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

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Overview

- Resonance energy transfer
- Energy transfer systems
    - Energy donors and properties
    - Polymer syntheses
    - Energy acceptors and properties
    - Sample preparation
- Spectral overlap of donors and acceptors
- Coumarin doped systems
    - Emission spectra of the Coumarin doped systems
    - Calculations
    - Energy transfer parameters of Coumarin systems
- Metalloporphine doped systems
    - Emission spectra of the porphine doped systems
    - Energy transfer parameters of porphine systems
    - Emission intensities of a Coumarin compared to a porphine
- Conclusions
- Acknowledgements

Energy Transfer

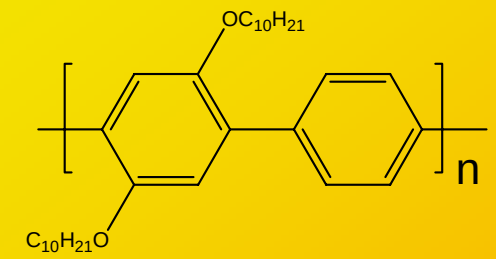
• For Förster energy transfer to occur, the emission spectrum of the donor must overlap the absorption spectrum of the acceptor.[1]

• Also known as resonance energy transfer, this process 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]

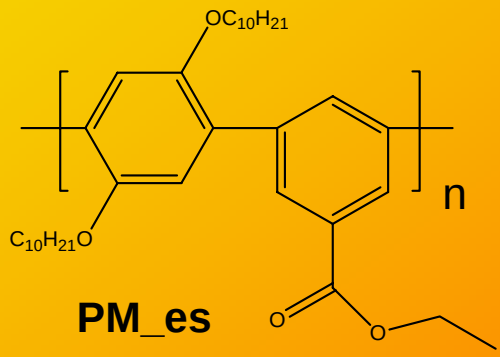
1. T. Förster, *Ann. Phys. (Leipzig)* **2**, 55, 1948. Translated by R. S. Knox.
2. J. R. Lakowicz, *Principles of Fluorescence Spectroscopy,* 2nd ed., Kluwer Academic / Plenum Publishers, New York, NY (1999).

Energy Donors

Structures of the polymers used.



P1

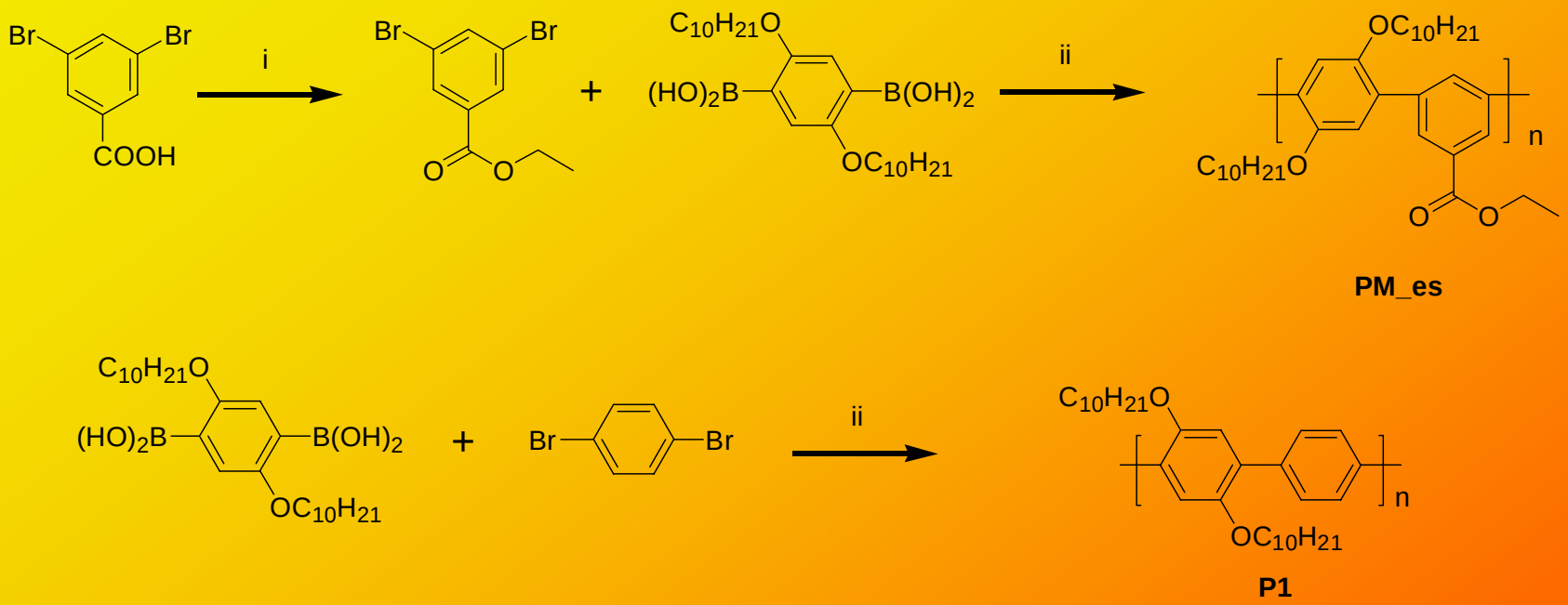


PM_es

Solution state (THF) photophysical properties of the polymers.

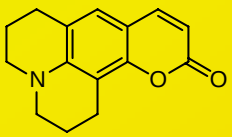
Polymers	Abs. Max (nm)	Emission				Singlet energy (eV)	Triplet energy (eV)
		Max (nm)	FWHM (nm)	ϕ_{FL}	τ (ns)		
P1	350	411	61.5	0.386	0.690	3.24	2.31
PM_es	330	392	61.5	0.662	1.665	3.41	2.47

Energy Donors - Syntheses

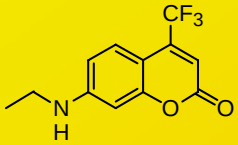


Scheme 1: The synthetic route to PM_es and P1 (i.) Ethanol/ PTSA refluxed 24hrs; (ii.) $Pd(PPh_3)_4$, 2M Na_2CO_3, Toluene, refluxed 72hrs).

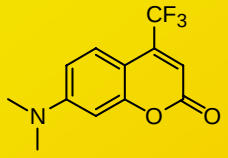
Energy Acceptors



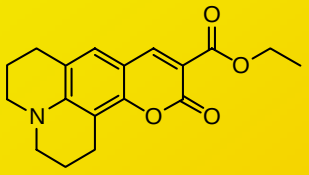
Coumarin 6H



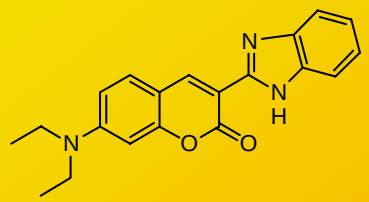
Coumarin 500



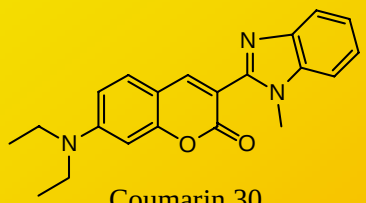
Coumarin 152



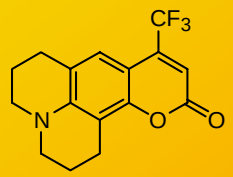
Coumarin 314



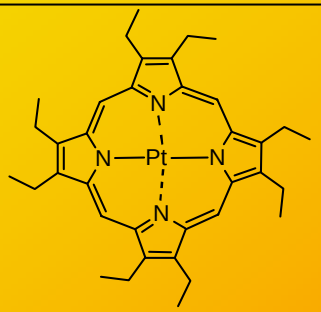
Coumarin 7



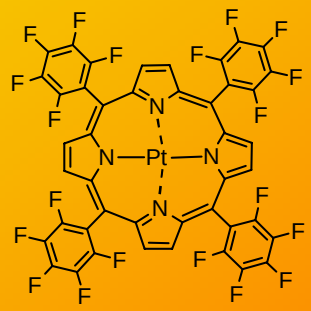
Coumarin 30



Coumarin 153



PtOEP



PtFTPP

Structures of the acceptors.

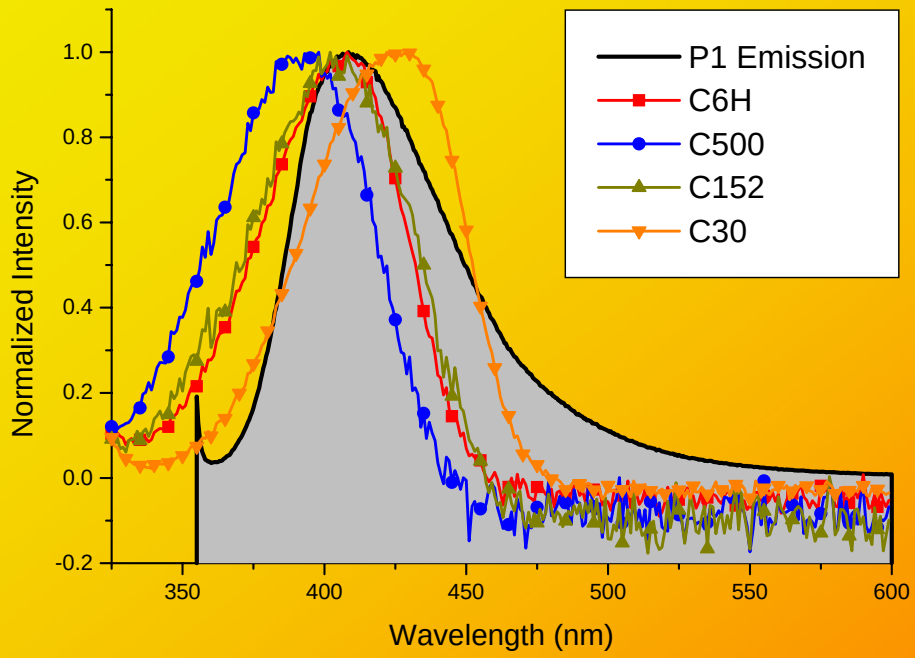
Solution state (THF) photophysical properties of the acceptors.

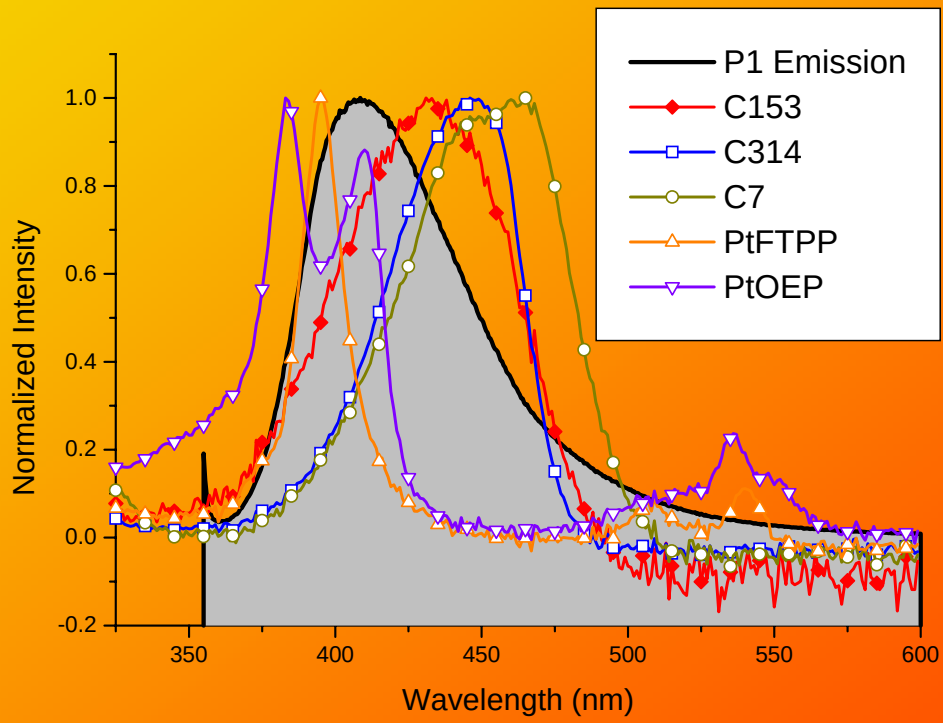
Dye	λ max	ε ($M^{-1}cm^{-1}$)
Coumarin 102	376	21373
Coumarin 480D	376	17900
Coumarin 6H	381	23660
Coumarin 500	383	18480
Coumarin 152	388	19133
Coumarin 30	406	39573
Coumarin 153	413	14537
Coumarin 314	427	28687
Coumarin 7	431	29750
Coumarin 337	437	38903
Coumarin 6	442	48070
PtFTPP	389	212856
PtOEP	380	217999

Sample Preparation

- A 25 w/v % solution of polystyrene in 2,2,2-trichloroethanol was made.
- In this solution, each of the polymers P1 and PM_es were dispersed in a 2.5 w/v % concentration.
- The acceptors were each dispersed in a 2.5 w/v % concentration as well.
- 1:1 Doping of donor to acceptor.
- The solutions were then spin cast onto quartz slides.

Overlay of P1 Emission with Absorbances of the Acceptors



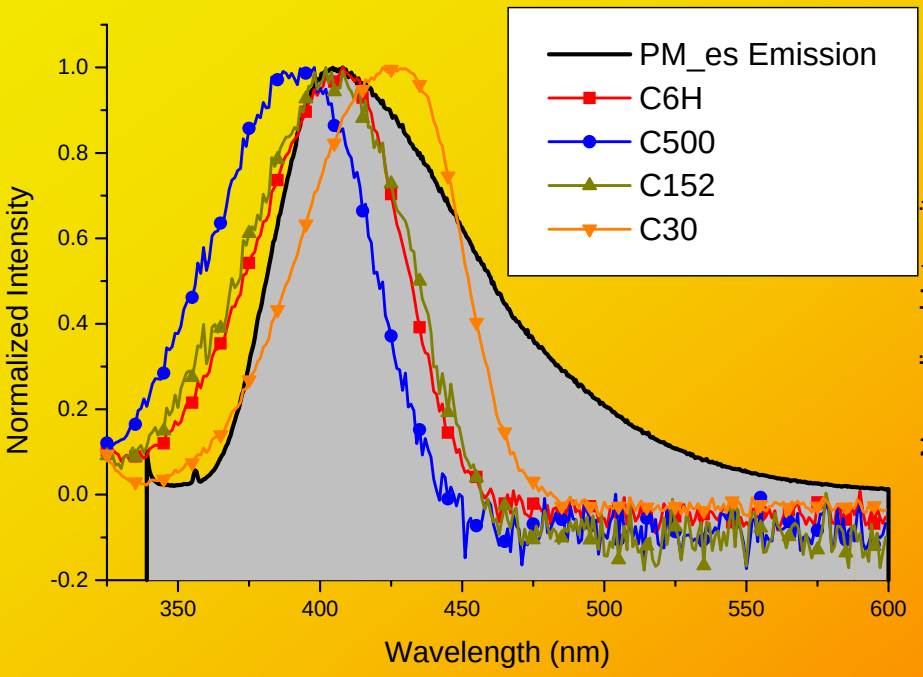


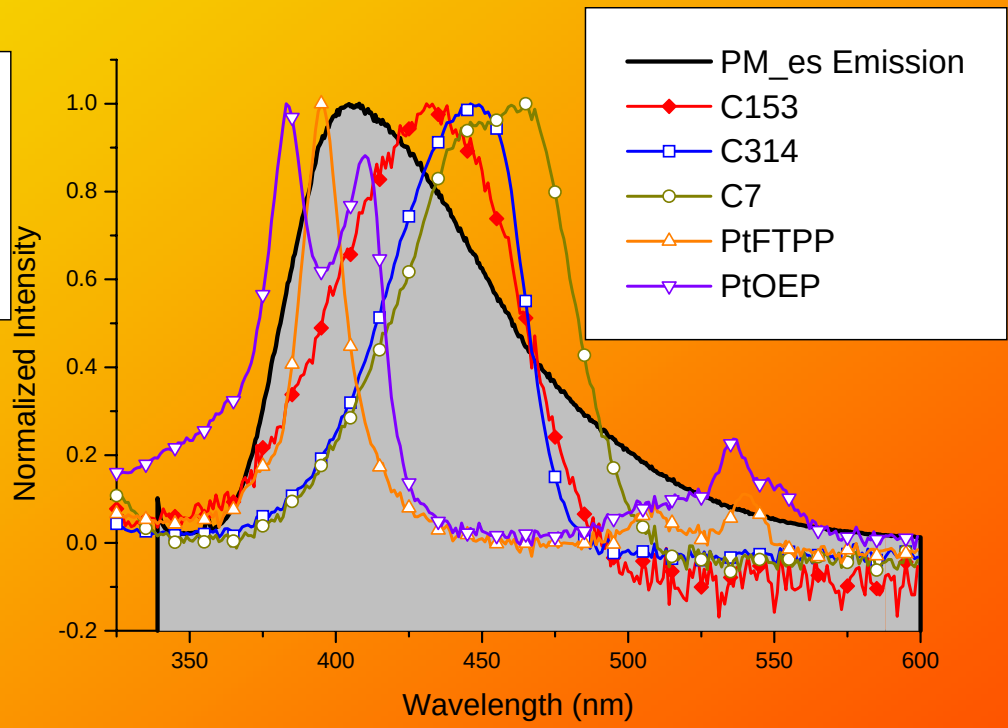
- Overlap from high to low energy side of donor emission.

- Brunner's work[3] showed that overlap on low energy side led to greater energy transfer efficiences.

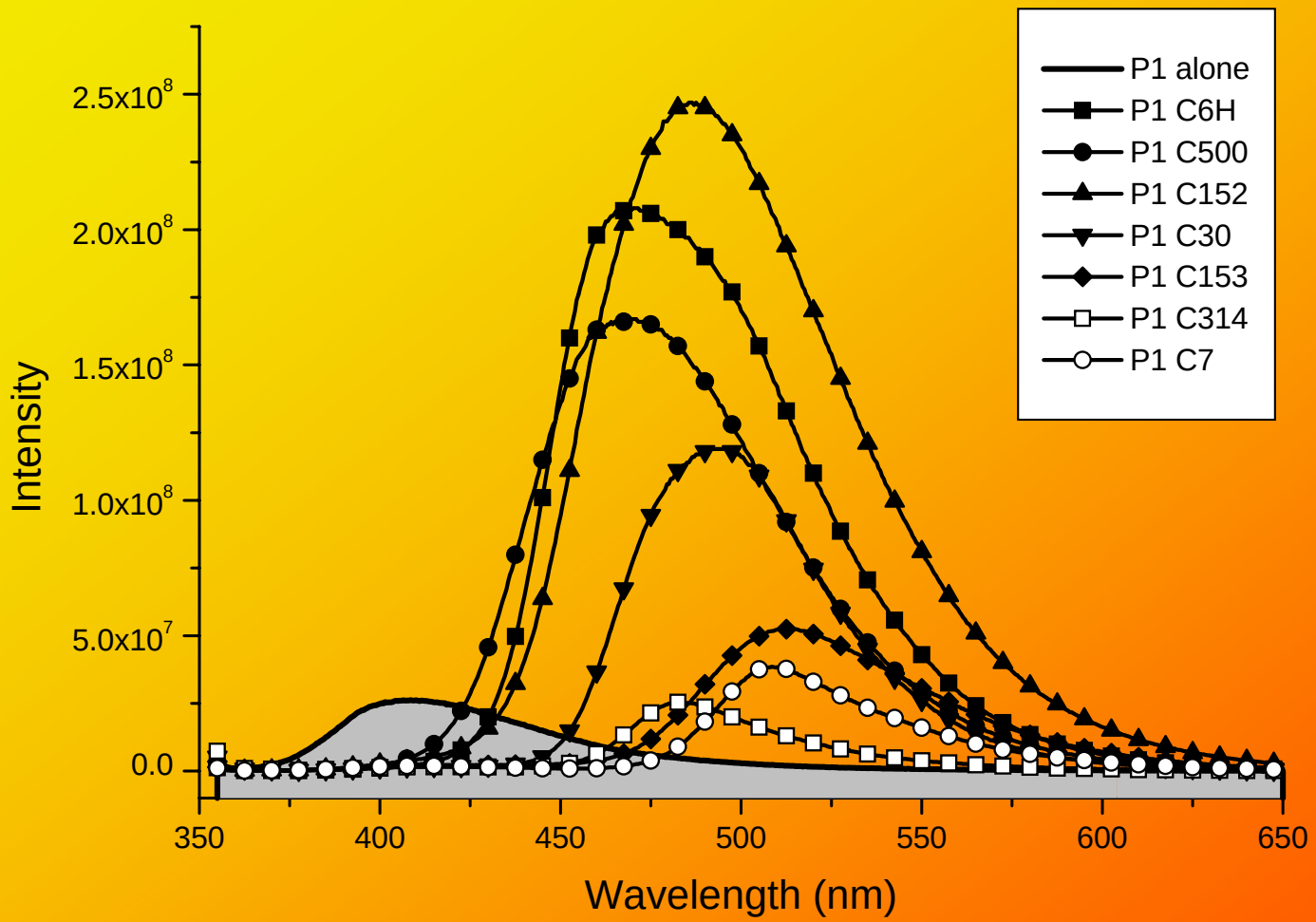
3. K. Brunner, J. A. E. H. van Haare, B. M. W. Langeveld-Voss, H. F. M. Schoo, J. W. Hofstraat, and A. van Dijken, *J. Phys. Chem. B* **106**, 6834 (2002).

Overlay of PM_es Emission with Absorbances of the Acceptors



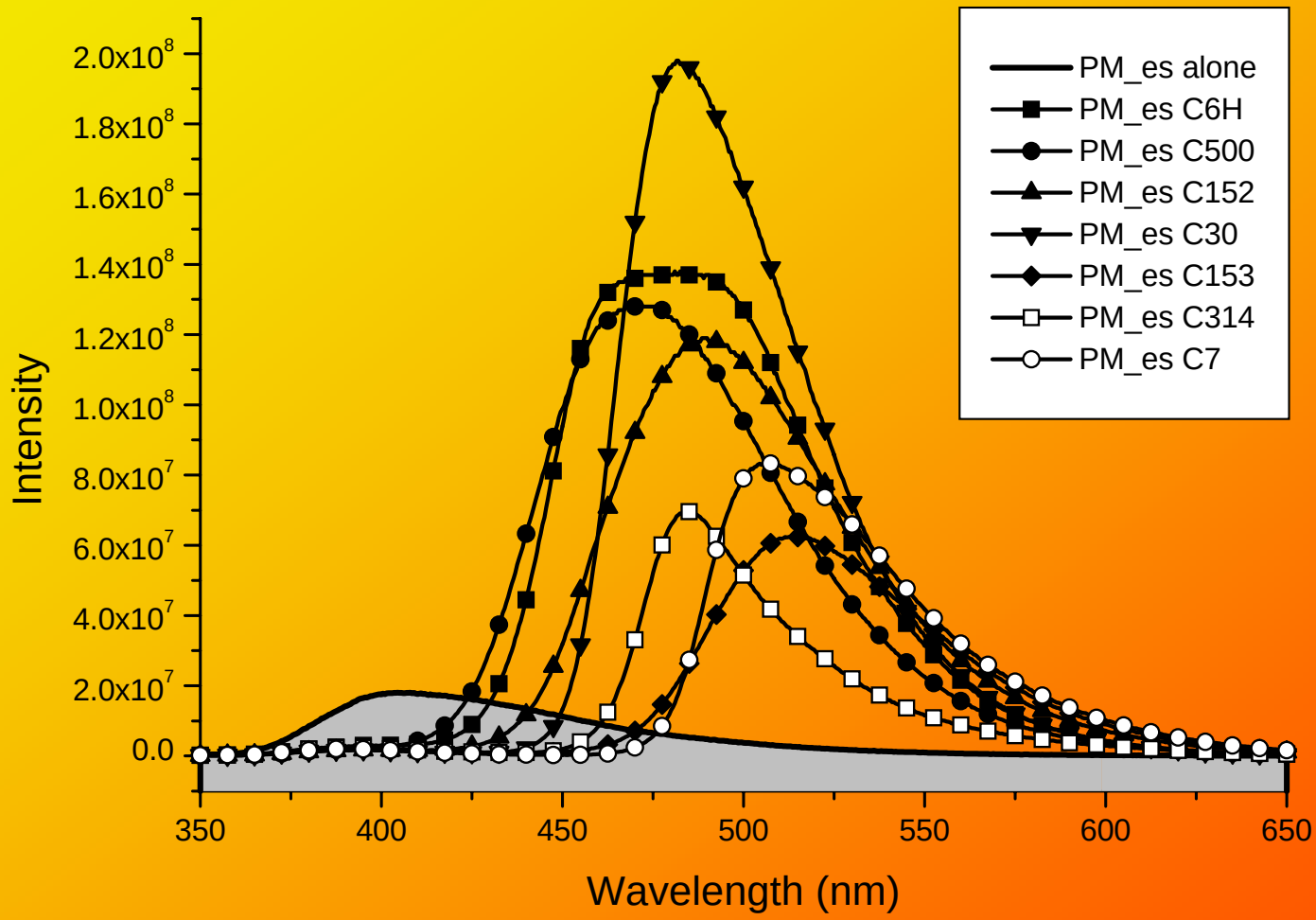


P1 – Coumarin Doped Systems



- Not corrected for direct excitation of the acceptors.

PM_es – Coumarin Doped Systems



Calculation of the Parameters

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

In Equation 1, *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.

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

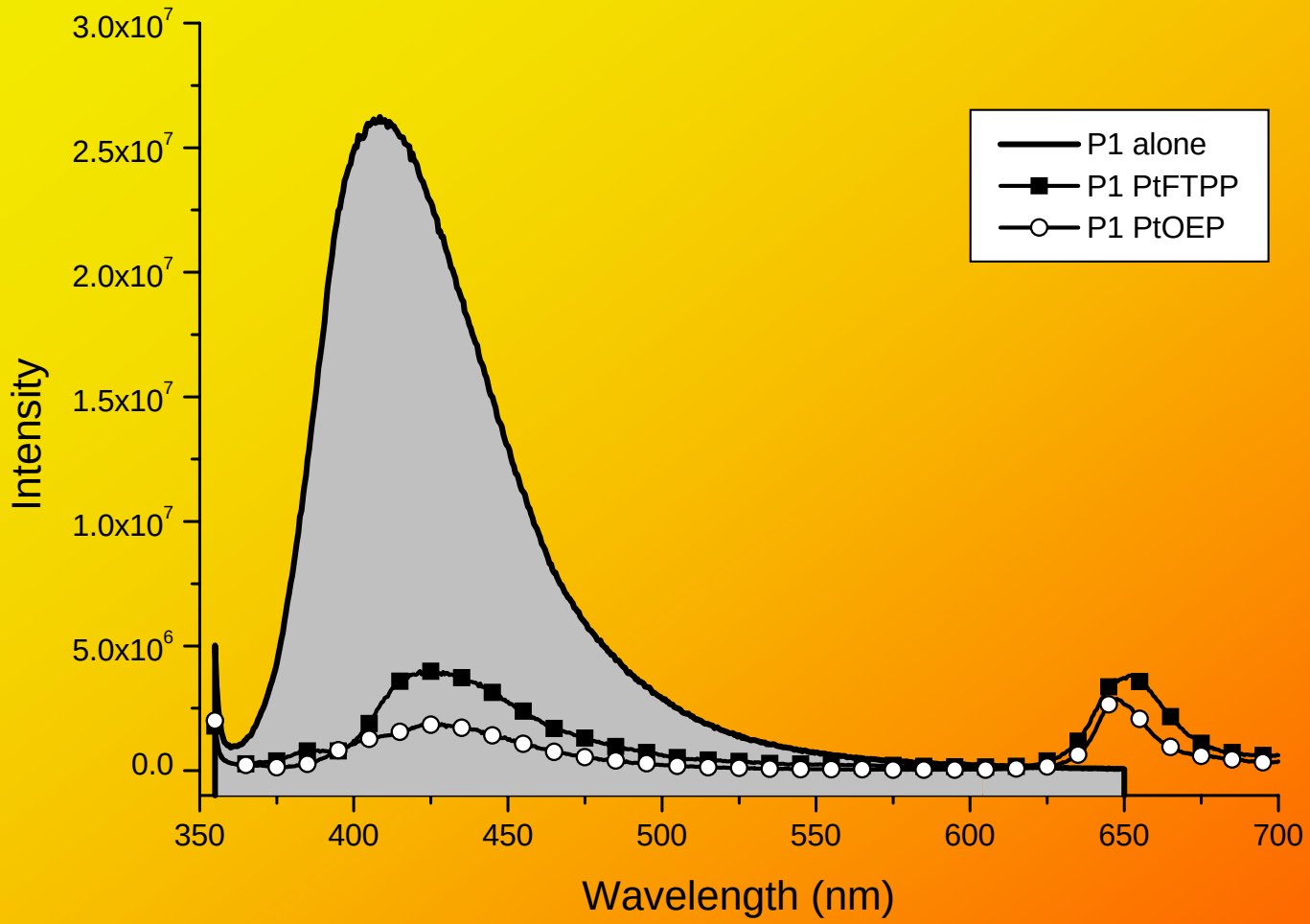
PhotoChemCAD calculated the overlap integrals (*J*) with Equation 2, where: *J* is the spectral overlap; is $f_s(\upsilon)$ the fluorescence intensity of the donor; $\varepsilon_A(\upsilon)$ is the molar absorption coefficient of the acceptor; and υ is the wave number of the donor emission spectrum and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

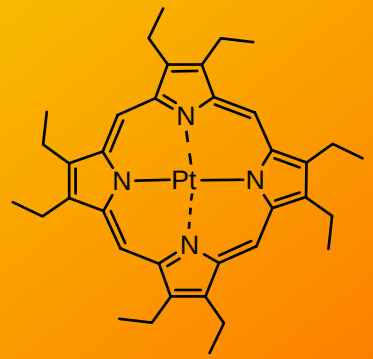
Energy Transfer Parameters of Coumarin Systems

Dye	***Abs. Max. (nm)***	***P1 – E(-14) J,cm^6/mmol***	***PM_es – E(-14) J,cm^6/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

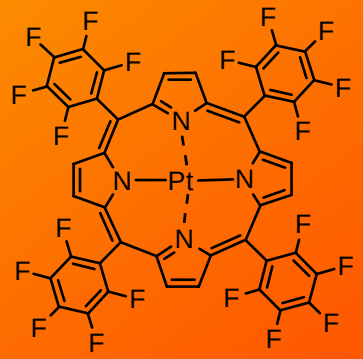
- Coumarin 500 and Coumarin 152 do not follow the trend of higher relative overlap integral leads to higher relative energy transfer efficiency.

P1 – Pt(II) Porphine Doped Systems





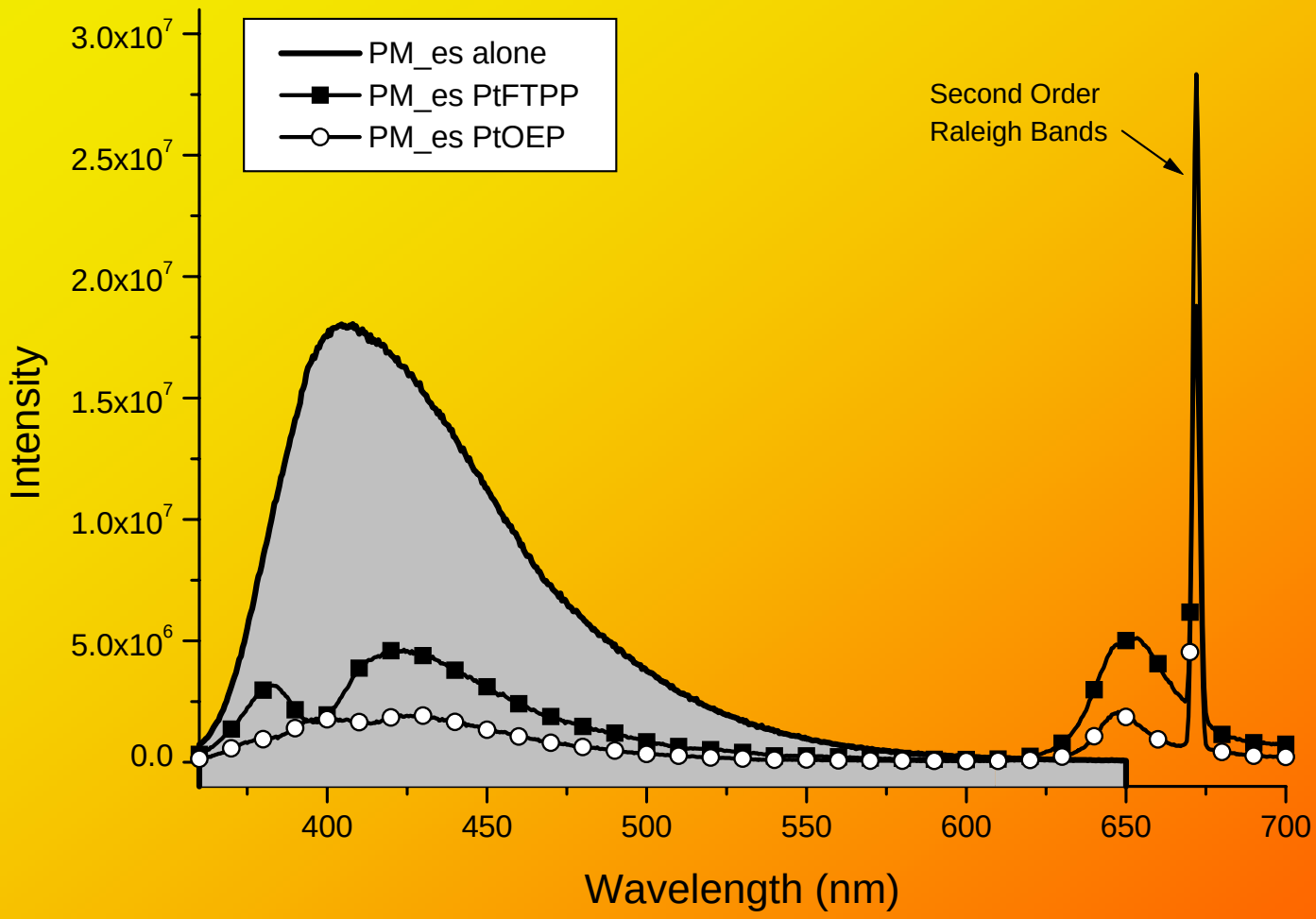
PtOEP

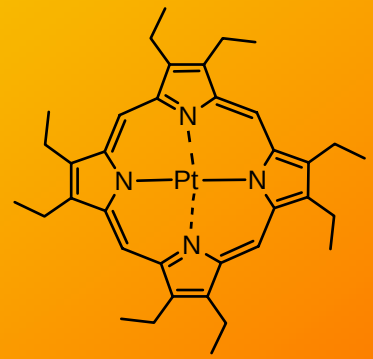


PtFTPP

- Same concentrations.
- High ET efficiencies.
- Low emission efficiencies.

PM_es – Pt(II) Porphine Doped Systems





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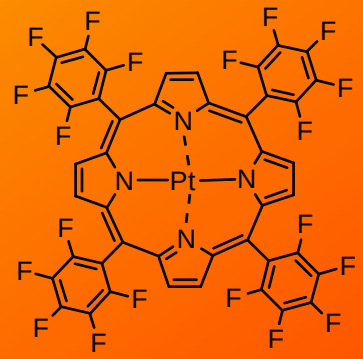


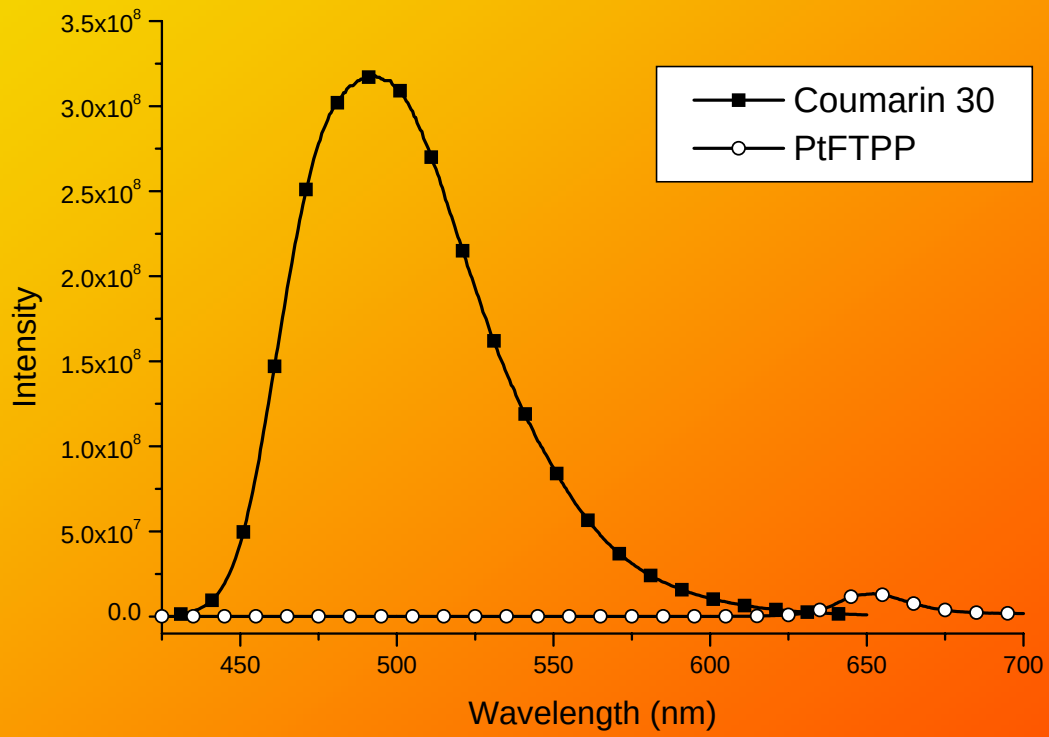
PtFTPP

Metalloporphine System Parameters

Dye	***Abs. Max. (nm)***	***P1 – E(-14) J,cm^6/mmol***	***PM_es – E(-14) J,cm^6/mmol***	***P1 – ET***	***PM_es – ET***
PtFTPP	395	22	20	0.904	0.855
PtOEP	383	28	26	0.949	0.902

• Overlap integrals are much higher than those for the Coumarin systems, because of the higher extinction coefficients.

• Intensities of emission from metalloporphines are much less than Coumarins.



Conclusions

- Energy transfer has been shown to occur from polyphenylenes as the energy donors to singlet energy accepting Coumarins and the triplet energy accepting metalloporphines.

- By dispersing the donor polymers and acceptor dyes in polystyrene, aggregation was prevented.

- Our studies did not follow Brunner's observations mostly due to the fact that the polymers used in this study did not aggregate.

- 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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