole ratio of donor (D) block to form the final copolymer –D-B-A-B-.

In a typical synthesis, for instance, 0.5 g of **D** (C_8H_{17} substituted) was mixed with excess amount of dialdehyde bridge unit **1** in 50 ml dry THF under inert gas. To the mixture was added drop wise lithium ethoxide solution (4.5 ml, 1.0 M in ethanol) via a syringe at room temperature. The base should be introduced at such a rate that the transient red-purple color produced upon the addition of base should not persist. The resulting solution was allowed to stir at room temperature for 48 hours more after the completion of base addition. The reaction mixture was then poured into a dilute aqueous HCl to neutralize the base, and then poured into 500 ml methanol. The precipitates were collected via filtration and washed with water, then dried under vacuum to yield a yellow and intense fluorescent solid –BDB-. NMR analysis indicated the complete disappearance of terminal phosphate groups from original donor block, and the appearance of new terminal aldehyde groups as well as new peaks belong to bridge protons. The synthesized -B-D-B- block and the acceptor block (A) (mole ratio 1:1) were then dissolved in 50 ml dry THF along with excess amount of t-BuOK. The mixture was stirred under room temperature in inert gas for 48 hours, then poured into 500 ml methanol. The precipitates were collected, washed with methanol, and dried under vacuum to yield a dark red and weakly fluorescent –DBAB- solid. The synthesis of diamine bridged final block copolymers will be reported separately.
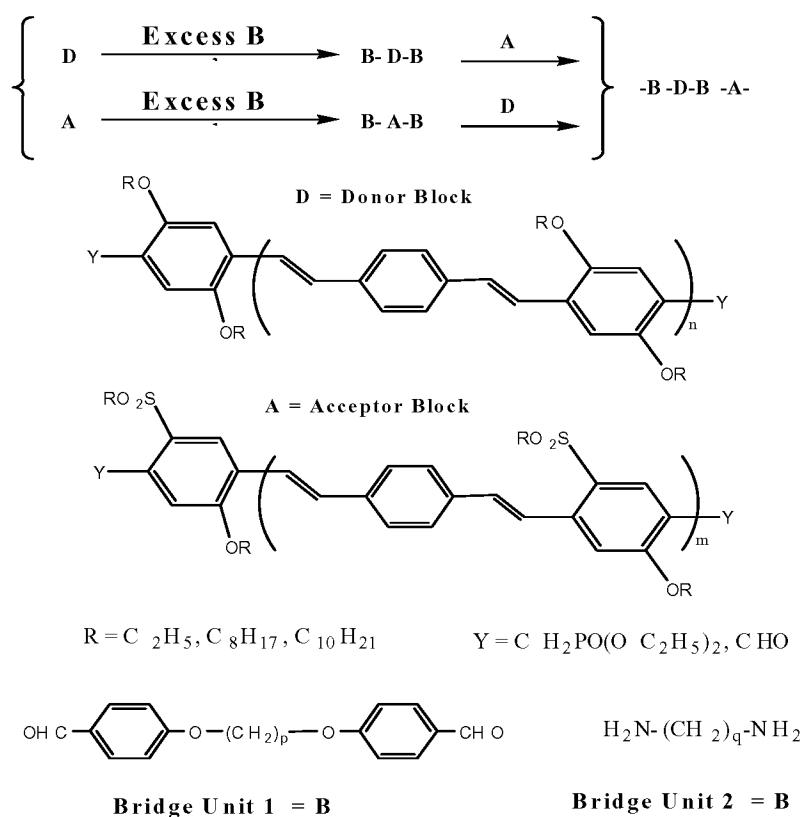
Scheme 2. Donor and Acceptor Block Copolymer Systems Studied

3. RESULTS AND DISCUSSION

The synthesized block copolymer –DBAB- has been characterized by NMR, GPC/MALDI, thermal, optical, electron microscopic, electrochemical and conductivity analysis.[33-34] In this paper, only synthesis and some optical characterizations is discussed.

In the synthesis of the –DBAB- block copolymers, very dry THF or DMF are necessary. If the solvent was not dried enough, the tiny water in the solvents may kill the base catalyst, and therefore, the reaction may go very slow or

not at all. For ^{1}H NMR characterization of –DBAB-, in comparison with BDB or BAB blocks, the aldehyde peaks at around 10 ppm were significantly reduced or disappeared,[33] yet other ^{1}H peaks of BDB or BAB blocks can still be found in the –D-B-A-B- spectra. Also, the BDB and BAB were soluble in THF, the synthesized DBAB is only partially soluble in THF. Most notably, while the BDB or BAB were light yellow-reddish color in solid state with very strong luminescence, the synthesized –DBAB- was brownish dark color in solid, and was very weakly luminescence as will be discussed next.

GPC analysis shows a polymer molecular weight corresponding to one structure unit of B-D-B-A (or A-B-D-B). Since the final block copolymer was only partially soluble in THF, and that filtering (0.2 μm) was done before the polymer solution was analyzed with GPC, therefore, the GPC results only reflected the soluble part of polymer sample, *i.e.*, there might be higher MW block copolymers that are not soluble well in THF and was filtered out. MALDI analysis also confirmed the existence of at least a –DBAB- unit. Though species with higher molecular weight then -A-B-D-B- was not obvious in MALDI data, however, it is also possible that higher MW species may be broke down during laser ablation.[35]

Figure 1 shows the PL excitation and emission of RO-PPV donor block dissolved in dichloromethane. In solvent, solvent-solute interaction is dominant in comparison to the solute-solute interactions, particularly at low concentration as in our case. As it can be seen, the excitation of donor block in dichloromethane is at about 480 nm (2.58 eV), and the emission maximum is at about 530 nm (2.34 eV). Interestingly, as shown in Figure 2, after coupling with two bridge **1** units, the excitation maximum blue shifted to about 460 nm (2.70 eV), and the emission blue shifted to 515 nm (2.41 eV). We speculate that, possibly due to the heavy mass or the long size of the two terminal bridges, the effective electronic conjugation of the donor block became shortened due to conjugation backbone distortion, thus energy gap increased. When in thin films states as shown in Figure 3, the excitation peak is further blue shifted to about 410 nm (3.02 eV), the emission peak instead red shifted to about 570 nm (2.18 eV). Also in comparison to solution, thin film peaks become much broadened as expected due to well-known inter-molecular electronic interactions. For the excitation blue shift, one possible mechanism is the electronic conjugation or main chain twist in solid state. For the emission red shift, a well known mechanism is the availability of more vibrational or lattice energy relaxation modes due to solid state molecular interactions. For optical properties of SF-PPV acceptor blocks, as shown in Figures 4-6, a similar trend was observed, *i.e.*, the excitation maximum was blue shifted from about 500 nm (2.48 eV) to 430 nm (2.88 eV), and then further to 370 nm (3.35 eV) respectively (note the shape of the peak was also affected by film morphology), yet the emission maximum first blue shifted from about 540 nm (2.30 eV) to about 490 nm (2.53 eV), then red shifted to about 590 nm (2.10 eV). For the final –DBAB- block copolymers, the PL emission was significantly quenched in comparison to the pristine donor or acceptor blocks. For instance, from a concentration calibrated PL analysis, an 80% PL emission quenching was found in dichloromethane, and over 99% PL emission quenching was found in DBAB films. It is obvious that the contacts between the donor and acceptor blocks in thin film state are much larger or more frequent then in solution. At the same time, the UV-VIS absorptions of final blocks are very similar to a simple overlap of the absorptions of individual blocks as shown in Figures 7 (dichloromethane) and Figure 8 (Thin film). These data demonstrated that ground state charge separated states were not obvious in –DBAB-. As shown in Scheme 1, if the photo induced exciton were nearby a donor/acceptor interface, or the exciton diffused to the donor/acceptor interface during its lifetime, then electrons and holes will be separated at the D/A interface with electrons dropped into the LUMO level of acceptor phase, and holes jumped into the HOMO level of donor phase, and this would result the PL emission quenching. Once the electrons and holes are effectively separated, the first important process of light harvesting is accomplished. For photovoltaic device purposes, the electrons and holes thus separated will be collected by respective electrodes having the same or close work function levels to the donor HOMO and acceptor LUMO levels. Such studies are ongoing and will be reported in the near future.

4. SUMMARY

Preliminary results on the design and synthesis of a novel –Bridge-Donor-Bridge-Acceptor- (-DBAB-) type conjugated block copolymer systems are presented. Specifically in our system, the donor block (or p-type) contains an electron donating alkyloxy derivatized polyphenylenevinylene (PPV) or RO-PPV, the acceptor block (or n-type) contains an electron withdrawing alkyl-sulfone derivatized polyphenylenevinylene (PPV) or SF-PPV, and the bridge block contains a very short non-conjugated or insulating aliphatic chain. The key synthetic strategy we developed includes the synthesis of terminally functional and desired sized individual copolymer blocks first, then couple the blocks together. In this way, the size of the separated polymer nano phases can also be controlled. While the RO-PPV

has a strong PL emission at around 530 nm (solution) and 570 nm (film), and SF-PPV has a strong PL emission at around 540 nm (solution) and 590 nm (film), the PL emissions of final -B-D-B-A- block copolymer films were quenched over 80% in solution and 99% in solid films. These results demonstrated the effective and efficient photo induced electron transfer and charge separation at the interfaces of donor and acceptor blocks. The system is therefore very promising for variety high efficiency light harvesting applications, including photovoltaic applications.

ACKNOWLEDGEMENTS

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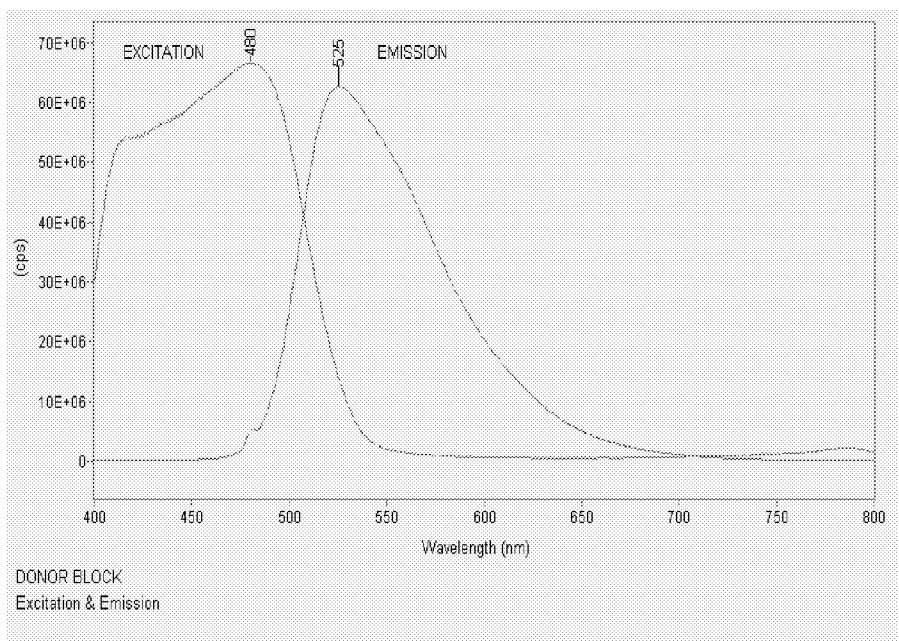35. G. Montaudo, *Mass Spectrometry of Polymers*, CRC Press, FL, 2002.

Figure 1. PL Excitation and Emission Spectra of D in dichloromethane
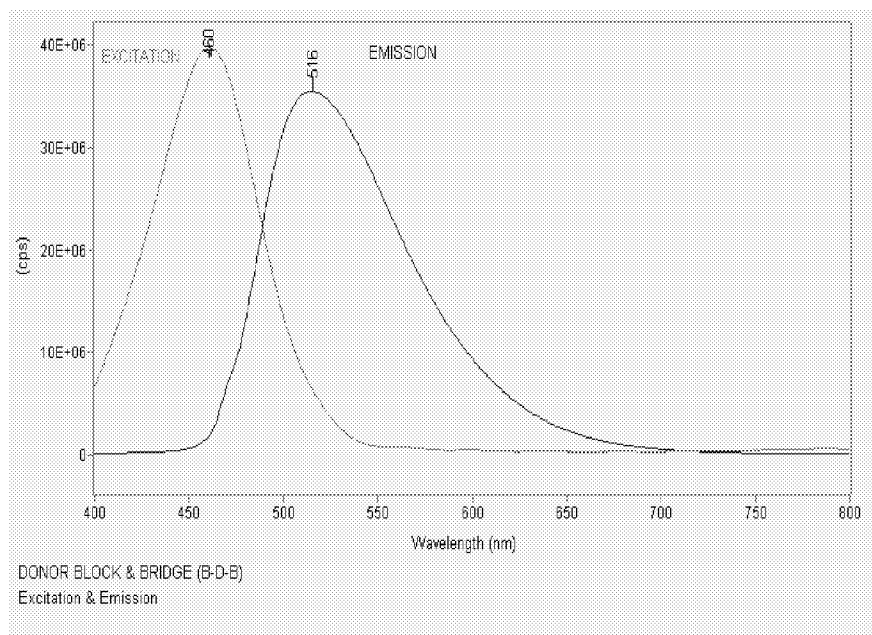

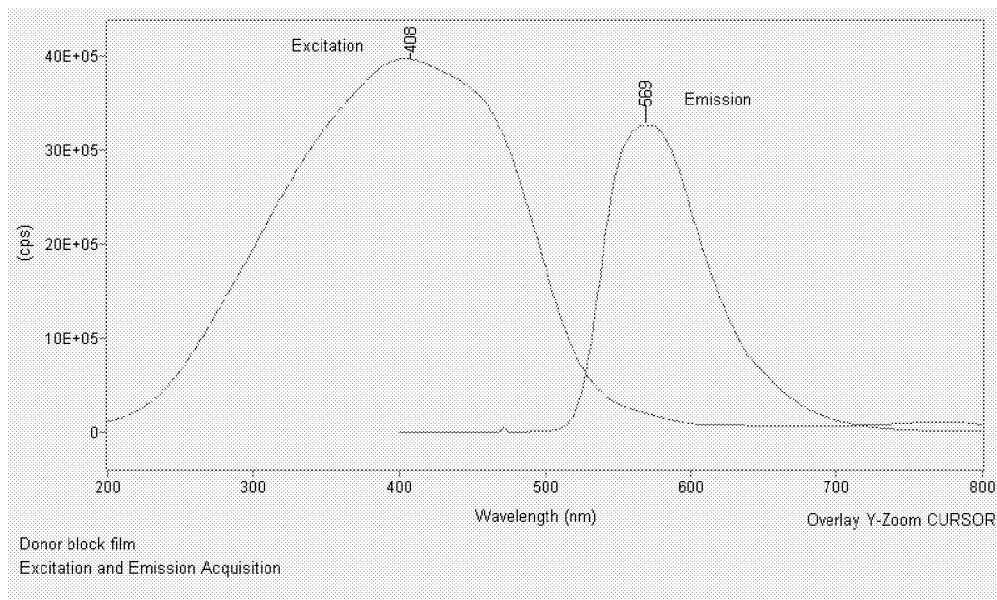Figure 2. PL Excitation and Emission Spectra of B-D-B in dichloromethane

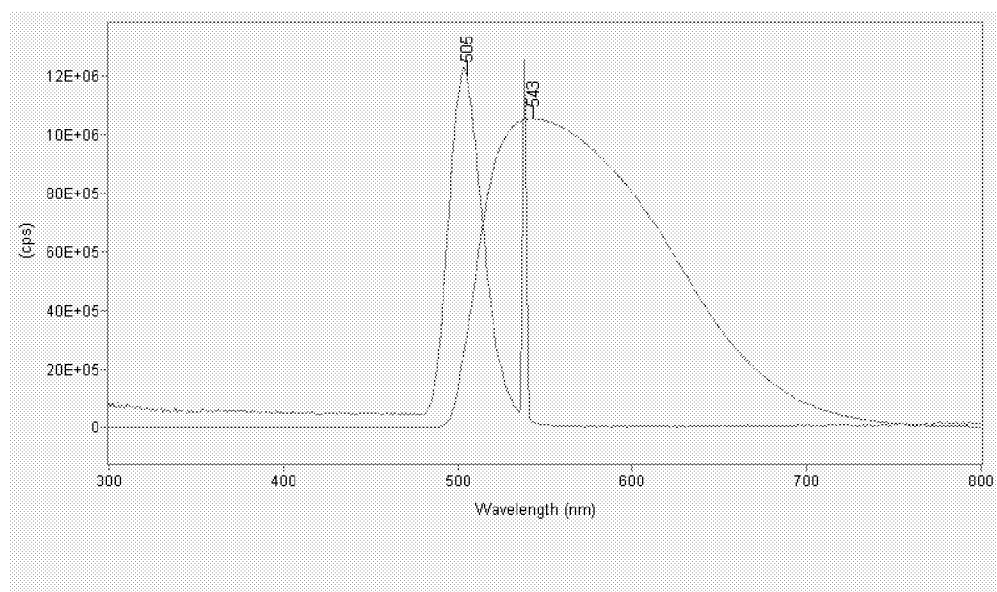Figure 3. PL Excitation and Emission Spectra of D Thin Film

Figure 4. PL Excitation and Emission Spectra of A in dichloromethane
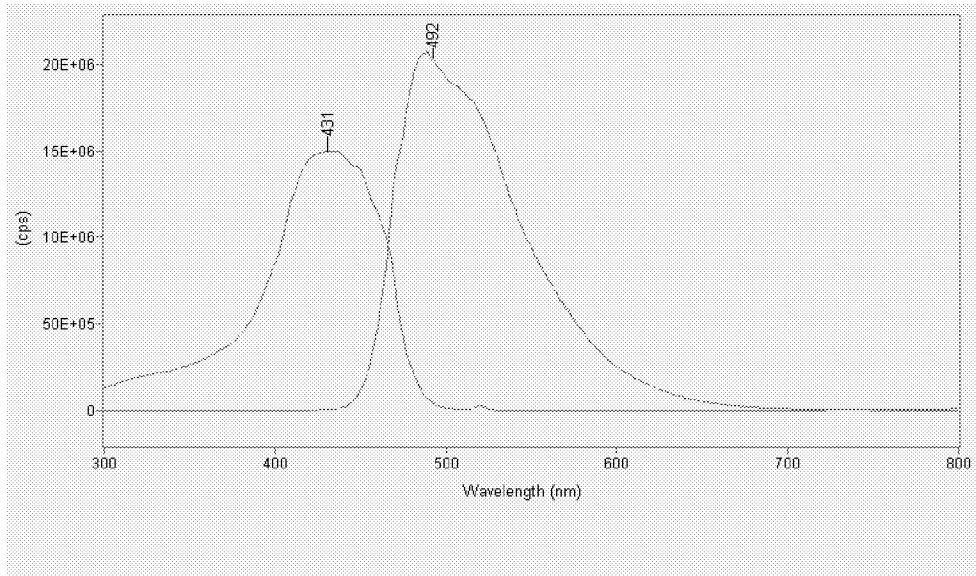(Note: sharp spike at 540 nm is due to reflected excitation beam)

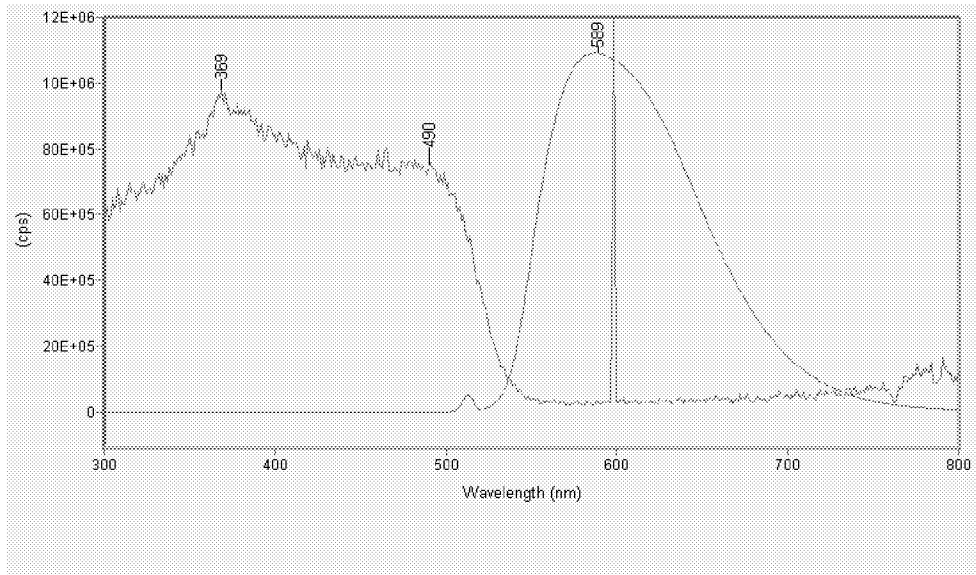Figure 5. PL Excitation and Emission Spectra of B-A-B in dichloromethane

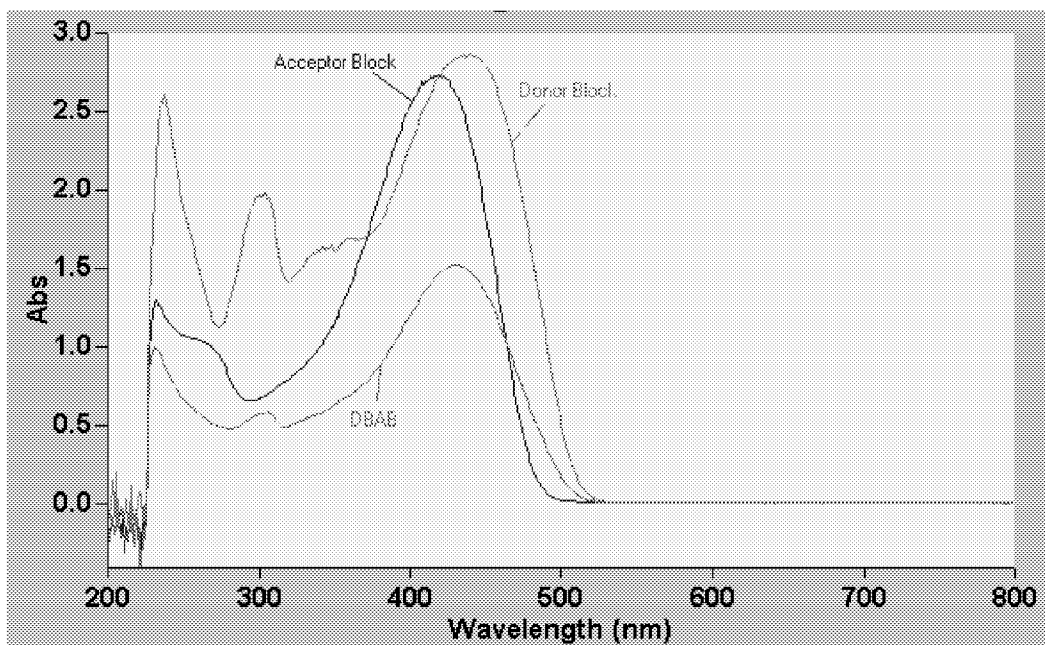Figure 6. PL Excitation and Emission Spectra of an A Thin Film
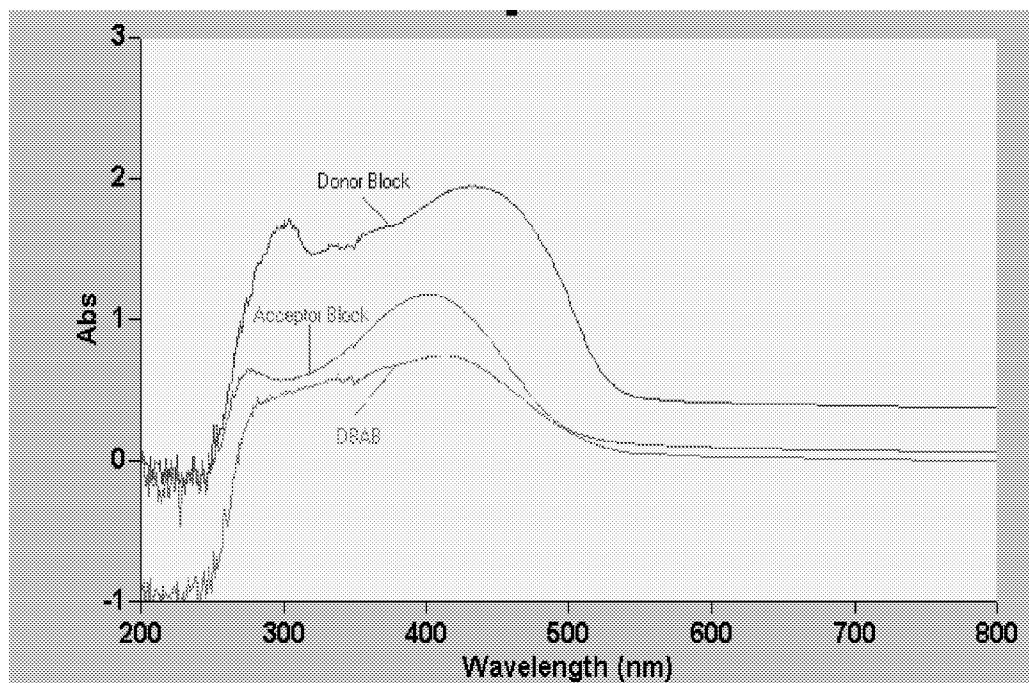
Figure 7. UV-VIS of D, A and DBAB in dichloromethane

Figure 8. UV-VIS of D, A and DBAB in dichloromethane