Energy transfer from polyphenylene-type polymers to a series of Coumarins and other acceptors

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ABSTRACT

Energy transfer studies were performed with polyphenylene-type polymers as the donating species and a series of organic dyes as the acceptors. The polymers were synthesized via Suzuki coupling of 2,5-didecyloxyphenyl-1,3-bisboronic acid with a corresponding dihaloarene. Coupling with 1,4-dibromobenzene produced a *para*-only polymer, while 3,5-dibromoethylbenzoate produced a polymer with alternating *para*- and *meta*-linkages. Several Coumarins served as singlet acceptors, while some porphyrins were used as triplet acceptors. Photophysical data and energy transfer parameters are presented.

Keywords: Energy transfer, polyphenylene, Coumarin, porphyrins, photophysical, Suzuki coupling, alternating para meta, singlet, triplet

1. INTRODUCTION

Conjugated polymers have received considerable attention in recent years for applications such as light-emitting diodes and other devices. Conjugated polymers have achieved optical and electrical properties similar to that of inorganic analogues, yet retained the ease of processability and mechanical properties of polymers. 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. This study is founded upon the concept of using dopants, e.g. organic dyes, to tune the emission color of a polymer.[1, 2, 3]

For Förster energy transfer to occur, the emission spectrum of the donor must overlap the absorption spectrum of the acceptor.[4] 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,[5] which is known as trivial energy transfer.

In this energy transfer study, polyphenylene-type polymers were used as the donating species. The polymers were an alkoxy-substituted poly(*para*-phenylene) (**P1**) and an alkoxy-substituted poly(*alt-para-meta*-phenylene) (**PM_es**), the structures of which are shown in Figure 1.
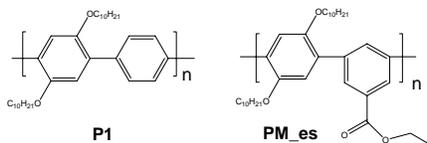

Figure 1: Structures of the polymers.

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The acceptors were commercially-available organic dyes, which included: Coumarin 102, Coumarin 480D, Coumarin 6H, Coumarin 152, Coumarin 30, Coumarin 153, Coumarin 314¸ Coumarin 7, Coumarin 337¸ Coumarin 6, Coumarin 500, platinum(II) meso-tetra(pentafluorophenyl)porphine (**PtFTPP**), and platinum(II) octaethylporphine (**PtOEP**). The structures of the laser dyes and metalloporphines are found in Figure 2.
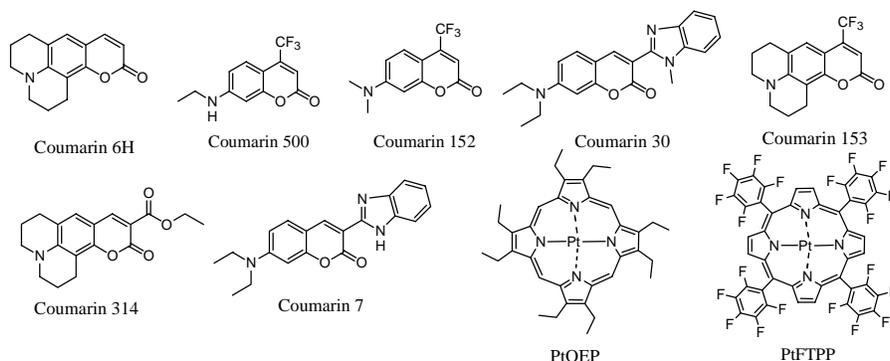

Figure 2: Structures of the acceptors.

2. EXPERIMENTAL

2.1 Materials. 1,4-Dibromobenzene, 3,5-dibromobenzoic acid, and all reagents were purchased from Aldrich. 2,5-didecyloxyphenyl-1,3-bisboronic acid[6] were synthesized according to published procedures. 3,5-dibromobenzoic acid was esterified using ethanol prior to polymerization. Polystyrene, Coumarin 102, Coumarin 480D, Coumarin 6H, Coumarin 152, Coumarin 30, Coumarin 153, Coumarin 314¸ Coumarin 7, Coumarin 337¸ and Coumarin 6 were purchased from Sigma-Aldrich. Coumarin 500 was purchased from Lambda Physik. Platinum(II) meso-tetra(pentafluorophenyl)porphine and platinum(II) octaethylporphine were purchased from Frontier Scientific. 2,2,2-Trichloroethanol was purchased from Lancaster Synthesis. Quartz slides were purchased from ChemGlass.

2.2 General Procedure for Polymerizations.[7] 2,5-Didecyloxyphenyl-1,3-bisboronic acid (0.001 mol) and corresponding dihaloarene (0.001 mol) were placed in an argon-flushed flask. THF (15 mL) and 1M aqueous Na_2CO_3 (15 mL) were added, degassed, and brought to reflux under argon. Palladium catalyst (35 mg) dissolved in THF (5 mL) was added and the reaction mixture was refluxed for two days. The organic phase was added to methanol, producing the polymer as a solid precipitate, which was further purified by reprecipitation in methanol.

2.3 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. Phosphorescence studies were carried out using the 1934D3 phosphorimeter in conjunction with the Fluorolog-3 system with a xenon flash lamp. 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. The quantum yield for emission in solution, determined according to the method described by Demas and Crosby[8] relative to quinine sulfate in 1.0M H_2SO_4 (0.546).[9] The singlet and triplet energies of the polymers were calculated according to published methods.[10]

2.4 Sample Preparation. A 25 w/v % solution of polystyrene in 2,2,2-trichloroethanol was made in which the polymers P1 and PM_es were each dispersed in a 2.5 w/v % concentration. The acceptors were each dispersed in a 2.5 w/v % concentration as well. The solutions were then spin cast onto quartz slides.

3. RESULTS AND DISCUSUION

The polymers P1 and PM_es were synthesized using 2,5-didecyloxyphenyl-1,3-bisboronic acid coupled with 1,4-dibromobenzene and 3,5-dibromoethylbenzoate via Suzuki coupling. The reactions are shown in Scheme 1.
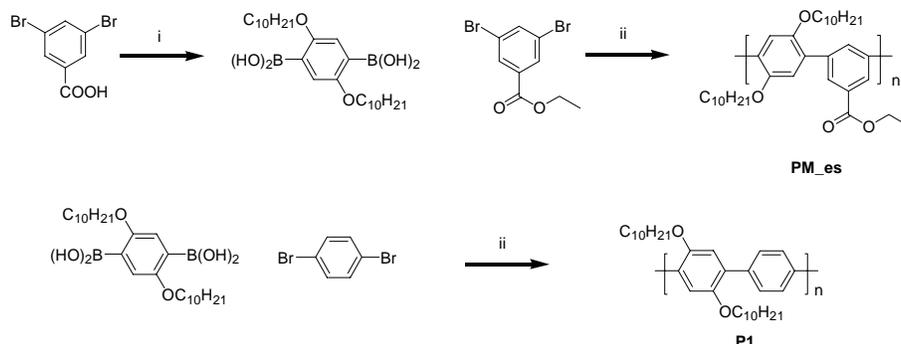
Scheme 1: The synthetic route to PM_es and P1 (i.) Ethanol/ PTSA reflux for 24hrs; (ii.) Pd(PPh$_3$)$_4$, 2M Na$_2$CO$_3$, Toluene, refluxed 72hrs).

The photophysical properties of the energy donating polymers are shown in Table 1. These properties were determined in solution studies. Small changes in emission maxima were noted in both polymers in the solid state while dispersed in polystyrene. The polymer P1's emission maximum shifted to 408 nm and PM_es' went to 404 nm. PM_es' absorption maximum also shifted to 334 nm, while P1 did not change.

Table 1. Photophysical properties of the polymers in THF solution.

Polymers	Abs. Max (nm)	Emission				Singlet energy (eV)	Triplet energy (eV)
		Max (nm)	FWHM (nm)	ϕ_{FL}	τ (ns)		
P1	350	411	61.5	0.386	0.690	3.24	2.31
PM_es	330	392	61.5	0.662	1.665	3.41	2.47

The spectral overlap of the polymer emissions and the dyes absorbances are illustrated in Figures 3 and 4. In Figure 3, the emission of polymer P1 is surrounded by absorbances of the dyes. The same is shown in Figure 4 for polymer PM_es. All of these spectra were determined in polystyrene dispersed films.
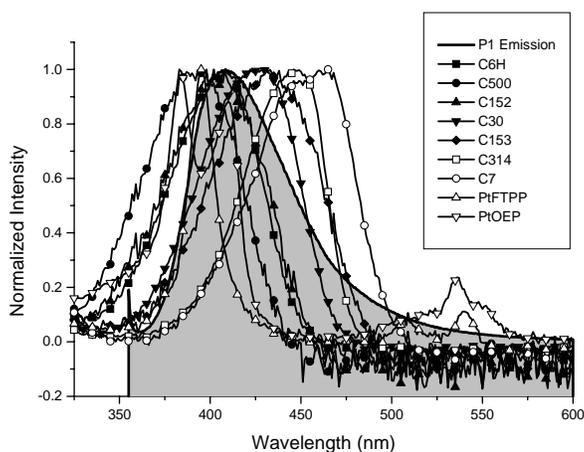

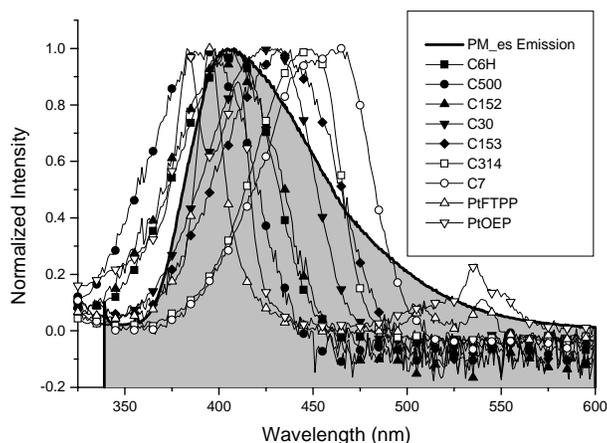Figure 3: Spectral overlay of emission spectra of polymer P1 with absorption spectra of the dyes.

Figure 4: Spectral overlay of emission spectra of polymer PM_es with absorption spectra of the dyes.

The dyes were chosen to overlap over the polymer emissions in specific areas. Some overlap the higher energy portions, as with PtFTPP, PtOEP, Coumarin 6H, Coumarin 500, and Coumarin 152. Some overlap most of the central area, as with Coumarin 30 and Coumarin 153. Others overlap the lower energy areas where the emissions have tails, as with Coumarin 314 and Coumarin 7. The metalloporphines have minor absorption bands in the tail regions of the polymer emissions.

The rationale behind the position of overlap was inspired by the work of Brunner and coworkers,[1] where acceptors with overlap in the lowest excimer region of polymer resulted in higher energy transfer efficiencies. Our findings will be discussed later.

In Figure 5, the emission spectra of the polymer P1 alone and when doped are shown. In all of these Coumarin doped systems, negligible to no residual emission was seen from the polymers at 408 nm.
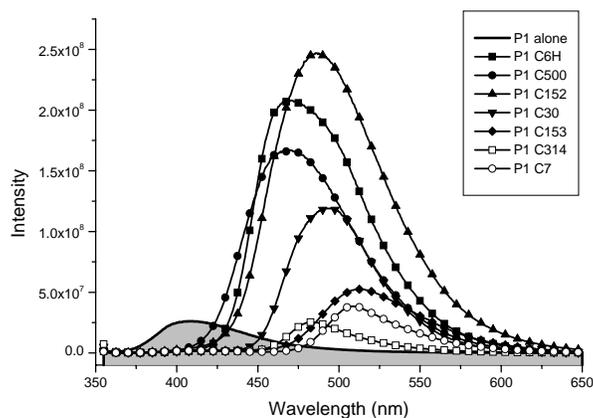

Figure 5: Emission spectra of the P1 doped systems, excited at 350 nm.

In Figure 6, the emission spectra of the polymer PM_es alone and when doped are shown. Again, residual emission from the polymer at 404 nm is negligible.
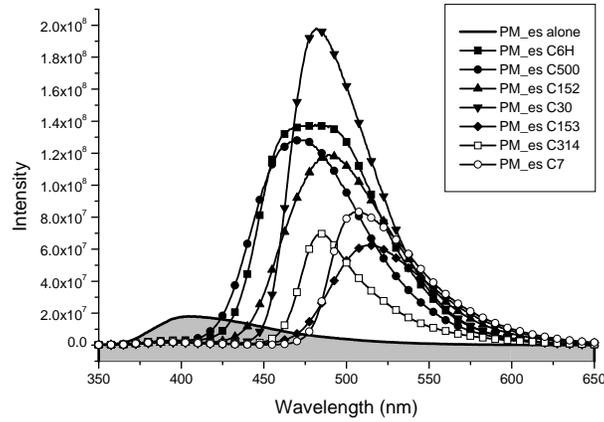
Figure 6: Emission spectra of the PM_es doped systems, excited at 334 nm.

The energy transfer efficiencies listed in Table 2 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.

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

(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,[11] and these data are summarized in Table 2.

Table 2. Energy transfer efficiencies and overlap integrals and the Coumarin doped polymer systems.

Dye	Abs. Max. (nm)	P1 – E(-14) J,cm⁶/mmol	PM_es – E(-14) J,cm⁶/mmol	P1 - ET	PM_es – ET
Coumarin 6H	381	6.2	5.6	0.925	0.830
Coumarin 500	383	2.6	2.4	0.819	0.841
Coumarin 152	388	4.0	3.6	0.854	0.916
Coumarin 30	406	9.6	8.7	0.943	0.919
Coumarin 153	413	3.6	3.4	0.924	0.904
Coumarin 314	427	5.9	5.6	0.942	0.885
Coumarin 7	431	6.7	6.7	0.926	0.912

PhotoChemCAD calculated the overlap integrals (J) 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.

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

(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 significant figures. Both the absorbance and fluorescence spectra were recorded at 1.00 nm

resolution with a spectral width of interest of 300 – 450 nm, and were baseline corrected. The program authors stated that the calculated values were consistent with prior calculations seen in the literature.[12]

The rate constant of energy transfer typically depends upon the overlap integral, which is the case for small molecule donors. However, conjugated polymers should have spectral overlap in the low energy region of the emission spectra of the polymer.[1] From the data listed in Table 2, only Coumarin 500 and Coumarin 152 had higher energy transfer efficiencies in PM_es than in P1, when their overlap integrals suggested the opposite would occur. According to Brunner's findings, Coumarin 337 and Coumarin 7 should have greater energy transfer efficiencies than those that absorb at lower wavelengths. One reason the data would not agree with Brunner's findings was that these polymers did not form aggregates. Therefore the low energy region of these polymers' emissions would not have as many long lived excited states as it would if aggregation did occur.

Figure 7 shows a depiction of the degree of overlap between the polymers and the acceptors in terms of the acceptor's absorption maxima. What is observed is that when a dopant has a large overlap with one polymer, it has a large overlap with the other. The same is true when there is less overlap.
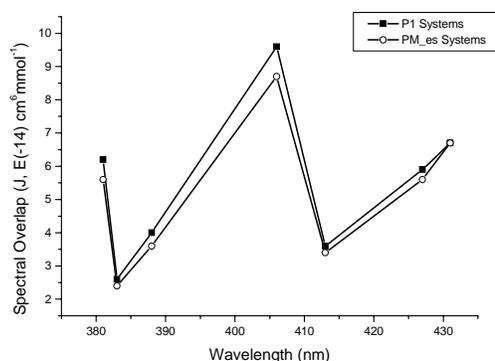

Figure 7: Spectral overlap with polymer versus absorption maxima of the Coumarin dopants.

Figure 8 shows the energy transfer efficiencies of the Coumarin doped systems in terms of the acceptor's absorption maxima. There is a very general trend of increasing energy transfer as the dopant's absorption maxima increases, at least for polymer P1.
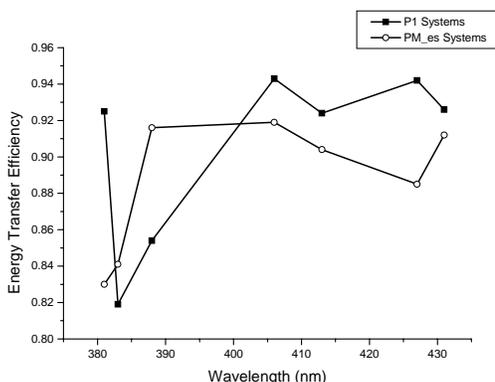

Figure 8: Energy transfer efficiency versus absorption maxima of the Coumarin dopants.

In Figure 9, energy transfer is shown to occur from both P1 and PM_es to PtFTPP and PtOEP. The sharp spikes located at 668 nm in Figure 9(b) are due to the second order Raleigh bands, resulting from exciting the polymer at 334 nm. Residual emission from the polymers was seen in all cases, though less in the systems where PtOEP was the

dopant. The PM_es doped systems also had unusual peak shapes in its residual emission, more so with PtFTPP as the dopant, as seen in Figure 9(b).
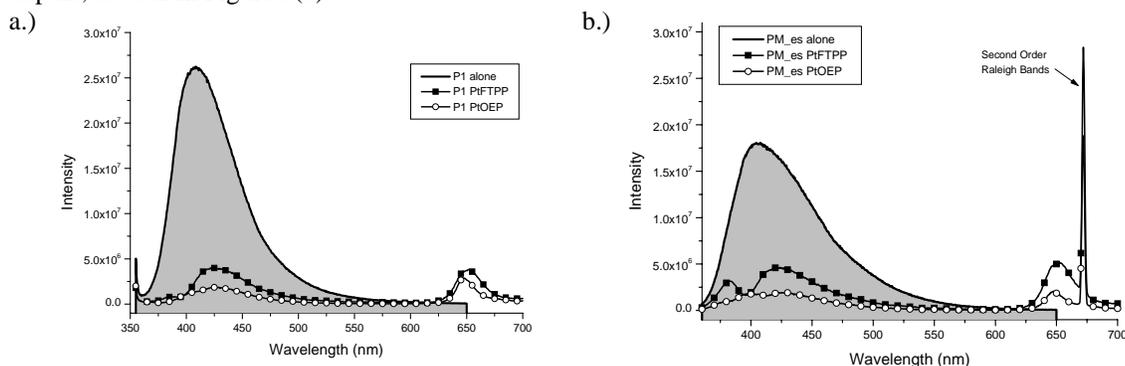
a.)

b.)

Figure 9: Emission spectra of P1 excited at 350 nm (a), and PM_es excited at 334 nm (b) when doped with platinum porphines.

Significant emission from the dyes was not observed, though the intensities from the porphines were much less than that of the Coumarins. Figure 10 illustrates this point by comparing the intensity of emission from a polystyrene film of Coumarin 30 with a polystyrene film of PtFTPP. Back in Figure 9, although the acceptor emission was not as intense as the Coumarin doped systems, significant reduction in polymer emission occurred.
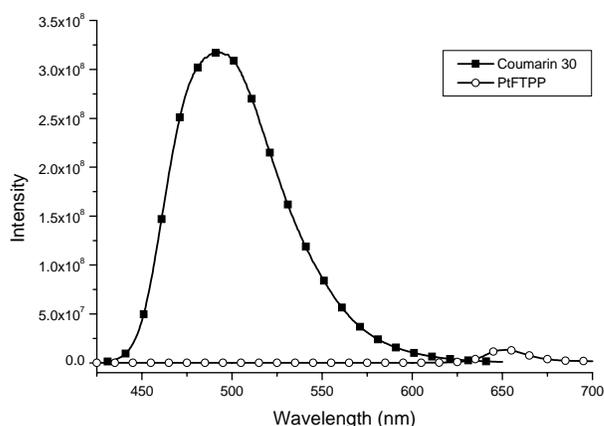

Figure 10: Emission spectra of Coumarin 30 and PtFTPP.

In these metalloporphine doped systems, The PtFTPP and PtOEP doped systems exhibited energy transfer as noted by the donor emission's reduction, and the efficiencies of these systems are listed in Table 3. Both dopants preferred P1 over PM_es by nearly five percent in each instance.

Table 3: Energy transfer efficiencies of the metalloporphine doped polymer systems.

Dye	P1 – ET	PM_es – ET
PtFTPP	0.904	0.855
PtOEP	0.949	0.902

4. CONCLUSION

Energy transfer has been shown to occur from polyphenylenes as the energy donors to singlet energy accepting Coumarins and the triplet energy accepting metalloporphines. Our studies did not follow Brunner's observations mostly due to the fact that the polymers used in this study did not aggregate. By dispersing the donor polymers and acceptor dyes in polystyrene, aggregation was prevented. For the most part, the efficiencies of energy transfer did correlate with the overlap integrals of the doped systems. The disparity noticed with Coumarin 500 and Coumarin 152 is undergoing further study.

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