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VISIBLE LIGHT-HARVESTING IN COVALENTLY-LINKED PORPHYRIN-CYANINE DYES

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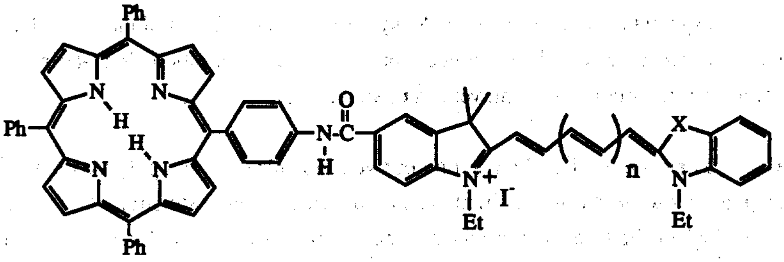
Abstract: We report the synthesis and properties of three members of a new class of photochemical model compounds containing a covalently-linked porphyrin and a cyanine dye. In compounds **1** and **2** the dye absorbs in the 450-570 nm region and energy transfer occurs with 80% efficiency *from the dye to the free base porphyrin.* In compound **3** the dye absorbs in the 650-780 nm region and energy transfer occurs with 80% efficiency *from the free base porphyrin to the dye.* The zinc-porphyrin-dyes exhibit both donor and acceptor quenching with only moderate yields of energy transfer. This work is a first step toward the development of an artificial phycobilisome.



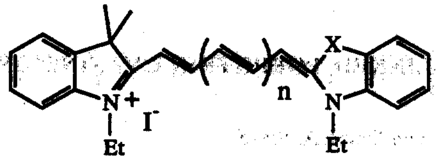
1: X = O, n = 0
PC3(I-O)

2: X = $C(CH_3)_2$, n = 0
PC3(I-I)

3: X = $C(CH_3)_2$, n = 2
PC7(I-I)

Introduction: Light-harvesting by antenna complexes is an integral photosynthetic process. Both the chlorophyll light-harvesting complexes and the phycobilisomes are comprised of hundreds of pigments which function in a cooperative manner to funnel photonic energy to the reaction centers.[1] Given the importance of photosynthetic light-harvesting it is surprising that few synthetic model systems have been prepared for absorption of visible light followed by energy transfer.[2-4] The major synthetic challenge is to create a structured-pool of chromophores that together perform efficient vectorial energy transfer. In the phycobilisome, for example, stacked arrays of bilin pigments absorb in the ~500-650 nm region and perform a multistep energy cascade with high quantum efficiency, ultimately sensitizing chlorophyll and thereby extending the spectral range for light-harvesting.[5] The bilin pigments are rigidly-positioned in proteins which self-assemble to give a functional phycobilisome unit. In creating an artificial phycobilisome it is desirable to preserve the paradigms of the natural system (high fluorescence quantum yields, rigid 3-dimensional organization of pigments, rapid energy transfer, self-assembly of the component parts, etc.), but from a functional standpoint there are no compelling reasons to limit the selection of pigments to bilin chromophores.

One especially intriguing class of photochemically-active abiotic molecules consists of the cyanine dyes.[6] The cyanines have an intense long wavelength absorption band (ε ~50-200,000 $M^{-1}cm^{-1}$), moderate fluorescence quantum yields, and negligible yields of triplet state formation.[7] The long wavelength absorption band can be tuned with precision from the near-UV to the near-IR by synthetic design. Each additional vinyl group in the polyene chain shifts the absorption about 100 nm to the red, and alteration of the terminal groups provides finer tuning (Figure 1). Wavelength tunability is unique to the cyanines and in conjunction with their absorption, fluorescence, and photochemical properties has led to diverse applications such as laser dyes,[8,9] fluorescent bioprobes,[10] and visible sensitizers in photography.[11]



4: X = O, n = 0 C3(I-O)
5: X = $C(CH_3)_2$, n = 0 C3(I-I)
6: X = $C(CH_3)_2$, n = 2 C7(I-I)

(where 3 and 7 refer to the number of carbons in the polyene chain)

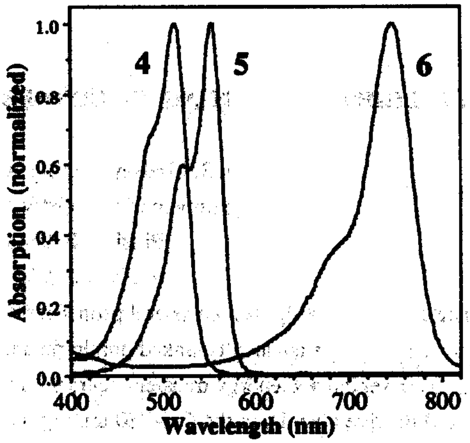
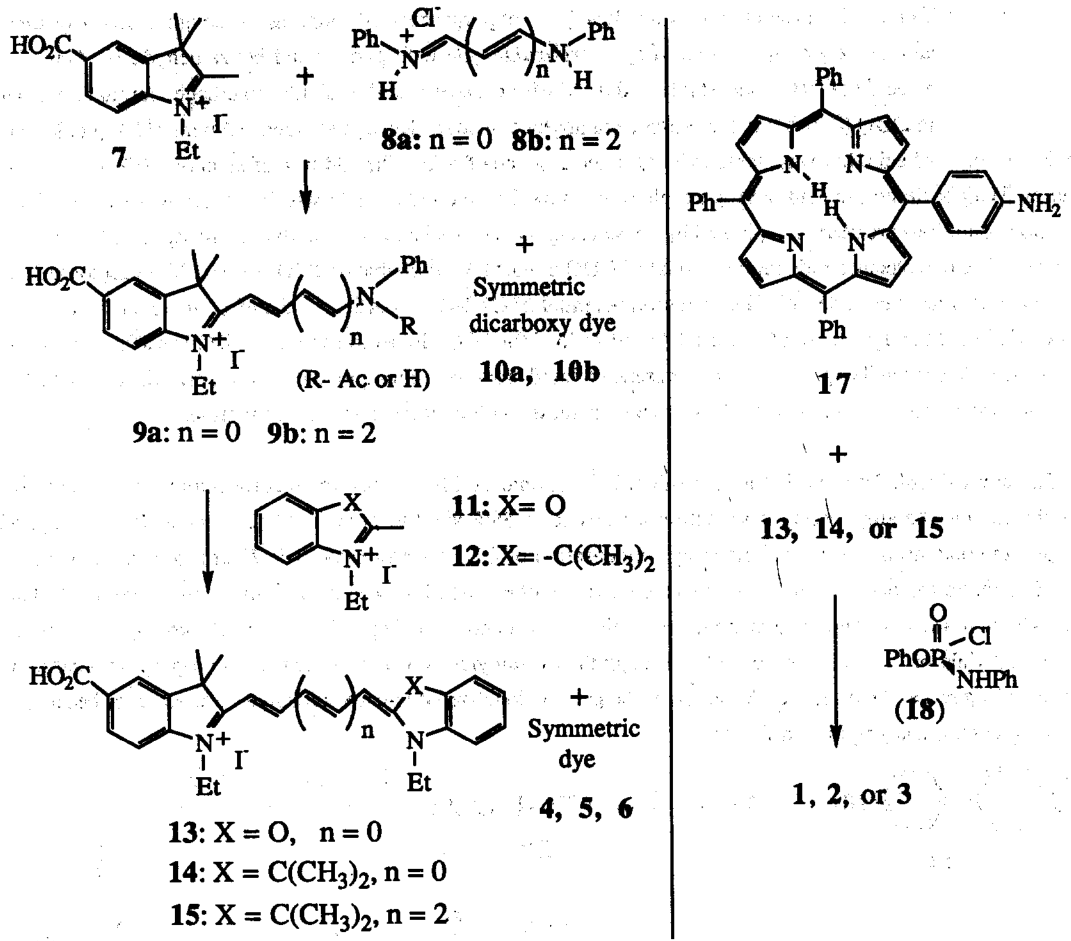


Figure 1. Wavelength tunability in cyanine dyes.

The rich photochemistry of the porphyrins and the cyanine dyes has propelled us to prepare the new class of compounds containing a porphyrin and a cyanine dye. To our knowledge this is the first example of the covalent incorporation of cyanine dyes into a synthetic photochemical model system. The elucidation of the photochemical properties of these bichromophoric molecules provides a foundation for the more ambitious long-term goal of constructing synthetic multichromophore assemblies for harvesting of visible light.

Synthesis: The asymmetric dyes are synthesized by reaction of two indolenines with a polyene dianil.[12] If both indolenines show equal reactivity toward the anil, a simultaneous condensation with stoichiometric quantities will give the asymmetric dye as 50% of the three dye products. Because the carboxy indolenine **7** is the most valuable component, the synthesis was performed by sequential additions of the two indolenines rather than by a simultaneous condensation. By addition of the second indolenine (**11** or **12**) after consumption of the carboxy indolenine to give the intermediate **9** (but prior to extensive formation of the symmetric dicarboxy dye **10**), the isolated yield of asymmetric dye (**13**, **14**, or **15**) was increased with respect to the carboxy indolenine.

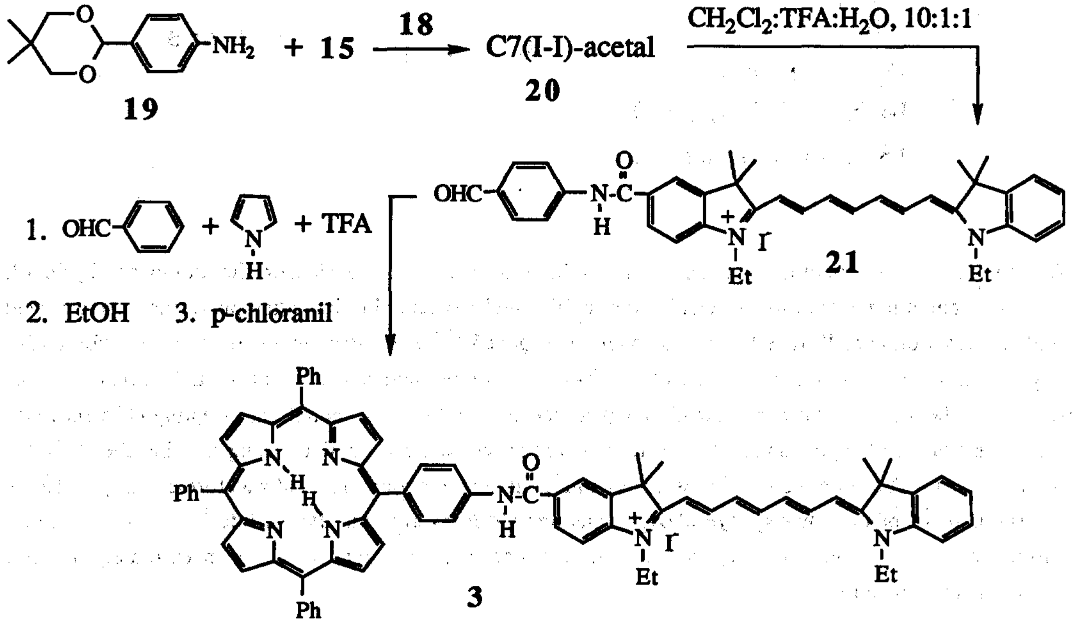
This approach gave good yields of the C3 asymmetric dyes (**13**, **14**), but their purification by column chromatography posed severe problems. Losses of up to 50% of total dye due to irreversible adsorption and band tailing with little separation were common on reverse phase HPLC (C8, aqueous acetonitrile or tetrahydrofuran). Silica gel chromatography (methylene chloride/methanol) gave reasonable separations with much less irreversible binding. The synthesis of the C7 dye (**15**) was performed analogously with facile reaction occurring at room temperature under base catalysis. The chromatographic separations were easier for the C7 dye and gave greater isolated yields. The C3 and C7 dyes have high solubilities in solvents such as dichloromethane (>0.01 M), acetone, and methanol.



We required a facile method for coupling the carboxy dyes **13**, **14**, and **15** with the amino-porphyrin **17**. Though aromatic amides are formed readily from aniline and the acid chloride, attempts to form the dye acid chloride for reaction with **17** failed. The phosphorous reagent **18**[13] was compatible with the dyes, afforded 50-75% yields in the reaction of the C7 dye with p-substituted anilines, and gave straightforward chromatographic separations. The amino-porphyrin generally coupled poorly with the dyes, though the coupling efficiency was much greater for the C7 dye than for the C3 dyes. No improvement was obtained using the zinc chelate of the amino-porphyrin. The coupling reaction was very mild, but the poor coupling yield was further complicated by the rearrangement of the carboxy dye-phosphorous anhydride to give the dye-anilide.[14] With the amino-porphyrin the yields of porphyrin-dye and dye-anilide were roughly equal, resulting in extremely difficult chromatographic separations.

Given the difficulties in chromatography and low yield of porphyrin-dye coupling, we sought *a direct synthetic pathway of condensing a prefunctionalized dye-carboxaldehyde* with pyrrole and benzaldehyde.[15] Omission experiments showed that C7(I-I) was stable to 0.02 M trifluoroacetic acid in dichloromethane, but that it reacted immediately with DDQ (0.01 M) in the presence or absence of acid. The dye also reacted with TCQ (p-chloranil) in the presence of acid, but was stable to TCQ in the absence of acid. The addition of ethanol (10% v/v) prior to adding TCQ buffered the acid, giving porphyrinogen oxidation conditions to which the dye was stable. These reaction conditions are readily explained by considering the electrochemical potentials of the dye and the quinone species. The one electron reduction potential of DDQ is +0.51 V while that of TCQ is +0.01 V (in acetonitrile vs saturated calomel electrode).[16] The oxidation potential of C7(I-I) is +0.46 V,[17] therefore the overall potentials for oxidation of the dye are +0.05 V for DDQ and -0.45 V for TCQ. In neutral solution DDQ is sufficiently potent to oxidize C7(I-I) but TCQ is not. In the presence of acid, however, both quinones will oxidize the dye, which is not unexpected since the quinone oxidant strength increases with increasing acid concentration.

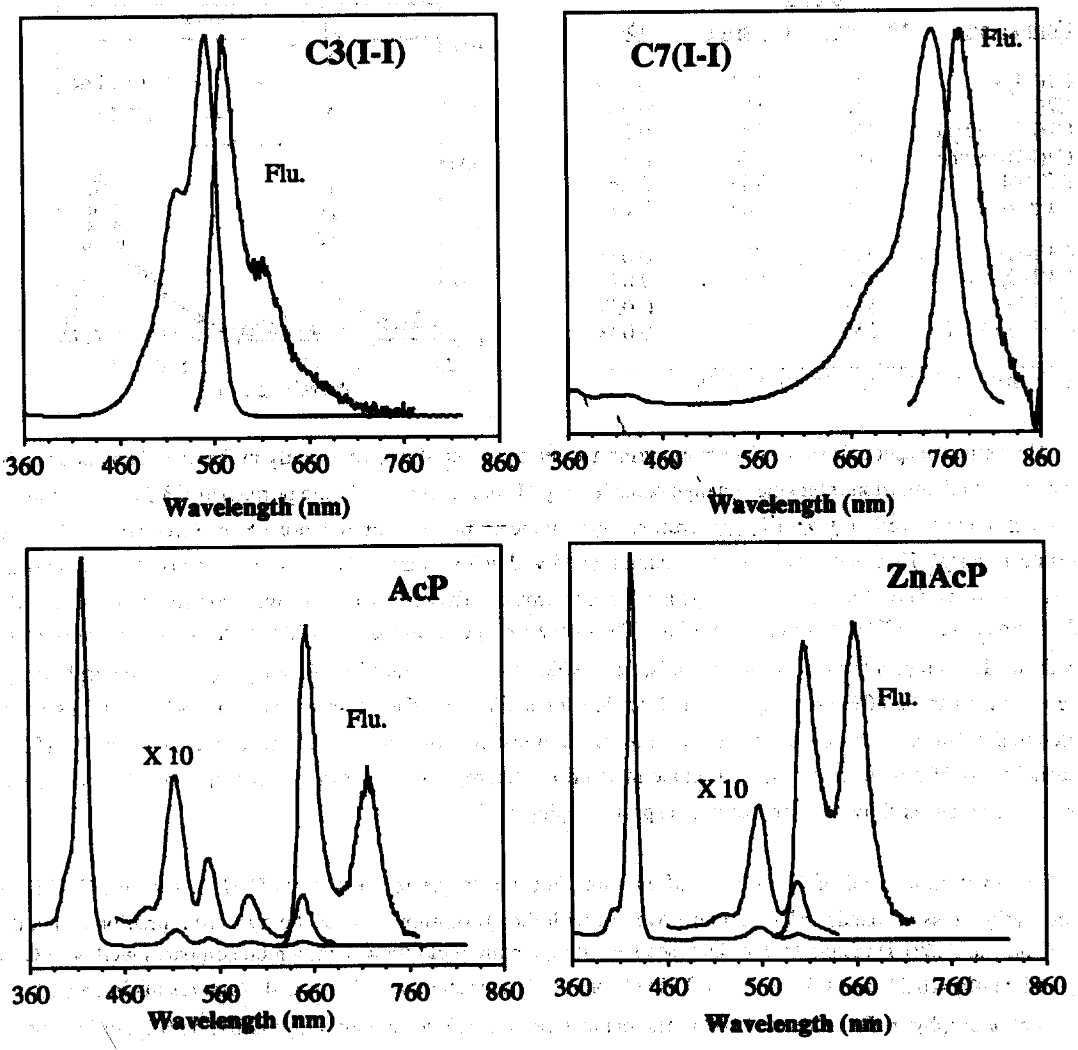
The aminoacetal **19** provided a convenient bifunctional building block for incorporating the dye with the porphyrin, and the amide coupling reaction proceeded in 58% yield to give the C7(I-I)-acetal **20**. The hybrid porphyrin condensation was performed by condensation of C7(I-I)-carboxaldehyde **21** at room temperature for 1h. The acidic solution was then neutralized by addition of ethanol, followed by addition of p-chloranil to initiate the oxidation process. The polarity imparted by the dye resulted in facile purification by chromatography, giving an overall yield of 12% based on pyrrole. Though the overall yield was higher via the amino-porphyrin carboxy-dye coupling route, the direct condensation of the prefunctionalized dye-carboxaldehyde was superior because of the simpler chromatographic purification.



Direct condensation of prefunctionalized dye-carboxaldehyde

Photochemical Results: The photochemical characterization of these compounds was performed in n-butyronitrile ($\varepsilon = 20$) to ensure dissociation of the dye and counterion. The absorption and emission spectra of the individual dyes and porphyrins (free base and zinc) are shown in Figure 2. The porphyrin absorption spectrum consists of the intense Soret band in the 420 nm region and the weaker visible bands (shown multiplied by 10). The Soret and visible bands derive from the S2-S0 and S1-S0 transitions, respectively. Illumination of the Soret band is followed by rapid relaxation to the S1 level, from which photochemistry and fluorescence emission occur. The dyes show a strong absorption band and a partially-overlapping emission band. The C3(I-O) absorption and emission spectra (not shown) mirror those of C3(I-I) but are translated 40 nm to shorter wavelength (Table 1).

Figure 2. Absorption and Emission Spectra (arbitrary intensities).



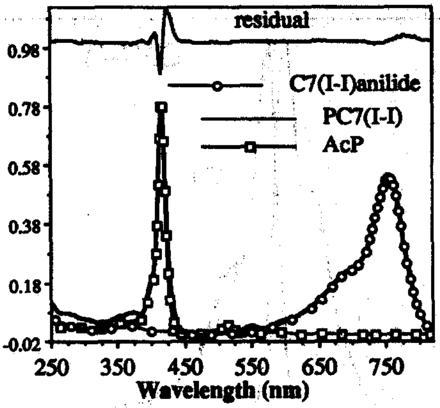
The absorption spectra of the porphyrin-dyes are nearly but not entirely the sum of the spectra of the component parts. The only noticeable change with dye attachment is a slight broadening of the porphyrin Soret band from 13 nm in the acetamidoporphyrin (AcP) to ~16 nm in the free base porphyrin-dyes. The slight (8 nm) wavelength shift in dye absorption in going from C7(I-I) to PC7(I-I), for example, is attributable entirely to the presence of the anilide substituent (Table 1). The spectrum of PC7(I-I) is matched well with the composite spectra of the AcP and the C7(I-I)-anilide, as shown by the small residual obtained by subtracting the dye and porphyrin spectra from the porphyrin-dye spectrum (Figure 3). The effects of substituents are quite weak in the C3 dyes (Table 1). Thus close absorption spectral matching is seen of component parts with each free base and zinc porphyrin-dye.

Table 1. Dye Substituent Effects (in PrCN).

Compound	λ max Absorption	λ max Emission	Φf
C7(I-I)[a]	740	771	0.28[b]
C7(I-I)	748	777	0.35
C7(I-I)-CO_2H	750	783	0.27
C7(I-I)-anilide	755	786	0.31
PC7(I-I)	756	785	0.26
ZnPC7(I-I)	756	787	0.07
C3(I-O)	512	534	0.046
C3(I-O)-CO_2H	513	537	0.046
C3(I-I)	553	571	0.057
C3(I-I)-CO_2H	555	572	0.048

a) In methanol. See ref. 18. b) Ref. 19.

Figure 3. Absorption spectrum of PC7(I-I).



The emission spectral bands of the porphyrins and the dyes also shift only slightly in the linked compounds, but the integrated emission intensities change considerably (Tables 2 and 3). In the porphyrin-C3 dyes the emission band of the dye overlaps the visible absorption bands of the porphyrin. Illumination of the Soret band in PC3(I-O) results in porphyrin fluorescence with a quantum yield within 15% that of AcP. Illumination of the dye (490 nm) results in weak fluorescence from the dye and strong porphyrin fluorescence. The dye fluorescence is quenched to 0.05 times that of C3(I-O) alone in solution. The excitation spectrum (λ_{em} = 720 nm) shows a very close match with the dye and porphyrin absorption bands, from which the energy transfer efficiency from dye to porphyrin can be estimated to be 80% (see experimental section for methods). The closely-related PC3(I-I) exhibits nearly identical features. The porphyrin shows normal fluorescence but the dye fluorescence yield in PC3(I-I) is quenched to 0.07 times that of C3(I-I) alone in solution. Energy transfer from dye to porphyrin also occurs with 80% efficiency, as shown by the excitation spectrum (Figure 4).

The absorption band of C7(I-I) is shifted about 200 nm to the red of that of C3(I-I), and in PC7(I-I) the porphyrin emission bands (650, 720 nm) overlap with the absorption band of the dye. Illumination of the dye (700 nm) in PC7(I-I) results in dye fluorescence with quantum yield Φ_f = 0.26, which compares well with C7(I-I)-anilide (Φ_f = 0.31) and C7(I-I) (Φ_f = 0.35) (Table 1). Illumination of PC7(I-I) at 417 nm results in only a small amount of porphyrin fluorescence (0.09 times that of AcP) and a large amount of dye emission (Figure 5). The excitation spectrum (370-596 nm) shows a close match with the absorption spectrum, from which the efficiency of energy transfer from porphyrin to dye is estimated to be 80%.

Figure 4. Energy transfer from dye to porphyrin.

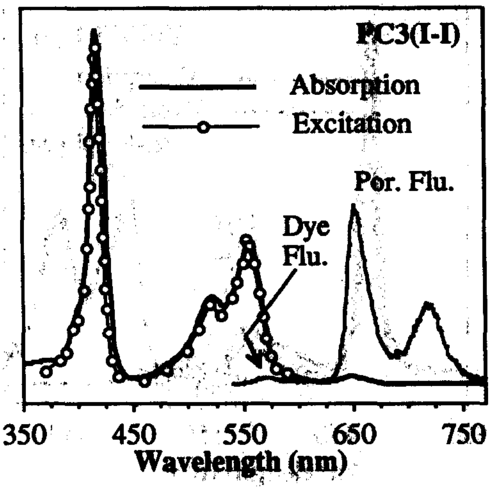
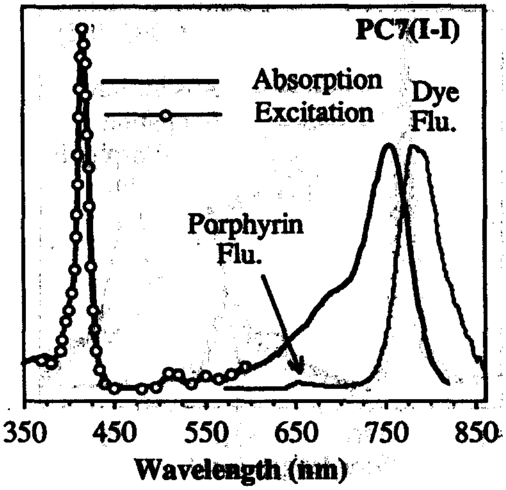


Figure 5. Energy transfer from porphyrin to dye.



The zinc-porphyrin-dyes were studied in a similar manner (Table 3). Illumination of the Soret band (424 nm) in ZnPC3(I-I) gave porphyrin fluorescence, but the yield was reduced to 0.14 times that of ZnAcP. Illumination of the dye (520 nm) resulted in both dye and porphyrin fluorescence, with the dye fluorescence intensity reduced to 0.07 times that of C3(I-I) (Figure 6). The emission spectrum upon illumination of the dye was shown by deconvolution to consist of 80-85% dye emission and 15-20% porphyrin emission, with total dye plus porphyrin emission equal to only 0.08 times that of C3(I-I) alone. Though the excitation spectrum (λ_{em} 660 nm) at first glance would appear to indicate ~70% energy transfer, two complications arise. First, the fluorescence quantum yields are approximately equal for the porphyrin (0.045 x 0.14) and the dye (0.057 x 0.07) in ZnPC3(I-I), and second, the dye emission band tails into the 660 nm region (Figure 2). Control experiments with C3(I-I) showed that over one-third of the emission detected from the excitation scan through the dye absorption band in ZnPC3(I-I) could be accounted for by the residual emission occurring directly from the dye in ZnPC3(I-I). Based on the 5-6:1 ratio of dye to porphyrin emission following excitation of the dye, we estimate the yield of energy transfer to be ~10%. It must be emphasized that the use of excitation spectroscopy to quantitate energy transfer in a system where the acceptor is highly quenched, as in ZnPC3(I-I), is fraught with pitfalls.

In ZnPC3(I-O) illumination of the Soret band gave porphyrin fluorescence with intensity 0.56 times that of ZnAcP. Illumination of the dye (490 nm) resulted in dye fluorescence with intensity 0.02 times that of C3(I-O), as well as porphyrin fluorescence, with the total emission from dye plus porphyrin equal to 0.21 times that of C3(I-O) alone (Figure 7). In ZnPC3(I-O) the dye emission band was well-separated from the porphyrin emission bands, and comparison of the excitation and absorption spectrum of ZnPC3(I-O) showed the efficiency of energy transfer to be 50%. Though the ratio of dye to porphyrin emission is ~1:16, the yield of energy transfer (50%) is still less than the extent of dye quenching (98%). In ZnPC3(I-O) the decreased porphyrin fluorescence does not result from selective B-state quenching, since identical porphyrin emission intensities were observed upon illumination of ZnPC3(I-O) at 424 nm (B-state) and 598 nm (Q-state).

Figure 6. ZnPC3(I-I).

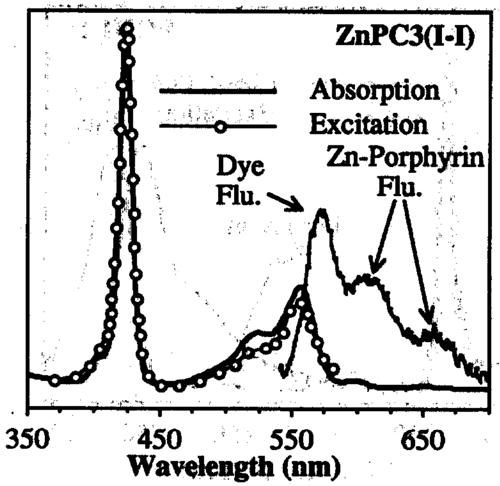


Figure 7. ZnPC3(I-O).

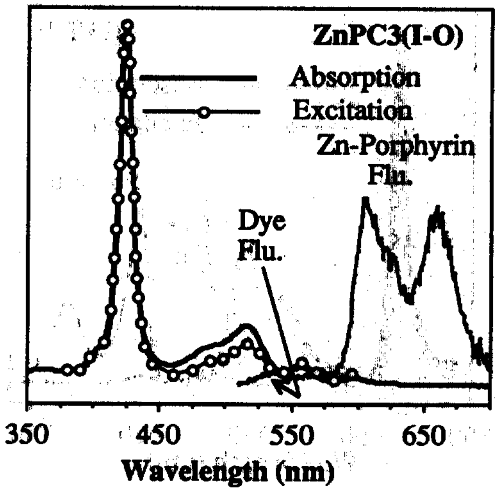
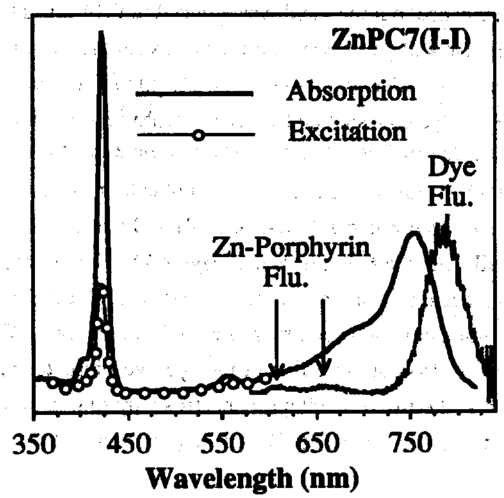


Figure 8. ZnPC7(I-I).



The unusual quenching of the acceptor and only partial energy transfer observed in the porphyrin-C3 dyes also occurred with ZnPC7(I-I). Illumination of the dye in ZnPC7(I-I) resulted in the characteristic dye fluorescence spectrum but the intensity was decreased to 0.2 times that of C7(I-I). Illumination of the zinc porphyrin gave porphyrin fluorescence with intensity 0.05 times that of ZnAcP, as well as a small amount of dye fluorescence. The excitation spectrum showed the efficiency of energy transfer in ZnPC7(I-I) was only ~20-30% (Figure 8). The extent of dye quenching in ZnPC7(I-I) was nearly identical to that of CuPC7(I-I). These results were obtained with a freshly prepared solution of ZnPC7(I-I). The photochemical stability of C7(I-I) as a laser dye has been reported to be quite high,[9,20] but we found that the C7 compounds slowly degenerated in dilute solution, with the least stability shown by ZnPC7(I-I).[21]

In summary, in the free base porphyrin-dyes the extent of donor quenching matched the extent of energy transfer as measured by comparison of the absorption and excitation spectra. In the zinc-porphyrin-dyes, the extent of donor quenching was greater than the yield of energy transfer, and most unexpectedly, the acceptor fluorescence was quenched by 2-7 fold (Table 3). This can be contrasted with the free base porphyrin dyes, where the acceptor (the porphyrin in the PC3 compounds, the dye in PC7(I-I)) exhibited fluorescence properties that were relatively insensitive to the presence of the donor. The energy transfer efficiencies in the zinc-porphyrin-dyes are low, and the net photochemical efficiencies are further decreased after taking into account the quenching of the acceptor.

Table 2. Fluorescence Quantum Yields (in PrCN).

Compound	Φf	Reference	Φf
AcP	0.12	TPP[a]	0.10 (ref. 22)
ZnAcP	0.045	ZnTPP[a]	0.04 (ref. 22)
C3(I-O)	0.046	Rh 6G[b]	0.95 (ref. 23)
C3(I-I)	0.057	Rh 6G[b]	0.95 (ref. 23)
C7(I-I)	0.35	C7(I-I)[c]	0.28 (ref. 19)

a) In toluene or PrCN. b) In EtOH. c) In MeOH.

Table 3. Energy Transfer Properties of Porphyrin-Dyes.

	Relative Φf[a]		
Compound	Donor[b]	Acceptor[b]	% Energy Transfer
PC3(I-O)	0.05	1.14	80
PC3(I-I)	0.07	0.90	80
PC7(I-I)	0.09	0.75	80
ZnPC3(I-O)	0.02	0.56	50
ZnPC3(I-I)	0.07	0.14	10
ZnPC7(I-I)	0.05	0.20	25

a) Yields are relative to unity for each of C3(I-O), C3(I-I), C7(I-I), AcP, and ZnAcP. See Table 2 for conversion to absolute quantum yields. b) The C3 dyes are donors; the C7 dye is an acceptor. The porphyrins are acceptors with C3 dyes and donors with the C7 dye.

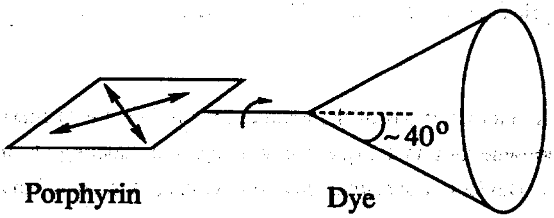
Discussion: Two possible interpretations of the photochemical data are 1) energy transfer proceeds via the Forster mechanism and the non-energy transfer quenching is due to competing electron transfer reactions, or 2) energy transfer proceeds via the Dexter mechanism of electron exchange and recombination of radical intermediates leads to quenching. This discussion focusses on mechanisms of energy transfer and the feasibility of electron transfer in the porphyrin-cyanine dyes.

In the Forster theory of energy transfer the rate of transfer is $k = 8.8 \times 10^{23}\kappa^2\Phi_f J n^{-4}\tau^{-1}R^{-6}$, where κ^2 is the orientation factor, Φ_f is the fluorescence quantum yield of the donor in the absence of the acceptor (Table 2), J is the spectral overlap term (Table 4), n is the solvent refractive index (n = 1.382 for butyronitrile), τ is the donor fluorescence lifetime, and R is the donor-acceptor center-to-center distance of separation in A.[24] The values of $\varepsilon_{\lambda max}$ (in $M^{-1}cm^{-1}$) used in calculating the spectral overlap term are 4×10^5 (AcP), 2×10^5 (C7(I-I)) and 5×10^5 (ZnAcP). κ^2 is a measure of the relative orientation of the donor-acceptor transition dipoles; it ranges from 0 (perpendicular) to 4 (colinear) and has a value of 2/3 for randomly-oriented chromophores. The porphyrin-C3 and porphyrin-C7 compounds have center-to-center distances (R) of ~19 and 21A, respectively, based on Corey-Pauling-Koltun models.

We make several assumptions. First, the relative orientation of the dye and porphyrin is not known, but molecular models show that rotation at the phenyl-amine or dye-carbonyl linkages enables the dye to sweep out the surface of a cone with a half-angle of ~40° with respect to the cone axis (defined by the porphyrin *meso*-position and the p-amino phenyl group) (Figure 9). We assume the conformationally-averaged 'dynamic limit' where each and every donor-acceptor pair samples all orientations by pivoting at the spacer unit.[25] Second, in some cases a single substituent conjugated with the porphyrin ring can rotate the polarization of the transition moment, but we ignore any perturbation due to the p-amide substituent.[26] Third, a correction in expected rate is necessary when the donor-acceptor distance is comparable to the size of the donor-acceptor π-systems. For chlorophyll-chlorophyll energy transfer at 20 A separation the rate modification can reach ± 30% depending on orientation, but we neglect any corrections to the point-dipole approximation.[27]

The value of the orientation factor κ^2 can be calculated using the above assumptions. The transition dipole of the dye lies along its longitudinal axis. In free base tetraphenylporphyrin the x and y transition dipole moments are polarized along the N-N axes (45° with respect to the cone axis, as shown in Figure 9).[28] The Q_x state is of lowest energy and is considered a single-dipole oscillator. As the dye sweeps out the cone surface κ^2 takes on values from 0.40 to 2.37, and in the dynamic limit each porphyrin-dye has an average κ^2 value of 1.28. In zinc tetraphenylporphyrin the Q_x and Q_y states are degenerate. This gives a planar oscillator, which can be treated as a combination of two linear orthogonal in-plane oscillators.[28] In the dynamic limit the κ^2 value for each zinc porphyrin-dye is also 1.28. (The participation of two oscillators in the energy transfer process in the zinc porphyrin is cancelled by their equal contribution to the fluorescence quantum yield.)

Figure 9. Structural model for Forster calculations.



These values were used to calculate R_o (the interchromophore distance at which energy transfer is 50% efficient), where Ro (in A) is defined by $(R_o)^6 = 8.8 \times 10^{23} \kappa^2 \Phi_f n^{-4} J$, and the expected transfer efficiency, T, where $T = (R_o/R)^6/[1 + (R_o/R)^6]$.[29]

Table 4. Forster Energy Transfer Calculations.

Donor	Acceptor	I (cm^{6}mmol^{-1})	Ro (A)	Expected Efficiency (T)	Observed Efficiency (Table 3)
C3(I-O)	AcP	5.5×10^{-14}	30	94%	80
C3(I-I)	AcP	3.7×10^{-14}	29	93%	80
AcP	C7(I-I)	2.1×10^{-12}	65	>99%	80
C3(I-O)	ZnAcP	6.9×10^{-14}	31	95%	50
C3(I-I)	ZnAcP	7.6×10^{-14}	33	96%	10
ZnAcP	C7(I-I)	8.9×10^{-13}	48	99%	25

The observed energy transfer efficiencies fall within the range expected by Forster theory (Table 4). It is interesting that C3(I-O) and C3(I-I) have very similar spectral overlap with AcP (J differs by < 1.5). The dyes have peak emission bands at 535 and 570 nm, respectively, but the four visible bands of AcP are spread over a range of 150 nm and thus overlap well with the emission bands of both dyes (Figure 2). The overlap term is ~50 times larger for the transfer from porphyrin to C7 dye, partly due to the greater extinction coefficient of the acceptor C7(I-I). The zinc-porphyrin-dyes have predicted transfer efficiencies in the same range as the corresponding free base compounds, but other quenching modes must be operative.

Electron transfer is one quenching mechanism that in principle can compete with energy transfer. For electron transfer to be a viable quenching mechanism, it must be both thermodynamically feasible and kinetically competitive. Porphyrins participate in a rich variety of electron transfer reactions,[22,30] and cyanine dyes function as sensitizers in the silver halide photographic process by a mechanism of photoinduced electron transfer from the dye.[11,31] Unfortunately very little fundamental research has been published concerning electron transfer reactions of cyanine dyes, at least compared with the extensive literature of the porphyrins. The cyanine dyes can be oxidized electrochemically[17,32] and the dye excited state can be quenched with electron acceptors.[33] We showed by Stern-Volmer analysis that the fluorescence quenching of C7(I-I) by benzoquinone in either butyronitrile or N,N-dimethylacetamide at room temperature occurs with rate constant of ~2×10^{10} M^{-1}s^{-1} (assuming $\tau = 1$ ns[34]). Tetraphenylporphyrin (TPP) and its zinc chelate (ZnTPP) react with benzoquinone with similar rate constants.[22] The fluorescence quenching experiment is consistent with a diffusion-controlled electron transfer reaction from the excited state of C7(I-I), in analogy with the reactivity pattern of the porphyrins.[22]

The feasibility of photoinduced electron transfer among the porphyrins and dyes can be assessed using the formula $\Delta E = E(h\nu) - E(D^+) + E(A^-)$ and the appropriate energy values obtained from model compounds (Figure 10). This expression must be used with caution.[35] In ZnPC3(I-I) the dye HOMO lies at over 0.23 V lower energy than the HOMO of the zinc-porphyrin. Upon excitation the half-occupied HOMO of the dye can oxidize the porphyrin ($\Delta E = +0.44$ V) which could explain the non-energy transfer quenching of the dye fluorescence.

Similarly, the excited porphyrin can reduce the dye ($\Delta E = +0.27$ V). Both electron transfer processes are more exothermic with the zinc than with the free base porphyrin ($\Delta E = +0.24$ V and -0.11 V, respectively). A comparison between C3(I-I) and C3(I-O) cannot be made because the electrochemical potentials of the latter were not found. However it is intriguing that of the two ZnPC3 compounds, ZnPC3(I-I) shows both the higher degree of acceptor quenching and the lower yield of energy transfer. In the porphyrin-C7 compounds the dye HOMO and LUMO are sandwiched between the HOMO and LUMO of the porphyrin. In ZnPC7(I-I) the excited porphyrin can either reduce ($\Delta E = +0.67$ V) or oxidize ($\Delta E = +0.31$ V) the dye, and in PC7(I-I) the same redox reactions have $\Delta E = +0.29$ and $+0.38$ V, respectively. In neither porphyrin-C7 compound, however, does this thermodynamic analysis provide a clear means for electron transfer mediated quenching of the excited C7-dye by the porphyrin.

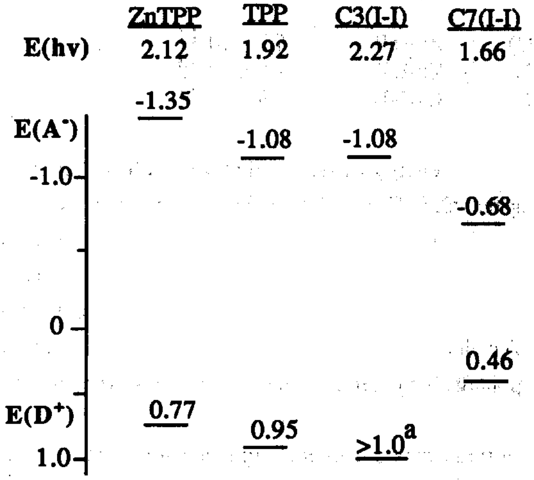


Figure 10. The electrochemical potentials are used to approximate the HOMO and LUMO energy levels.[35] The porphyrin electrochemical potentials are versus the saturated calomel electrode.[22] The cyanine dye potentials[17] were corrected by 20 mV from the Ag/AgCl electrode to the SCE standard. a) A value of 1.0 V is used for $E(D^+)$ of C3(I-I) in the calculations.

The kinetics of electron transfer are difficult to predict. A structurally-related porphyrin-quinone separated by a single phenyl group undergoes electron transfer quenching with quantum yield 0.98 (free base) and 0.965 (zinc).[36] Using $k_1/k_2 = \exp[-\alpha(d_1-d_2)]$ with α equal to 1.0 A^{-1}, d defined as the edge-to-edge distance (6.5 A in the porphyrin-dye, 4 A in the porphyrin-quinone), and porphyrin singlet state lifetimes of 10 (free base) and 2 (zinc) ns, the expected quantum yields at 6.5 A would be 71% and 77%, respectively.[22,30] Though electron transfer to benzoquinone may represent a best-case scenario, this kinetic analysis indicates electron transfer can compete with energy transfer at 6.5 A if the acceptor can play the dual role of a Forster energy transfer acceptor as well as an electron acceptor.

An alternative mechanism for energy transfer is the Dexter mechanism of electron exchange.[37] The rate of transfer is $k = k_0\exp(-2R/L)J'$, where R is the donor-acceptor edge-to-edge distance of separation, L is an effective average Bohr radius, and J' is the spectral overlap term. Some major differences from Forster theory are that a) the distance dependence falls off exponentially rather than as the inverse sixth power, b) the donor fluorescence quantum yield is not a factor, and c) the spectral overlap term J' is normalized with respect to the acceptor absorption intensity. Electron exchange can occur in either a concerted process or via stepwise electron transfer reactions involving radical intermediates (D^+A^- or D^-A^+). Recombination of the radicals to give the ground state rather than the excited state is one mechanism for quenching the electron exchange energy transfer process.[38,39]

Electron exchange energy transfer and electron transfer are both dependent on orbital overlap. Electron exchange involves both the LUMO's and the HOMO's of the donor and acceptor, while electron transfer involves only the donor-acceptor LUMO's. The participation of two pairs versus one pair of orbitals leads to a correspondence between the rate expressions for electron exchange energy transfer and electron transfer.[40] Both electron transfer and electron exchange are very sensitive to the distance parameters (α, L), but our lack of knowledge of orbital interactions at long distances renders calculation difficult. However, rapid energy transfer via electron exchange has been observed in bichromophoric model compounds having a donor-acceptor distance of separation of 5-10 A.[40]

The thermodynamic constraints of electron exchange are not well-developed experimentally. If neither electron transfer step can occur to an orbital at a higher energy level, then the HOMO and LUMO of the acceptor must either be isoenergetic with or sandwiched between the levels of the HOMO and LUMO of the donor. In this view electron exchange energy transfer from excited C3(I-I) to ZnTPP is precluded on thermodynamic grounds, for example, but transfer from ZnTPP to C7(I-I) is allowed (Figure 10). The presence of only one accessible orbital results in the electron transfer quenching processes described previously. This simple concept can be tested through the synthesis of a family of porphyrin-dyes with similar spectral overlap (J') but where the redox levels of the dyes are systematically varied.

Few covalently-linked porphyrin model compounds have been prepared that undergo energy transfer. One compound contains anthracene (λ_{abs} 256 nm) and a porphyrin with an intervening conjugated polyene chain. A broadened absorption spectrum is observed and illumination of anthracene results in both anthracene and porphyrin-like emission.[3] A more closely-related group of compounds are the carotenoid-porphyrins.[4] Energy transfer from carotenoid to porphyrin has been observed in yields of up to 80%. The carotenoids have very low fluorescence quantum yields ($\Phi_f \leq 10^{-3}$), and the energy transfer efficiency depends critically on the relative orientation of the donor (carotenoid) and the acceptor (porphyrin). It is noteworthy that in some carotenoid-porphyrin systems the porphyrin fluorescence was quenched by 75% by the polyene group.[4]

Summary and Future Directions: The free base porphyrin dyes show high yields of energy transfer and the direction of energy transfer, from dye-to-porphyrin or from porphyrin-to-dye, can be selected based on the choice of dye. Thus the porphyrin can function as either an energy donor or an energy acceptor. In photosynthesis a reaction center chlorophyll is the terminal acceptor of the photonic energy from the antenna complexes. Energy transfer from a cyanine dye to a porphyrin mimics in a primitive fashion the antenna function of the phycobilisome. Energy transfer from a porphyrin to a cyanine dye illustrates the photochemical versatility of this family of compounds. Efficient energy transfer occurs despite the fact that in each case the donor has a low fluorescence quantum yield (< 12%). Furthermore, the free base porphyrin functions well as an acceptor in spite of its weak extinction coefficients in the visible region. Energy transfer is the predominant pathway for depopulating the donor excited state in the free base porphyrin-cyanine dyes. In the zinc chelates electron transfer may partially account for the discrepancy between the high amount of donor quenching and the low yield of energy transfer. Experiments using transient spectroscopy are required to elucidate the contribution of electron transfer reactions to the observed results. The energy transfer efficiencies for both the free base and zinc compounds fall within the range expected for Forster theory, but these data are insufficient to discriminate between mechanisms of dipole-dipole coupling and electron exchange. The synthesis and characterization of porphyrin-dyes in other 3-dimensional geometries, with larger interchromophore distances, and with varying redox potentials will establish further groundwork for preparing multichromophore systems for visible light-harvesting.

Experimental:

General. Methylene chloride, chloroform, pyrrole, and triethylamine were distilled from calcium hydride. Trifluoroacetic acid, acetic anhydride, and pyridine were distilled and used within two weeks. Benzaldehyde was distilled under reduced pressure and stored at 0°C. Butyronitrile was distilled from P_2O_5. Other commercial reagents were used as received.

^{1}H NMR spectra were obtained at 300 MHz (IBM FT-300) in deuteriochloroform. IR spectra were recorded on a Nicolet 5DXB spectrometer. UV-vis absorption spectra were obtained on either an HP 8451A photodiode array spectrometer or an IBM 9430 scanning spectrophotometer and, unless otherwise noted, were taken in butyronitrile. Routine fluorescence analysis was performed with a Gilford Fluoro IV spectrofluorometer. Mass spectral analyses were obtained by ^{252}Cf fission fragment mass spectrometry. Melting points are uncorrected. Chromatographic separations were performed with a Harrison Research Chromatotron Model 7924T or by gravity elution silica gel (Si 60, 70-230 or 230-400 mesh) column chromatography.

The identity of the counterion in each isolated dye is not known. For yield calculations we have assumed the counterion is I^-. Because of its high mass this should provide a conservative estimate of the actual dye yield. The ^{1}H NMR signals in the aromatic and olefinic regions of the porphyrin-dyes were heavily overlapped, causing difficulty in assignment. The aliphatic signals and the N-H peak in the amide linked dyes could be assigned, though integration was complicated in some cases due to broad overlapping signals. Definitive proof of structure was based on absorption spectroscopy and ^{252}Cf fission fragment mass spectrometry. The latter gave intense parent ion peaks (M- counterion) for the dyes and the porphyrin-dyes. The zinc chelates of porphyrins and porphyrin-dyes were prepared at room temperature.[22]

1-ethyl-2,3,3-trimethyl-5-carboxy-3-H-indolium iodide (7). Modified versions of procedures developed by Southwick and Grzywinski were used for the preparation of 7 from p-hydrazinobenzoic acid.[41] 1.55 g of p-hydrazinobenzoic acid and 3 mL 3-methyl-2-butanone were refluxed in 15 mL 95% ethanol for 30 min to give the hydrazone upon cooling (1.97 g, 94%). mp 191-193°C; Abs (CH_2Cl_2:EtOH, 3:1) 314 nm. Subsequent reaction in 15 mL refluxing glacial acetic acid under N_2 for 3.5 h followed by removal of solvent gave a red oil which crystallized on cooling from 8 mL ethyl acetate/petroleum ether (3:1), giving 2,3,3-trimethyl-5-carboxy-3-H-indole in 71% yield. mp 210-212°C; ^{1}H NMR δ 1.30 (s, 6H, $C(CH_3)_2$), 2.30 (s, 3H, CH_3), 7.58 (d, J = 8 Hz, 1H, Ar-H [7]), 7.99 (d, J = 2 Hz, 1H, Ar-H[4]), 8.07 (dd, J = 8, 2 Hz, 1H, Ar-H[6]); IR (KBr) 1685 (s, sh, C=O); Abs (CH_2Cl_2:EtOH, 3:1) 274 nm. Reaction of the 3-H indole (1.3 g, 6.4 mmol) with ethyl iodide (2 mL, 25 mmol) in refluxing acetonitrile (15 mL) for 20 h proceeded with difficulty, giving 736 mg of 7 (32%) as a stable, crystalline, non-hygroscopic solid upon precipitation with ether. The starting 3-H indole was recovered in 40% yield from the mother liquor. mp 233-234°C (dec); ^{1}H NMR δ 1.64 (t, J = 8 Hz, 3H,

$CH_2\underline{CH}_3$), 1.69 (s, 6H, $C(CH_3)_2$), 3.15 (s, 3H, CH_3), 4.77 (q, J = 8 Hz, 2H, $\underline{CH}_2CH_3$)7.77 (d, J = 8 Hz, 1H, Ar-H[7]), 8.26 (d, J = 2 Hz, 1H, Ar-H[4]), 8.31 (dd, J = 8, 2 Hz, 1H, Ar-H[6]); IR (KBr) 1725 cm^{-1} (s, sh, C=O); Abs (CH_2Cl_2:EtOH, 3:1) 232, 330 nm. The similar reaction of 1.14 mL phenylhydrazine and 1 mL 3-methyl-2-butanone afforded 1.12 g of 2,3,3-trimethyl-3-H-indole as a clear liquid after distillation (75°C, 3 mm Hg). Alkylation of 0.5 g 2,3,3-trimethyl-3-H-indole with 1 mL ethyl iodide in 2 mL CH_3CN gave 0.965 g (97%) of **12** as a white granular solid.

3,1'-Diethyl-3,3'-dimethyl-5'-carboxy-indoxacarbocyanine iodide (13). Samples of **7** (100 mg, 0.279 mmol, 1 equiv) and **8a** (54.3 mg, 0.35 mmol, 1.25 equiv) were added to a 15 mL round-bottom flask containing 2 mL acetic anhydride, 1 mL glacial acetic acid and sodium acetate (110 mg, 1.3 mmol). The solution was refluxed under N_2 for 1.5 h. By absorption spectroscopy **7** had been consumed (λ_{max} = 330 nm) and the symmetric dicarboxylic acid dye was present in ~4% yield (λ_{max} = 518 nm, assuming $\varepsilon = 10^5$ $M^{-1}cm^{-1}$). After cooling to room temperature **11**[42] (121 mg, 0.42 mmol, 1.5 equiv) was added as a solid in one portion. After 1 h under reflux the total dye yield reached 46% (assuming $\varepsilon = 10^5$ $M^{-1}cm^{-1}$ for all three dyes) then the volatile components were removed (2.5 mm Hg, 60°C). The viscous orange product was chromatographed (Si 60, 70-230 mesh, 3 x 15 cm, 5-60% gradient of MeOH in $CHCl_3$) affording 38 mg of a metallic green solid (26%). $C_{25}H_{27}N_2O_3I$, 403.2 calcd mass ($M-I^-$), 403.2 obsd; ^1H NMR d 1.47 (t, J = 8 Hz, 3H, $CH_2\underline{CH}_3$), 1.61 (t, J = 8 Hz, 3H, $CH_2\underline{CH}_3$), 1.72 (s, 6H, $C(CH_3)_2$), 4.16 (q, J = 8 Hz, 2H, $C\underline{H}_2CH_3$), 4.56 (q, J = 8 Hz, 2H, $C\underline{H}_2CH_3$), 5.70 (s, br, CH=CH), 6.02 (s, br, CH=CH), 7.01-7.51 (m, 5H, Ar-H), 8.01 (s, 1H, Ar-H), 8.10 (d, J = 8 Hz, Ar-H), 8.44 (t, J = 8 Hz); Abs λ in nm (log ε), 512 (4.97, 54 nm fwhm).

1,1'-Diethyl-3,3,3',3'-tetramethyl-5-carboxyindocarbocyanine iodide (14). Samples of **7** (100 mg, 0.279 mmol, 1 equiv) and **8a** (54 mg, 0.348 mmol, 1.25 equiv) were added to a 15 mL round-bottom flask containing 2 mL acetic anhydride, 1 mL glacial acetic acid, and sodium acetate (100 mg, 1.22 mmol, 4 equiv). The solution was refluxed under N_2 and after 1 h **7** (λ_{max} = 330 nm) had been consumed. The solution was cooled to room temperature and **12** (132 mg, 0.417 mmol, 1.5 equiv) was added as a powder. The mixture was refluxed and after 1.5 h the total dye yield reached ~40% (λ_{max} = 558 nm, assuming $\varepsilon = 10^5$ $M^{-1}cm^{-1}$ for all three dyes). Then the volatile components were removed (1.5 mm Hg, 60°C) and the dark viscous residue was chromatographed (Si 60, 70-230 mesh, 3 x 15 cm, 5-45% gradient of MeOH in $CHCl_3$) giving 55.6 mg (36%) of a metallic green solid. $C_{28}H_{33}N_2O_2I$, 429.3 calcd mass ($M-I^-$), 429.3 obsd; ^1H NMR δ 1.41 (t, 6H, $CH_2\underline{CH}_3$), 1.70 (s, 12H, 1.72, $C(CH_3)_2$), 3.04 (s, br), 4.16-4.38 (m, 4H, $C\underline{H}_2CH_3$), 6.51-6.54 (m, br), 7.01-7.39 (m), 7.98-8.38 (m); Abs λ in nm (log ε), 555 (5.06, 55 nm fwhm).

1,1'-Diethyl-3,3,3',3'-tetramethyl-5-carboxyindotricarbocyanine iodide (15). Samples of **7** (100 mg, 0.279 mmol, 1 equiv) and **8b** (95 mg, 0.351 mmol, 1.25 equiv) were added to a 15 mL round-bottom flask containing 3 mL acetic anhydride and 1 mL pyridine. After stirring at room temperature for 1 h an absorption spectrum showed only a trace of **7** (λ_{max} = 330 nm). A solid sample of **12** (130 mg, 0.42 mmol, 1.5 equiv) was added in one portion, and the red solution turned deep blue within 5 min. After 1 h the total dye yield had leveled off at approximately 81% (λ_{max} = 756 nm, assuming ε = 200,000 $M^{-1}cm^{-1}$).[12] The volatile components were removed (2.0 mm Hg, 75°C) then the dark residue was chromatographed (Si 60 70-230 mesh, 3 x 15 cm, 5-50%

gradient of MeOH in CH_2Cl_2) affording 98 mg (58.1%) of a metallic red solid. $C_{32}H_{37}N_2O_2I$, 481.3 calcd mass (M-I$^-$), 481.5 obsd; ^{1}H NMR δ 1.13-1.41 (m, 6H, $CH_2\underline{CH_3}$), 1.67 (s, 12H, $C(CH_3)_2$, 3.96 (s, br, 2H, $\underline{CH_2}CH_3$), 4.19 (s, br, 2H; $\underline{CH_2}CH_3$), 5.98 (d, J = 8 Hz); 6.4-7.4 (m), 7.5-8.1 (m); IR (KBr) 3500 (br, O-H), 1702 (w, C=O); Abs λ in nm (log ε), 750 (5.31, 64 nm fwhm).

5,10,15-triphenyl-20-(4-acetamidophenyl)porphyrin (16), AcP. A 2 L three neck round-bottom flask was charged with 1 L CH_2Cl_2. Samples of benzaldehyde (760 µL, 7.5 mmol, 7.5 mM), 4-acetamidobenzaldehyde (410 mg, 2.5 mmol, 2.5 mM), and pyrrole (700 µL, 10 mmol, 10 mM) were added and the condensation was initiated by addition of trifluoroacetic acid (1.4 mL, 20 mmol, 20 mM). After stirring at room temperature under N_2 for 1.5 h the oxidation was initiated by addition of p-chloranil (1.85 g, 7.5 mmol) and the mixture was stirred at room temperature for 1 h. The reaction was neutralized with triethylamine (2.8 mL, 20 mmol) and then concentrated to 200 mL by rotary evaporation. Silica gel (15 g, Si 60, 70-230 mesh) was added, the remaining solvent was removed under vacuum, and the resulting dark gray powder was added to the top of a silica column poured with CH_2Cl_2. Elution with CH_2Cl_2 afforded tetraphenylporphyrin, and 20% EtOAc in CH_2Cl_2 gave 520 mg of total porphyrin products. **16** was purified by centrifugal chromatography and recrystallized from 15 mL CH_2Cl_2:MeOH (1:1). 283 mg, 17% yield; ^{1}H NMR δ -2.79 (s, 2H, N-H), 1.50 (s, 3H, CH_3), 7.5-8.22 (m, 19H, Ar-H), 8.84 (m, 8H, β-pyrrole); Abs λ in nm (log ε), 417 (5.54, 13 nm fwhm), 514, 548, 590, 648.

5,10,15-triphenyl-20-(4-aminophenyl)porphyrin (17). 135 mg (0.2 mmol) of the amide **16** was dissolved in 14 mL trifluoroacetic acid. 15 mL conc HCl was then added and the solution was heated at 80°C for 21 h. The mixture was diluted with H_2O and extracted 5 times with CH_2Cl_2 to remove the green porphyrin di-acid. The combined CH_2Cl_2 fractions were washed with H_2O and 10% Na_2CO_3, dried over $MgSO_4$, concentrated and chromatographed (2 mm silica rotor, CH_2Cl_2:MeOH 50:1) to give 98 mg of **17** (77%). In lieu of chromatography the product could be precipitated from 5 mL CH_2Cl_2:MeOH (1:4). ^{1}H NMR δ -2.7 (br s, NH), 4.0 (s, 2H, NH_2), 7.0 (d, J = 10 Hz, 2H), 7.75 (m, 8H), 8.0 (d, J = 10 Hz, 2H), 8.20 (m, 6H), 8.83 (m, 6H, β-pyrrole), 8.93 (d, J = 5 Hz, 2H, β-pyrrole); Abs λ max 418 nm (CH_2Cl_2:EtOH, 3:1).

PC3(I-O) (1). Samples of dye **13** (19 mg, 0.036 mmol, 1 equiv) and triethylamine (15 µL, 0.10 mmol) were added to a 4 mL conical vial containing 200 µL CH_2Cl_2. The mixture was stirred for 5 min at room temperature, then porphyrin **17** (45 mg, 0.072 mmol, 2 equiv) was added as a solution in 1.5 mL CH_2Cl_2 followed by the addition of phenyl N-phenylphosphoramidochloridate **18** (15 mg, 0.056 mmol, 1.5 equiv) as a solid in one portion. The mixture was stirred in the dark for 16 h under N_2. After concentration by rotary evaporation and preliminary chromatography (Si 60, 230-400 mesh, 2.5 x 10 cm, 5% MeOH in CH_2Cl_2), the desired product was isolated by centrifugal chromatography (1 mm silica rotor, 2-35% gradient of MeOH in $CHCl_3$). 2.6 mg (6.3%); $C_{69}H_{56}N_7O_2I$, 1014.5 calcd mass (M-I$^-$), 1015.3 obsd; ^{1}H NMR δ -2.93 (s, 1H, N-H), -2.79 (s, 1H, N-H), 1.40 (t, J = 8 Hz, $CH_2\underline{CH_3}$), 1.89 (s, $C(CH_3)_2$), 3.09 (q, J = 8 Hz, 4H, $\underline{CH_2}CH_3$), 3.6-4.3 (m), 6.5-9.0 (m); Abs λ in nm (log ε), 416 (5.31), 516 (4.83).

PC3(I-I) (2). Synthesis of 2 was performed according to the procedure for 1 starting with 26.1 mg of 14 and 59.0 mg of 17 affording 5.6 mg (11%) of 2. $C_{72}H_{62}N_7OI$, 1040.5 calcd mass $(M\text{-}I^-)$, 1041.4 obsd; ^1H NMR δ −2.77 (s, -NH), 0.8-1.9 (complex multiplets), 4.16-4.26 (m, $C\underline{H}_2CH_3$), 7.0-9.0 (m); IR (KBr) 3500 (br, O-H), 1702 (w, C=O); Abs λ in nm (log ε), 417 (5.45, 16 nm fwhm), 556 (5.14).

PC7(I-I) (3). Synthesis of 3 was performed according to the procedure for 1 starting with 35.3 mg of 15 (0.058 mmol) and 73 mg of 17. After coupling for 1.5 h analysis by TLC ($MeOH:CH_2Cl_2$, 1:4) showed two new dye components and no starting material. The crude reaction mixture was then purified by centrifugal chromatography (1mm silica gel rotor, 5-20% gradient of MeOH in CH_2Cl_2) to give 15 mg (20%) of 3. $C_{76}H_{66}N_7OI$, 1092.5 calcd mass $(M\text{-}I^-)$, 1093.4 obsd; ^1H NMR (600 MHz) δ −2.8 (br s, NH), 1.25-1.8 (complex m), 4.23 (m, J = 5.5 Hz, $C\underline{H}_2CH_3$), 6.05 (br d), 6.2 (br s), 6.5 (br t), 6.6 (br s), 6.95 (d, J = 10.9 Hz), 7.08 (d, J = 10.9 Hz), 7.18 (t, J = 8.2 Hz), 7.25 (d, J = 8.2 Hz), 7.3 (t, J = 8.2 Hz), 7.75 (m), 8.29 (d, J = 10.9 Hz), 8.42 (d, J = 10.9 Hz), 8.54 (br m), 8.82 (d, J = 5.5 Hz, β-pyrrole), 8.85 (s, β-pyrrole), 8.92 (d, J = 5.5 Hz, β-pyrrole), 9.55 (s, NH); Abs λ in nm (log ε), 417 (5.40, 16 nm fwhm), 756 (5.13).

2-(4-aminophenyl)-5,5-dimethyl-1,3-dioxane (19). p-Bromobenzaldehyde (3.7 g, 20 mmol) and potassium phthalimide (3.7 g, 20 mmol) were added to a flask containing 200 mL N,N-dimethylacetamide. CuI (3.81 g, 20 mmol) was added and the mixture was refluxed for 24 h under N_2 and shielded from ambient lighting. After cooling to room temperature, the solution was poured onto 800 g of ice yielding a light-orange precipitate. 80 mL of 10N HCl was added and the mixture was filtered. The precipitate was suspended in CH_2Cl_2 and heated on a steam bath to dissolve p-phthalimidobenzaldehyde (solubility ~4g/100 mL CH_2Cl_2). Filtration gave a filtrate containing p-phthalimidobenzaldehyde[43] (homogeneous by silica TLC, CH_2Cl_2:EtOAc, 1:1). 2.2 g (44%); ^1H NMR (60 MHz) δ 7.5-8.0 (m, 8H), 10.1 (s, 1H).

p-Phthalimidobenzaldehyde (1.5 g, 6 mmol) and 2,2-dimethyl-1,3-propanediol (624 mg, 6 mmol) were added to 60 mL CH_3CN. Upon dissolution, p-toluenesulfonic acid monohydrate (23 mg, 0.12 mmol) was added and then the solvent was removed by distillation until a dry solid residue was obtained. The crude product was recrystallized from CH_3CN to give 1.573 g (78% yield) of the acetal. mp 195-200°C; ^1H NMR δ 0.8 (s, 3H, CH_3), 1.3 (s, 3H, CH_3), 3.6 (d, J = 10 Hz, 2H, CH_2), 3.8 (d, J = 10 Hz, 2H, CH_2), 5.5 (s, 1H, CH), 7.5-8.0 (m, 8H). 12 mL of 0.2 M N_2H_4 in MeOH (2.4 mmol N_2H_4) was added to 396 mg (1.18 mmol) of the phthalimide acetal with stirring at room temperature. The initial bright yellow slurry changed to a pale yellow solution within 5 min. TLC at 1 h (CH_2Cl_2:EtOAc, 20:1) showed a new component (R_f = 0.2) and no remaining phthalimide acetal (R_f = 0.6). The addition of CH_2Cl_2 gave a yellow mixture, which upon filtration through Celite gave a white precipitate (phthalhydrazide) and a yellow filtrate. The filtrate was evaporated to give a yellow solid which was washed with pet ether and collected on a fluted filter. 152 mg (62%); mp 89-93°C; ^1H NMR δ 0.8 (s, 3H, CH_3), 1.3 (s, 3H, CH_3), 3.6 (d, J = 10 Hz, 2H, CH_2), 3.7 (d, J = 10 Hz, 2H, CH_2), 5.3 (s, 1H, CH), 6.6 (d, J = 10 Hz, 2H), 7.3 (d, J = 10 Hz, 2H).

C7(I-I)-acetal (20). 45 mg (0.074 mmol, 1 equiv) of 15 was added to a 1 mL Kontes micro-ware vial. 300 µL of CH_2Cl_2 and 20 µL (0.15 mmol, 2 equiv) of triethylamine were added to give a homogeneous solution. 30 mg (0.15 mmol, 2 equiv) of aminoacetal 19 followed by 22 mg (0.082 mmol) of 18 were then added and the reaction was stirred at room temperature for 2.5 h. TLC (CH_2Cl_2:MeOH, 10:1) showed only a trace of **15** (R_f = 0.1) and a new dye component (R_f = 0.3). The product was chromatographed (Si 60, 230-400 mesh, 15 x 3 cm, 5-10% gradient of MeOH in CH_2Cl_2) giving 35 mg of the acetal which was homogeneous by TLC (58% yield). ^1H NMR δ 0.8 (s, CH_3), 1.35 (s, CH_3), 1.4 (br t, $CH_2\underline{CH_3}$), 1.5 (br t, $CH_2\underline{CH_3}$), 1.7 (s, $C(CH_3)_2$), 3.4 (d, J = 10 Hz, OCH_2), 3.6 (d, J = 10 Hz, OCH_2), 4.0 (br m, $\underline{CH_2}CH_3$), 4.2 (br m, $\underline{CH_2}CH_3$), 5.4 (s, O_2CH), 6.0-7.0 (m), 7.15 (d, J = 10 Hz), 7.25 (m), 7.4 (m), 7.5 (d, J = 10 Hz), 7.75 (m), 7.85 (m), 8.0 (d, J = 10 Hz), 8.1 (s), 8.2 (s), 8.25 (s), 9.0 (s, NH); Abs λ max 756 nm.

Direct condensation to prepare PC7(I-I) (3). Prior to forming the porphyrin, the acetal **20** was hydrolyzed to the aldehyde **21** by dissolving 40 mg (0.05 mmol) of acetal dye (**20**) in 2 mL CH_2Cl_2. Then 200 µL of TFA:H_2O (1:1 by vol) was added and the reaction was stirred at room temperature for 1 h. The solution was taken up in CH_2Cl_2, washed with 5 mL each of saturated $NaHCO_3$ and brine, dried over $MgSO_4$, and evaporated to give 35 mg of dye carboxaldehyde. This was not characterized but was used directly in the porphyrin reaction.

Samples of **21** (35 mg, 0.05 mmol), benzaldehyde (15 µL, 0.15 mmol), and pyrrole (14 µL, 0.2 mmol) were added to 20 mL CH_2Cl_2 under N_2. Trifluoroacetic acid (31 µL, 0.4 mmol) was added and the reaction was stirred for 1 h at room temperature. The solution was then buffered by addition of 2 mL ethanol, then the oxidation was initiated by addition of p-chloranil (37 mg, 0.15 mmol). After 1 h at room temperature the crude reaction was chromatographed (Si 60, 70-230 mesh, 10 x 2 cm), eluting TPP and excess quinone with CH_2Cl_2 followed by dye components with CH_2Cl_2 containing 5-10% MeOH. The desired product was contained in the first five 4-5 mL fractions. Further purification by centrifugal chromatography (1mm silica rotor, 15% MeOH in CH_2Cl_2) gave considerable tailing. Fractions containing the porphyrin-dye were combined and evaporated, affording 8 mg (12%) of **3** which was identical by absorption spectroscopy and TLC with an authentic sample.

C7(I-I)-anilide (22). Aniline (10 µL, 0.100 mmol) and **15** (20 mg, 0.033 mmol) were coupled according to the procedure for **20** to yield 14.3 mg (64%) of **22**. $C_{38}H_{42}N_3OI$, 556.3 calcd mass (M-I^-), 556.3 obsd; ^1H NMR δ 1.35 (t, J = 5 Hz, $CH_2\underline{CH_3}$), 1.45 (t, J = 5 Hz, $CH_2\underline{CH_3}$), 1.7 (pair s, $C(CH_3)_2$), 4.0 (m, J = 5 Hz, $\underline{CH_2}CH_3$), 4.3 (m, J = 5 Hz, $\underline{CH_2}CH_3$), 6.0-6.7 (m), 7.1-7.85 (m), 8.0 (d, J = 10 Hz), 8.2 (d, J = 10 Hz), 8.35 (s), 9.3 (s, NH); Abs λ max 755 nm.

Fluorescence Measurements: Fluorescence yield measurements were performed with a SPEX Fluorolog 212 fluorometer. The instrumental configuration employed a Rhodamine 6G quantum counter for excitation (<600 nm) and a Hamamatsu R928 photomultiplier cooled to -15 C for emission. Both excitation and emission monochromators contained ruled gratings (1200 lines/inch) blazed at 500 nm. Spectra were collected at room temperature using excitation and emission slit widths of 0.5 mm (giving ~1 nm spectral resolution). The data were collected in the single photon counting mode. Peak areas were integrated after correcting for photomultiplier dark current and converting the raw data to the wavenumber scale.

The fluorescence experiments were performed at ~0.25 µM (A ~0.1) for Soret illuminations. Excitation into the Soret region was done reliably in spite of its very narrow absorption band. Fluorescence yields with ≤ 12%

variability were obtained upon Soret and visible illumination for the two pairs of compounds (TPP and AcP, 417 and 512 nm; ZnTPP and ZnAcP, 424 and 558 m). The dyes were generally illuminated into the short wavelength shoulder (C3(I-O), 490 nm; C3(I-I), 520 nm; C7(I-I), 700 nm) so that the entire dye emission trace could be captured. In these cases the concentration was adjusted so that the long-wavelength peak absorption was < 0.1 to avoid the inner filter effect. The only case in all six compounds where overlapping absorption bands presented a problem was in PC3(I-I). The absorption shoulder of the dye (520 nm, ε 69,000 $M^{-1}cm^{-1}$) overlapped with the first visible band of the porphyrin (514 nm, ε 17,000 $M^{-1}cm^{-1}$; ε_{520} ~14,600 $M^{-1}cm^{-1}$). The yield estimates were corrected accordingly.

Estimates of the efficiency of energy transfer are bracketed by 1) comparison of the donor fluorescence yield in the donor-acceptor complex with that of the donor free in solution, and 2) the matching of the donor-acceptor absorption and excitation spectra. The extent of donor quenching provides an upper estimate on the extent of energy transfer, assuming constancy of the rate constants for fluorescence, intersystem crossing, and internal conversion in the free donor and the donor in the donor-acceptor complex. The excitation spectra are used to assess whether energy transfer can account for the full complement of donor quenching. A shortfall between the degree of donor quenching and the excitation spectra-derived yield of energy transfer implies non-energy transfer mode(s) of donor quenching. One difficulty in using excitation spectra was that the instrumentally-corrected excitation spectrum of a simple porphyrin did not precisely mirror the corresponding absorption spectrum. When the corrected excitation spectrum (Spex Fluorolog) of AcP or ZnAcP was overlaid with the corresponding absorption spectrum (HP 8452), a precise match of the Soret bands resulted in the excitation spectrum overshooting the absorption spectrum in the visible region (500-600 nm) by 20-30%. This may be due in part to baseline problems and limitations in instrumental dynamic range. Until more precise measurements are available we have conservatively scaled all the excitation spectra by this correction factor. Thus we interpret the near-perfect absorption-excitation match seen with PC3(I-I), for example (Figure 4), as an energy transfer efficiency of ~80%. This value is in reasonable agreement with the 93% yield of donor quenching. The porphyrin-C7 compounds are analyzed similarly, though the present instrumental configuration employs a rhodamine 6G quantum counter which does not permit excitation scans beyond 600 nm. The spectral overlap terms were computed by numerical integration.

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