Energy Transfer from Polyphenylene-Type Polymers to a Series of Organic 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.

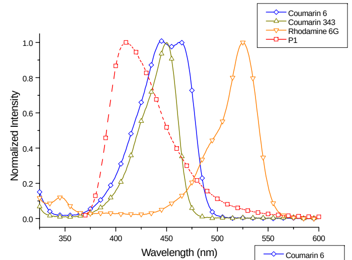
RESONANCE ENERGY TRANSFER

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]

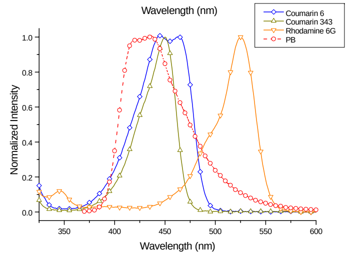
[1] Förster, Th., *Ann. Phys. (Leipzig)*, **1948**, *2*, 55-75. Translated by R. S. Knox.
[2] Lakowicz, J. R., *Principles of Fluorescence Spectroscopy, Second Edition*, Kluwer Academic / Plenum Publishers, **1999**, p. 13.

Overlaid Spectra of Polymer Emissions with Dye Absorbances

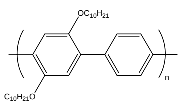
P1



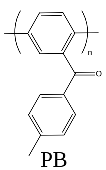
PB



DONORS

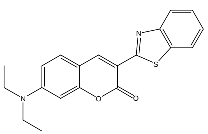


P1

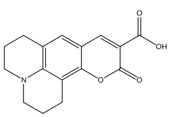


PB

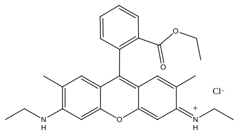
ACCEPTORS



Coumarin 6

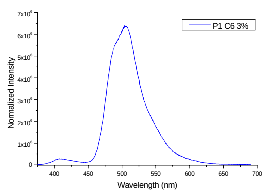


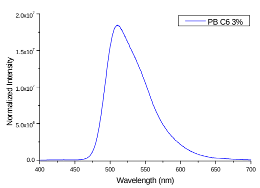
Coumarin 343



Rhodamine 6G

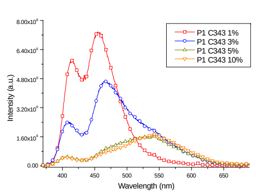
Emission Spectra from Polymers Doped with Coumarin 6

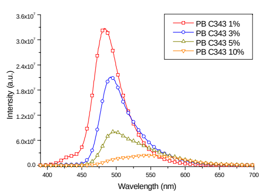




- P1 shows residual emission, while PB shows none.
- PB has more overlap than P1 with Coumarin 6.

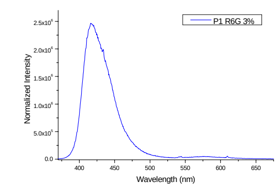
Emission Spectra from Polymers Doped with Coumarin 343

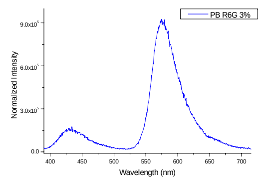




- P1 shows residual emission, while PB shows much less.
- Due to PB's larger overlap with Coumarin 343.
- Aggregate formation at higher concentrations.

Emission Spectra from Polymers Doped with Rhodamine 6G





- P1 shows no dye emission, while PB shows energy transfer.
- PB has greater overlap than P1.
- P1 though does overlap with Rhodamine 6G, but apparently not enough to cause dye emission.

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

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

Dye	***P1 - J,cm6/mmol***	***PB - J,cm6/mmol***	***P1 – ET***	***PB - ET***
Coumarin 6	1.117 E -13	1.538 E -13	0.980	0.985
Coumarin 343	1.392 E -13	1.255 E -13	0.935	0.845
Rhodamine 6G	0.345 E -13	1.247 E -13	0.805	0.962

OBSERVATIONS

- Resonance energy transfer is possible from polymers to dyes.
- PB has greater overlap than P1 for all of the acceptors.
- Greater overlap leads to less or no residual emission from the polymer.
- Overlap in the low energy / excimer region of the polymer leads to better energy transfer.
- At high concentrations, dye emission decreases, which is most likely due to aggregate formation and quenching.

FURTHER STUDIES

- Further experiments will involve dispersing the donors and acceptors in an inert matrix, e.g. polystyrene.
- Also, smaller increments of doping will be used to find the optimal concentrations.
- Refractive indices of the polymer films needed to determine the Forster radii of each system.

CONCLUSIONS

- We have demonstrated energy harvesting from conjugated polymers to light-emitting dopants.
- Possible uses include OLEDs and chemical sensors.
- We have confirmed the concept that amount of energy transfer depends on degree of overlap as well as the location of the overlap.

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