Energy Transfer Studies of Polyphenylene-Type Polymers to a Series of Dyes.

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ABSTRACT

Energy transfer from two polyphenylene-type polymers to a series of organic dyes was studied. One of the polymers was synthesized via Suzuki coupling of 1,4-phenyldiboronic acid with 1,4-dibromobenzene to obtain polyphenylene. The other polymer was a polybenzophenone generated by a nickel-mediated coupling of 2,5-dichloro-4'-methylbenzophenone. These polymers were used as the energy donors. A variety of Coumarins and other dyes were used as acceptors. Photophysical data and energy transfer parameters were determined.

INTRODUCTION

Considerable attention has been focused on conjugated polymers and their use in light-emitting diodes and other devices. Conjugated polymers have the ease of processability and advantageous mechanical properties, as well as optical and electrical properties similar to that of inorganic analogues. Polymers can be made to emit different colors with high photoluminescence efficiencies with relative ease. The electrical and optical properties can be varied by chemical design, as well.

Conjugated polymers can be optically excited to produce singlet excited states. Radiative decay can occur from the singlet state and in absence of non-radiative decay mechanisms, can be very efficient. Designing a polymer to emit in the red region usually leads to less photo and chemically stable materials. It is better to use singlet dyes with high quantum yield of emission as dopants, because red-emitting small molecules are typically more robust.

For Förster energy transfer to occur, the emission spectrum of the donor must overlap the absorption spectrum of the acceptor [1]. The process, known as resonance energy transfer (RET), occurs when the donor and acceptor are coupled by a dipole-dipole interaction, rather than the emission from the donor molecule being absorbed by the acceptor molecule [2], which is known as trivial energy transfer.

In this study, polyphenylene-type polymers were used as the energy donors. The polymers were an alkoxy-substituted poly(*para*-phenylene) (**P1**) and a poly(4'-methylbenzophenone) (**PB**). The energy acceptors were commercially-available organic dyes, which included: Coumarin 6, Coumarin 343, and Rhodamine 6G. The structures of the compounds are shown in Figure 1.
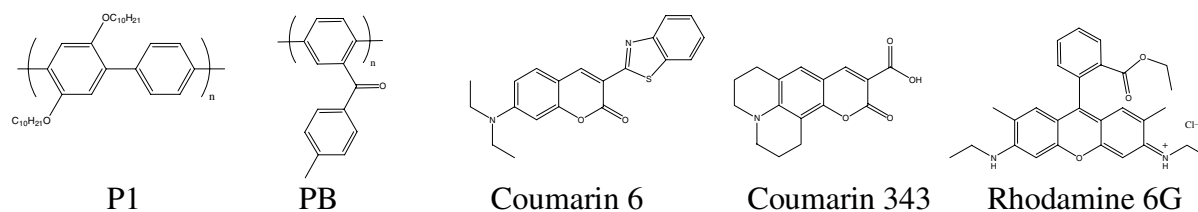

P1   PB   Coumarin 6   Coumarin 343   Rhodamine 6G

Figure 1. Structures of the polymers and dyes.

This study is founded upon the concept of using dopants, e.g. organic dyes, to tune the emission color of a polymer [3 – 13].

EXPERIMENTAL DETAILS

Materials

Coumarin 6, Coumarin 343, Rhodamine 6G, and 1,4-dibromobenzene were purchased from Sigma-Aldrich. Reagent grade chloroform was purchased from Mallinckrodt.

Polymerizations

The polymer poly(4'-methyl-2,5-benzophenone) (**PB**) was synthesized by polymerizing 2,5-dichloro-4'-methylbenzophenone via nickel-mediated coupling as per the published procedure [14]. The polymer poly(2,5-didecyloxyphenyl-1,4-phenylene) (**P1**) was synthesized via Suzuki coupling of 2,5-didecyloxybenzene-1,4-diboronic acid [15] and 1,4-dibromobenzene, as per the published procedure [16].

Photophysical Measurements

Steady state emission spectra were recorded using a Fluorolog-3 model FL3-21 with a 450W xenon lamp source, double grating excitation monochromator, single grating emission monochromator, and a room temperature R928 PMT serving as the detector. Plots were generated using GRAMS/32 and DataMax software. Absorbance spectra were generated using OLIS modernized Cary 14 UV/Vis/NIR spectrophotometer equipped with deuterium and tungsten lamps for UV and Vis/NIR regions. Singlet energies (Es) of the polymers and the dyes were calculated as described by Turro [17] and summarized in Table I.

Table I. Singlet energy values of donors and acceptors.

	Donors		*Acceptors*		
	P1	*PB*	*Coumarin 6*	*Coumarin 343*	*Rhodamine 6G*
Es (eV)	3.24	3.25	2.59	2.69	2.31

RESULTS AND DISCUSSION

The polymers used had similar photophysical properties in solution; the absorbance maxima of P1 and PB were 350nm and 370nm respectively. When exciting at these wavelengths, blue photoluminescence was obtained, which was attributed to fluorescence due to its short lifetime. The quantum yield of emission for P1 was 0.43, while for PB it was 0.115. The position of the emission spectra for the polymers make them ideal candidates to be used in energy transfer studies with selected singlet dyes, as seen in Figure 2. The singlet energies of the polymers and dyes are given in Table I, the donors have higher energy and the energy gap between the donor and acceptor is sufficient to prevent thermal depopulation, *i.e.* back energy transfer, of the acceptor-excited states.
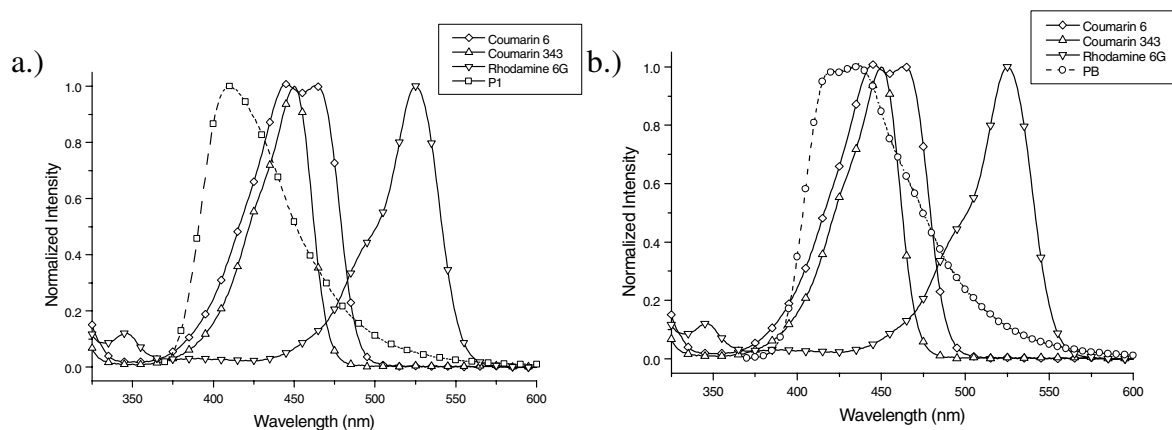
Figure 2. Overlaid spectra of the fluorescence of the polymer P1 (a) and PB (b) with the absorbances of the dyes.

The energy transfer efficiencies listed in Table II are calculated from Equation 1, where ET is the energy transfer efficiency, F_{da} is the fluorescence intensity of the donor in the presence of the acceptor, and F_d is the fluorescence intensity of the donor alone.

$$ET = 1 - \left(\frac{F_{da}}{F_d} \right) \qquad (1)$$

Equation 1 does not account for quenching or increase in intensity from the acceptor. It only accounts for the loss of energy from the donor through the polymer emission's loss of intensity. The overlap integrals (J) for the polymers with their respective dyes were calculated with PhotoChemCAD [18], and these data are summarized in Table II.

Table II. Energy transfer efficiencies and overlap integrals of the polymers with respect to 3% doping of the dyes.

Dye	P1 - J,cm^6/mmol	PB - J,cm^6/mmol	P1 - ET	PB - ET
Coumarin 6	1.1 E-13	1.5 E-13	0.980	0.985
Coumarin 343	1.4 E-13	1.3 E-13	0.935	0.845
Rhodamine 6G	0.35 E-13	1.3 E-13	0.805	0.962

The overlap integrals (J) were calculated in PhotoChemCAD with Equation 2, where: J is the spectral overlap; $f_s(\upsilon)$ is the fluorescence intensity of the donor; $\varepsilon_A(\upsilon)$ is the molar absorption coefficient of the acceptor; and υ is the wave number of the donor emission spectrum and the acceptor absorbance spectrum.

$$J = \int_0^\infty \frac{f_s(\upsilon)\varepsilon_A(\upsilon)}{\upsilon} d\upsilon \qquad (2)$$

The accuracy of the J values obtained by the program is dependent upon the resolution of the respective absorption and fluorescence spectra, and can not be any more accurate than the extinction coefficient, therefore they are usually restricted to two decimal places. Both the absorbance and fluorescence spectra were recorded at 1.00nm resolution with a spectral width of interest of 450nm, and were baseline corrected. The program authors stated that the calculated values were consistent with prior calculations in the literature [19].

It is popular belief that the rate constant of energy transfer depends upon the overlap integral. This may be true for small molecule donors, but in conjugated polymers the spectral overlap should occur at the low energy region of the emission spectra of the polymer [3]. Coumarin 6 and Rhodamine 6G have higher Js with PB than P1, thus the ET are higher for the PB/dye systems. Conversely, Coumarin 343 has a larger J and a higher ET with P1. The polymer P1 has weak overlap with Rhodamine 6G, thus it has a low ET when compared to the other dyes. P1/Coumarin 6 has a lower J than P1/Coumarin 343, but the latter has a lower ET. This can be further explained by the fact that the Coumarin 6 overlap with the polymer P1 extends more towards the low energy region than with Coumarin 343. The systems PB/Coumarin 6 and PB/Coumarin 343 follow the popular belief that ET depends on J. Consider the PB/Rhodamine 6G system, in which the J is the same as the PB/Coumarin 343 system, yet the ETs are significantly different. This can be explained by the fact that Rhodamine 6G overlaps with the lowest excimer emission region of PB. As per studies by Brunner et $al.$ [3], overlap in this region has higher efficiency.

The polymer film of P1 doped with Coumarin 6 (Figure 3a) shows residual emission. In the polymer film of PB with Coumarin 6 (Figure 3b) though, very little residual emission is seen. The spectra illustrate how a better donor-acceptor pair, as determined by a larger overlap integral, can have more efficient energy transfer.
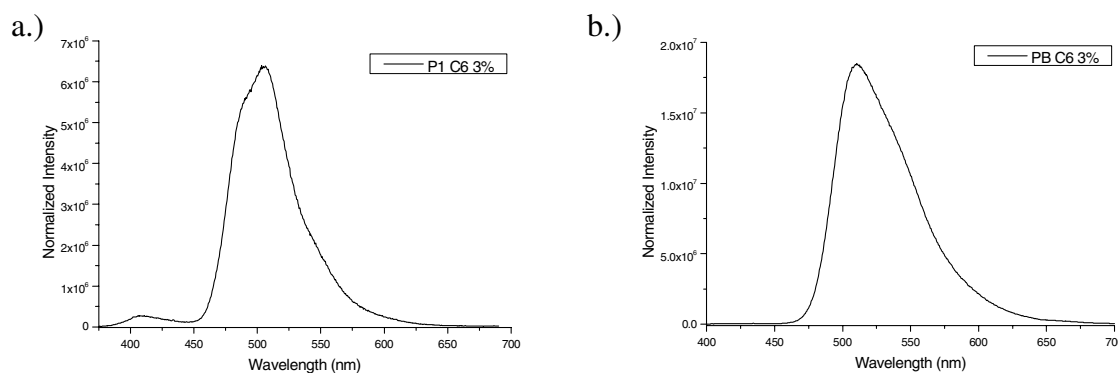
a.)

b.)

Figure 3. Fluorescence spectra of P1 (a) and PB (b) in the presence of Coumarin 6.

In Figure 4, the emission spectra of the polymer films doped with Coumarin 343 show PB to be superior to P1. This disagreed with our calculations that stated that P1 should have a better overlap with PB. At higher doping concentrations, the residual emission decreases, but the dye emission also decreases, which is most likely due to aggregate formation and quenching. There is a new peak at higher wavelengths that is due to aggregate formation. The spectra suggest that P1 supported aggregate formation better than PB, which could allow for the discrepancy of the fact that P1 has better overlap.
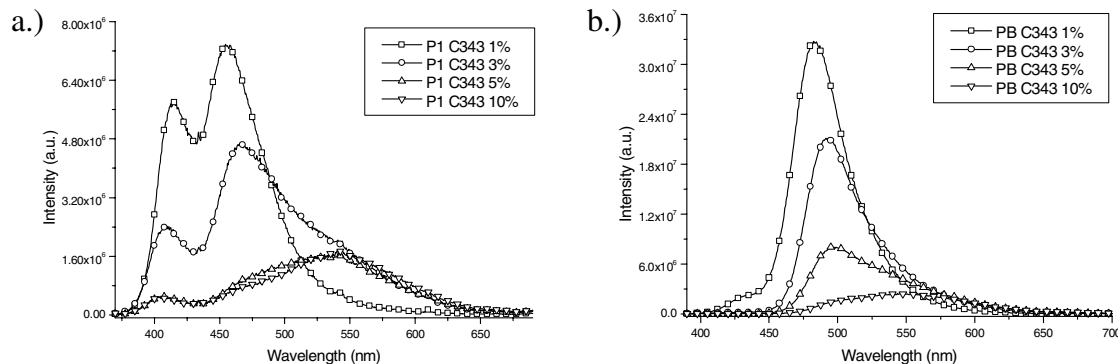
Figure 4. Fluorescence spectra of P1 (a) and PB (b) in the presence of Coumarin 343.

In all samples, the dyes overlapped better with PB than with P1. With the Coumarins, energy transfer took place. In the case of Rhodamine 6G though, only the polymer PB was able to transfer energy to it, as illustrated in Figure 5. The polymer film of P1 doped with Rhodamine 6G shows no dye emission at all, despite proper spectral overlap. The polymer emission is significantly quenched in the presence of Rhodamine 6G, implying the presence of an efficient non-radiative decay process. The film of PB with Rhodamine 6G shows emission from the dye, as well as residual emission from PB.
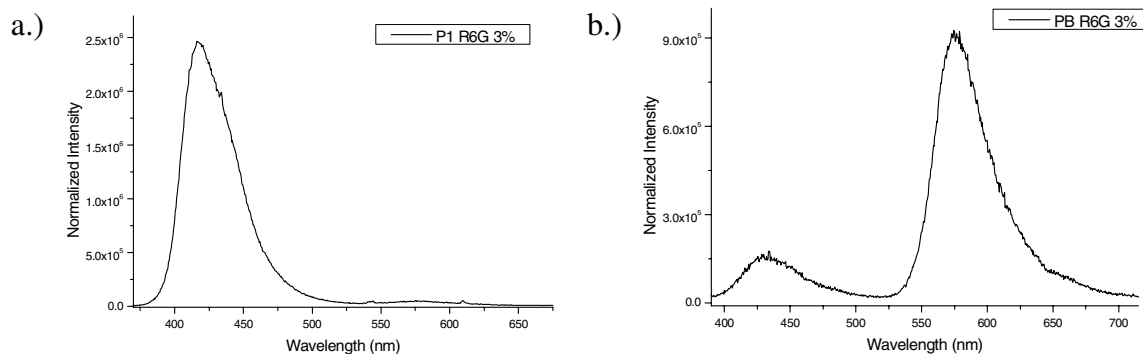

Figure 5. Fluorescence spectra of P1 (a) and PB (b) in the presence of Rhodamine 6G.

CONCLUSIONS

We have demonstrated energy harvesting from conjugated polymers to light-emitting dopants. The possible uses for this research includes: organic light emitting diodes (OLEDs) and chemical sensors. Resonance energy transfer is possible from these polymers to common laser dyes. In nearly all samples, PB performed better than P1, although both polymers had similar singlet energies, the greater spectral overlap of PB with the acceptors led to higher transfer efficiencies. We have confirmed that not only the spectral overlap, but the location of overlap is important in energy transfer efficiencies. At high concentrations, dye emission decreases, which is most likely due to dye aggregate formation and quenching.

ACKNOWLEDGEMENTS

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