

TRANSFER OF EXCITATION ENERGY BETWEEN PORPHYRIN CENTERS OF A COVALENTLY-LINKED DIMER*

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(Received 1 December 1977; accepted 3 February 1978)

Abstract—Three covalently-linked porphyrin hybrid dimers were synthesized, each containing a metallo-tetraarylporphyrin [Zn(II), Cu(II), or Ni(II)], and a free base tetraarylporphyrin. Transfer of singlet excitation energy from the metalloporphyrin center to the free base porphyrin center was determined by measuring fluorescence properties. The Zn hybrid dimer displayed excellent intramolecular transfer of energy ($\geq 85\%$) from the excited singlet state of the Zn(II) chromophore to the free base chromophore. No evidence for such transfer of the excited singlet state energy was found in the Ni(II) or Cu(II) analogues. From our experimental data, the fluorescence quantum yield of the Zn hybrid dimer was the same as for the free base monomer porphyrin (0.11; Seybold and Gouterman, 1969). Thus, the covalent attachment of another fluorescent porphyrin center effectively doubled the antenna size without decreasing the quantum yield even though the fluorescence quantum yield of the Zn(II) containing monomer was substantially less (0.03, according to Seybold and Gouterman, 1969) than that of the free base porphyrin.

The donor-acceptor distance and the rate constant for energy transfer were calculated using the Förster equation. Assuming random orientation, a donor-acceptor distance of 15 Å was calculated with an associated rate constant (k_{et}) for energy transfer of $1.9 \times 10^9 \text{ s}^{-1}$.

INTRODUCTION

The syntheses of several different covalently-linked porphyrin dimers have been recently reported (Anton *et al.*, 1976; Boxer and Closs, 1976; Wasielewski *et al.*, 1976; Collman *et al.*, 1977; Kagan, 1976). The interest in such complexes has been stimulated because the primary electron donor unit in photosynthesis has become well characterized as an aggregate of several chlorophyll (Chl) or bacteriochlorophyll (Bchl) molecules (see review by Loach, 1976). It appears that the study of well-defined, covalently-linked dimer, trimer and possibly tetramer complexes will be required in order to understand these primary electron donor units in photosynthesis. Covalently-linked porphyrin dimers are also being studied as models for oxygen binding and oxidase and nitrogenase systems (Collman *et al.*, 1977). In addition, electron transport reactions between metalloporphyrin centers are of great importance in oxidative metabolism, particularly in electron transport systems such as in mitochondria. Use of covalently-linked porphyrin complexes as model systems for studying

possible mechanisms of electron transfer promises to lead to a greater understanding of these important reactions.

Singlet-singlet energy transfer between non-conjugated but covalently-linked aromatic chromophores has been extensively studied (Birks, 1970). Energy transfer between covalently-linked metalloporphyrins has also been probed in one study (Schwartz *et al.*, 1972); however, singlet-singlet energy transfer was not observed in this work. In addition to probing their oxidation-reduction and photo-chemical properties, the covalently-linked dimer complexes should also be useful in studying transfer of excitation energy between chromophoric centers whose distance from each other can be precisely controlled.

In this paper, we report a highly efficient energy transfer of the excited singlet state in the covalently-linked porphyrin hybrid dimer, from one metalloporphyrin (zinc) to a free base porphyrin. When the metals in the metalloporphyrin were nickel or copper, no energy transfer was observed.

MATERIALS AND METHODS

The synthesis of the Cu and Ni hybrid dimers has been previously described (Anton *et al.*, 1976). The Zn hybrid dimer was synthesized using the same pathway, inserting Zn instead of Cu or Ni at the appropriate time. The method used for insertion of Zn was as described by Dorough *et al.* (1951). C, H, and N analyses, made on the

*This investigation was supported by research grants from the U.S. Public Health Service (GM 11741) and the National Science Foundation (PCM 74-12588 A02).

†Recipient of a Research Career Development Award from the U.S. Public Health Service (5 K04 GM 70133).

‡Supported by the National Science Foundation (PCM 76-11657).

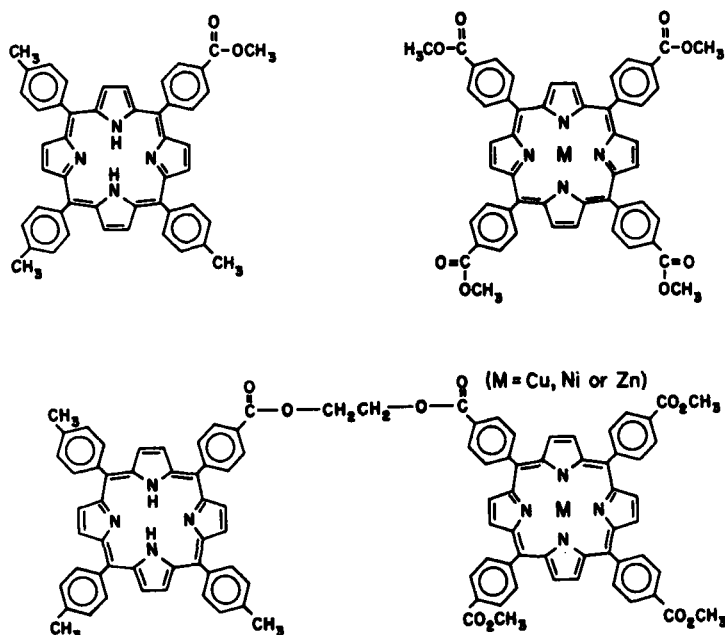


Figure 1. Structures of compounds used in study: upper left, 5-(4-carbomethoxyphenyl)-10,15,20-tritylporphyrin, upper right, Cu, Ni, or Zn 5, 10, 15, 20-tetra(4-carbomethoxyphenyl) porphyrin; bottom, Cu, Ni, or Zn hybrid dimer

Zn hybrid dimer ($\text{Zn C}_{101}\text{H}_{72}\text{N}_8\text{O}_{10}$) at Microtech Laboratories, Skokie, IL, showed good agreement with the expected composition. The calculated values were: C, 74.74; H, 4.47; N, 6.90, whereas the observed values were: C, 74.07; H, 4.33; N, 6.71.

Fluorescence excitation and emission spectra were recorded either with a laboratory-constructed instrument (Shimony *et al.*, 1967) or with a commercial instrument (Perkin-Elmer Model MPE-3). Both sets of data provided the same conclusions, but all the spectra presented here are from the commercial instrument as it directly provided the spectra corrected for the sensitivity of the photo-multiplier and the transmission characteristics of the mono-

chromator (Rebeiz *et al.*, 1975). All the emission spectra were recorded with an excitation bandwidth of 6 nm and an emission bandwidth of 3 nm. All the excitation spectra were recorded with an emission bandwidth of 6 nm and an excitation bandwidth of 3 nm. All the measurements were made at room temperature.

Lifetime of fluorescence was measured with an instrument constructed in the laboratory of Dr. Ken Kaufmann. This is a picosecond instrument similar to that previously used by Kaufmann *et al.* (1975). The samples were excited with 530 nm ps laser flashes, and the fluorescence decay signals were displayed on a ns time scale. An interference filter with 10 nm bandwidth (670 or 725 nm) or a red cut-

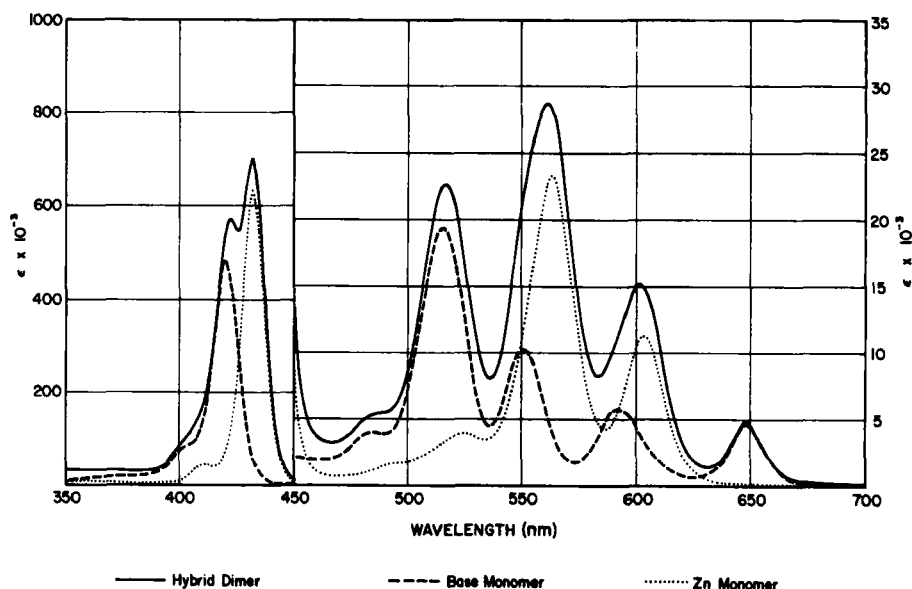


Figure 2. Experimentally determined absorption spectra for Zn hybrid dimer in benzene containing 1% pyridine (solid line), free base monomer in benzene (dashed line), and Zn monomer in benzene containing 1% pyridine (dotted line).

Table 1. Experimentally determined extinction coefficients

Free base monomer	λ (nm)	421		515	551	592	648
	$\epsilon_{mM}(\text{cm}^{-1})$	481		19.4	10.3	5.78	4.66
Zn monomer	λ (nm)		432		563		604
	$\epsilon_{mM}(\text{cm}^{-1})$		635		23.4		11.2
Zn hybrid dimer	λ (nm)	422	432	516	561	601	649
	$\epsilon_{mM}(\text{cm}^{-1})$	575	701	22.6	28.7	15.2	4.79

off filter which transmitted all wavelengths above 610 nm was placed before the photodetector to exclude the scattered exciting light.

Characterization of the Dimer. The chemical structures and purity of the hybrid dimers were established by measuring the absorbance spectra, NMR spectra and molecular weight by gel permeation chromatography. The structures of the compounds used in the study are shown in Fig. 1. The experimentally determined absorbance spectra for the Zn hybrid dimer and the monomers of which it is composed are shown in Fig. 2. Table 1 lists the experimentally determined extinction coefficients of these compounds. The data for the monomers agree well with previous spectral data for tetraphenylporphyrin and Zn(II) tetraphenylporphyrin (Dorough *et al.*, 1951), although our data for the Zn monomer may be slightly lower (less than 10%) due to solubility problems.

The absorption spectrum for the free base monomer was measured in reagent grade benzene while the absorption spectra of the Zn monomer and Zn hybrid dimer were measured in reagent grade benzene containing 1% pyridine. A computer addition of the monomer spectra is shown in Fig. 3 along with the experimentally obtained spectra for the Zn hybrid dimer. The absorbance spectra obtained for the porphyrin dimer appears to be simply the sum of the free base porphyrin spectra and the metalloporphyrin spectra. Good agreement is found at all wavelengths.

The gel permeation chromatography was carried out in tetrahydrofuran using two columns (62 cm long \times 1 cm outside diameter) packed with EM-Gel OR-PVA2000 (supplied by E. Merck, Darmstadt, Germany). The flow rate was 1.3 ml/min. Bands were detected by continuously

monitoring the absorbance at 254 nm. The gel permeation chromatography elution patterns for the Zn hybrid dimer, the Zn monomer, and *trans*-stilbene are shown in Fig. 4. A plot of log molecular weight vs elution volume is shown in Fig. 5. A least squares analysis gave a straight line with a correlation coefficient of -0.99 .

The NMR spectra for the monomers were recorded on a Varian T-60 spectrometer. The solvent used for the free base monomer was 99.8% chloroform-D. The solvent used for the Zn monomer was 99.8% chloroform-D containing a drop of deuterated pyridine to increase solubility. Due to its lower solubility, the Zn hybrid dimer spectrum was recorded on a Varian CFT-20 spectrometer (Varian Associates, Palo Alto, CA) with signal averaging and a 15 s time delay between scans. The recorded spectrum was the average of 100 scans. The solvent used for the Zn hybrid dimer was 99.8% chloroform-D. The chloroform-H peak was used as an internal standard assigned a Δ value of 7.20. This peak is marked with an asterisk in all the spectra. The NMR data for the monomers and for the Zn hybrid dimer are shown in Fig. 6. The NMR spectrum for the dimer is clearly the sum of the spectra of its two halves. The integrated areas for the ethylene, tolyl methyls, and carbomethoxy protons were found to be in the expected ratio of 4:9:9.

RESULTS

Fluorescence emission and excitation spectra were measured for the Zn monomer, the free base monomer, a mixture of the two monomers having

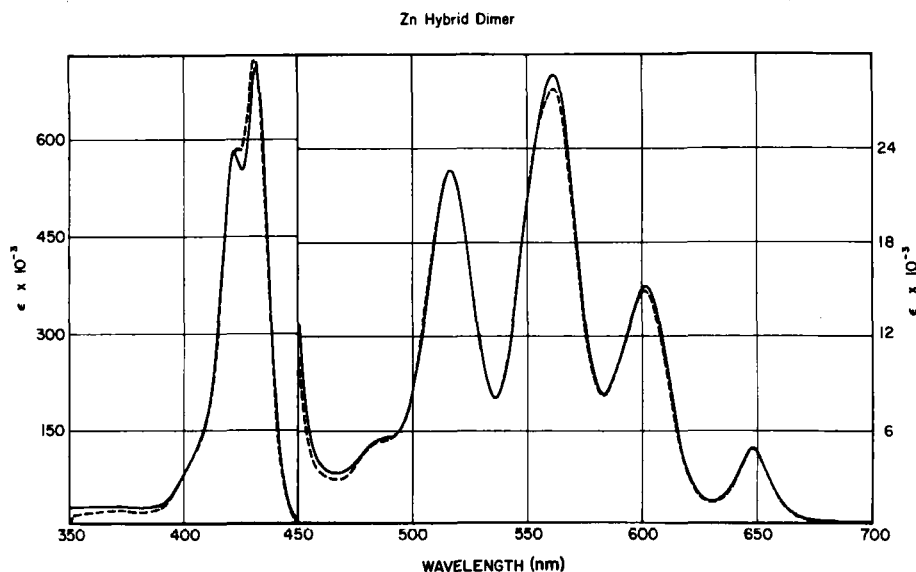


Figure 3. Computer simulation (dashed line) and experimentally determined absorption spectra (solid line) of Zn hybrid dimer in benzene.

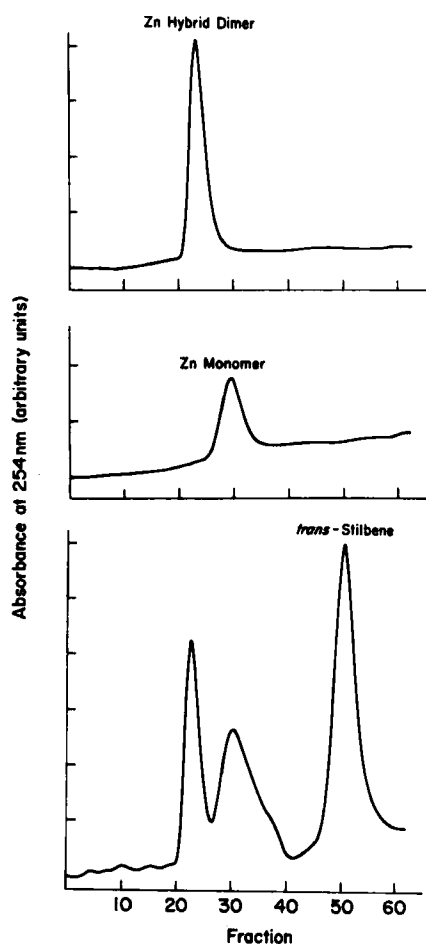


Figure 4. Gel permeation chromatography elution patterns for the Zn hybrid dimer, Zn monomer, and for a mixture of the dimer, monomer, and *trans*-stilbene.

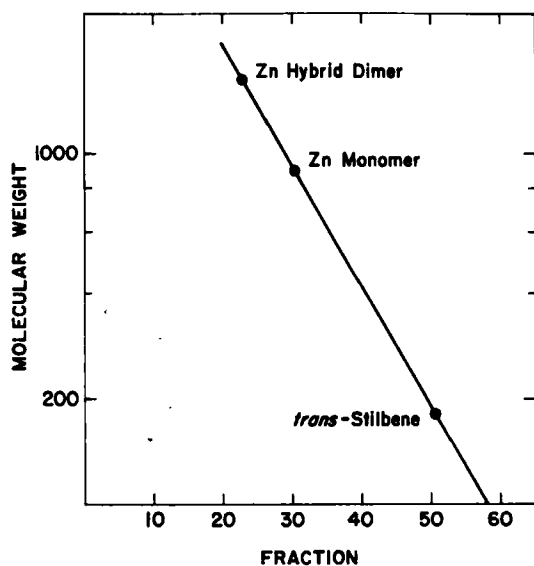


Figure 5. Least squares plot of log molecular weight vs elution volume for the Zn hybrid dimer, Zn monomer, and *trans*-stilbene separated by gel permeation chromatography.

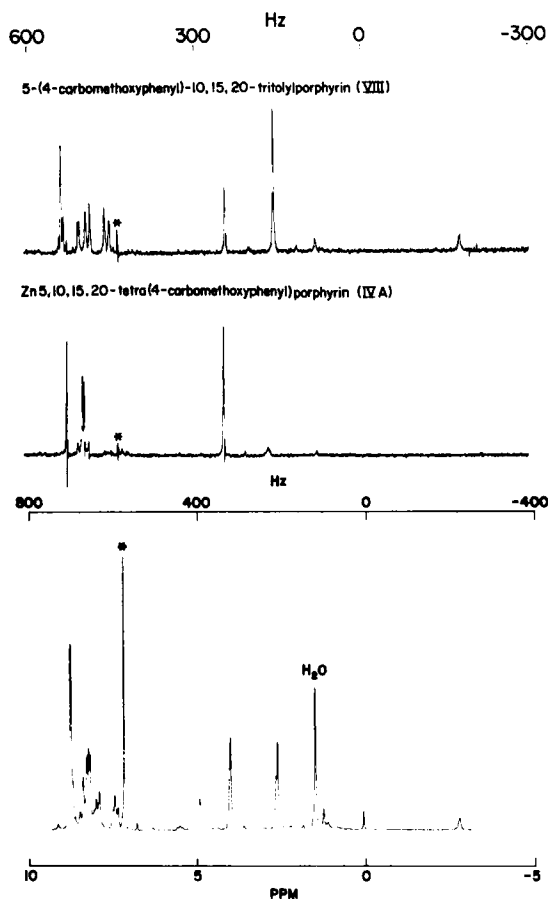


Figure 6. NMR Data for: *Top*, Free base monomer. $\Delta = 8.91$ – 8.68 (*m*, 8H, β -pyrrole); 8.37 (AB quartet, 4H, carbomethoxyphenyl-2,3,5,6-protons); 8.08 (*d*, 6H, $J = 8.0$ Hz, tolyl-2,6-protons); 7.52 (*d*, 6H, $J = 8.0$ Hz, tolyl-3,5-protons); 4.05 (*s*, 3H, methyl ester); 2.63 (*s*, 9H, methyl); -2.80 (*s*, 2H, pyrrole N-H). *Middle*, Zinc monomer. $\Delta = 8.80$ (*s*, 8H, β -pyrrole); 8.30 (AB quartet, 16H, carbomethoxyphenyl-2,3,5,6-protons); 4.09 (*s*, 12H, methyl esters). *Bottom*, Zinc hybrid dimer. $\Delta = 8.75$ (*s*, 16H, β -pyrrole); 8.53– 7.38 (*m*, 32H, phenyl protons); 4.95 (*s*, 4H, ethylene); 4.01 (*s*, 9H, methyl esters); 2.61 (*s*, 9H, methyls); -2.78 (*s*, 2H, pyrrole N-H).

approximately equal absorbances and for the covalently-linked hybrid dimer.

These compounds were dissolved in benzene containing 1% pyridine in order to ensure good solubility and therefore maximal independence of porphyrin centers and a maximally red shifted Soret band for the Zn chromophore. Figure 7 shows the emission spectra obtained. The solutions containing monomers were excited at wavelengths corresponding to the maxima of their respective Soret bands. The Zn monomer (λ excitation, 432 nm) gave an emission spectrum with peaks at 616 and 669 nm. The free base monomer (λ excitation, 422 nm) gave an emission spectrum with peaks at 659 and 725 nm. The relative intensities of the peaks for the individual monomers were independent of the wavelength used for excitation. The data for the free base monomer is in good agreement with the results of Seybold and Gouterman

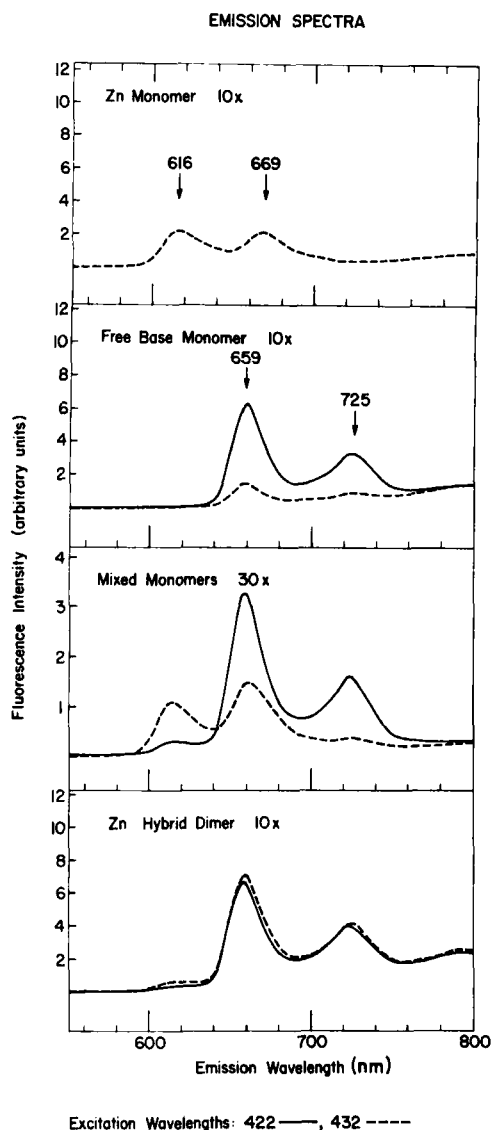


Figure 7. Fluorescence emission spectra for Zn monomer, free base monomer, mixed monomers, and Zn hybrid dimer in benzene containing 1% pyridine. The Zn monomer, free base monomer, and Zn hybrid dimer solutions were 0.30 ± 0.02 O.D. at the maximum of absorbance in the Soret region. The solution of mixed monomers was prepared by mixing together equal volumes of the above monomer solutions. Excitation wavelengths were 422 nm (solid line) and 432 nm (dashed line).

for TPP (1969). The data for the Zn monomer shows two emission peaks as does the data reported for Zn TPP by Seybold and Gouterman (1969) and also by Gurinovich *et al.* (1969). However, the relative intensities and the position of the maxima are somewhat different in each of these reports. The four carboxymethoxy groups on the phenyl rings attached to the methine bridge carbon atoms in our derivative may account for some of the differences.

As expected, the dilute solution of mixed monomers gave an emission spectrum in which the relative peak intensities were very much wavelength dependent. Clearly, when the mixed monomers were excited at

422 nm (the free base monomer Soret maximum), the emission spectrum was due almost entirely to the free base monomer. When the mixed monomers were excited at 432 nm (the Zn monomer Soret maximum), the emission spectrum was due almost entirely to the Zn monomer.

In the case of the hybrid dimer, however, the results were quite different. The emission spectrum observed is almost independent of excitation wavelength and corresponds to that of the free base monomer emission spectrum. Excitation of the Zn porphyrin chromophore in the hybrid dimer leads to emission from the free base chromophore. This clearly establishes a very high energy transfer from Zn porphyrin to the free base porphyrin center.

Figure 8 shows the excitation spectra of fluorescence obtained for the compounds studied. For the

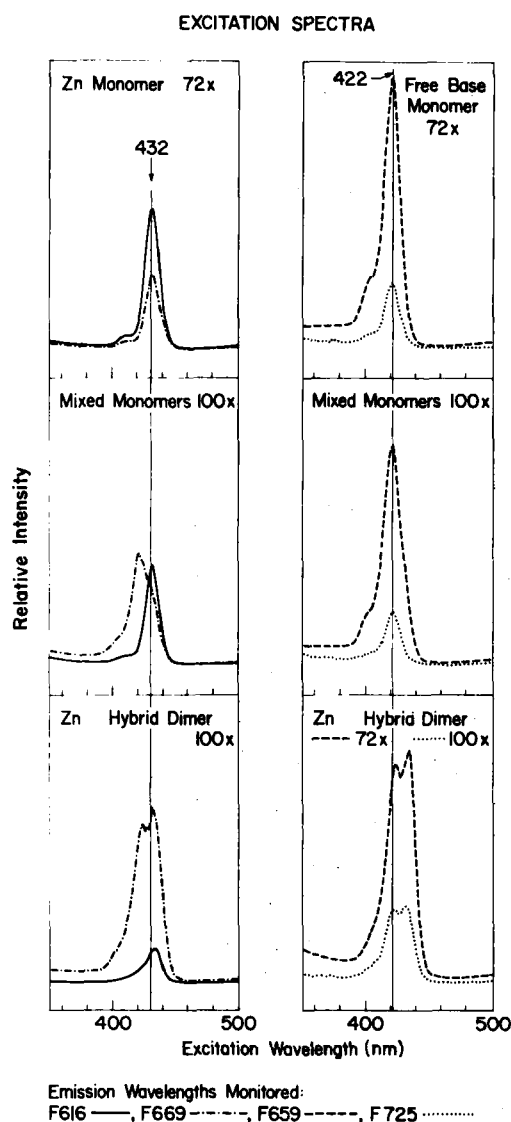


Figure 8. Fluorescence excitation spectra for Zn monomer, free base monomer, mixed monomers, and Zn hybrid dimer in benzene containing 1% pyridine. The concentration of samples prepared were as in Fig. 7. Emission wavelengths monitored were 616 nm (solid line), 669 nm (dot-dashed line), 659 nm (dashed line), and 725 nm (dotted line).

Zn monomer, the emission wavelengths monitored were 616 and 669 nm. For the fluorescence at both wavelengths, an excitation maximum was obtained at 432 nm which corresponds to the Soret band of the Zn monomer. For the free base monomer, the emission wavelengths monitored were 659 and 725 nm. For the fluorescence at both of these wavelengths, an excitation maximum was obtained at 442 nm which corresponds to the Soret band of the free base monomer.

For the mixed monomers and the Zn hybrid dimer, the emission wavelengths monitored were 616, 669, 659 and 725 nm. The 616 nm emission of the mixed monomers shows an excitation maximum at 432 nm clearly indicating that the Zn monomer is responsible for this emission. The 616 nm emission of the Zn hybrid dimer (which is much diminished) also shows an excitation maximum near 432 nm indicating that the Zn porphyrin chromophore is responsible for the emission. The 669 nm emission of the mixed monomers shows an excitation spectra in which the maxima can be attributed primarily to the free base monomer because of the intense 659 nm band from the free base porphyrin which overlaps with the less intense 669 band of the Zn porphyrin. There is also a shoulder which can be attributed to an independent contribution by the Zn monomer. The 669 nm emission of the hybrid dimer, on the other hand, shows two excitation maxima which must be attributed more equally to the free base porphyrin chromophore and the Zn porphyrin chromophore. The 659 and 725 nm emissions of the mixed monomers show an excitation maximum at 422 nm indicating in this case that the free base monomer is responsible for these emissions. On the other hand, the 659 and 725 nm emissions of the Zn hybrid dimer show two distinct excitation maxima again corresponding almost equally to the Zn porphyrin chromophore and the free base porphyrin chromophore.

Figure 9 shows the excitation spectra for the 659 and 725 nm emissions of the Zn hybrid dimer in the 450–700 nm region of the spectra. Clearly, the excitation spectra most closely resemble the sum of the Zn porphyrin chromophore and the free base porphyrin chromophore (cf. Fig. 2). This again indicates that in the Zn hybrid dimer, light absorbed by both chromophores substantially contribute to the emission monitored due to the free base porphyrin. The data, therefore, show that there is efficient transfer of excited singlet state energy from the Zn porphyrin chromophore to the free base porphyrin chromophore in the Zn hybrid dimer.

If one compares (see Fig. 7) the emission spectra for the mixed monomers and Zn hybrid dimer due to excitation at 432 nm, one sees that there is an 85% ($\pm 5\%$) quenching of the 616 nm band of the Zn porphyrin chromophore fluorescence in the Zn hybrid dimer. Correspondingly, if one compares the emission band at 725 nm due to the free base monomer in the mixed monomer system with the same band in

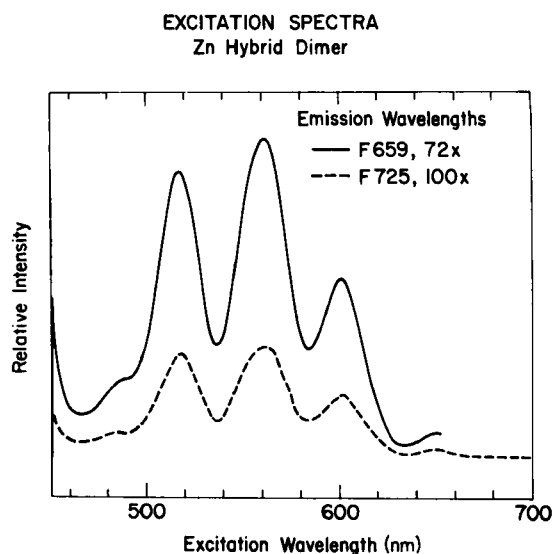


Figure 9. Fluorescence excitation spectra for the Zn hybrid dimer in benzene containing 1% pyridine in the region between 450 nm and 700 nm. The solution had a maximum of 0.30 at 561 nm. Emission wavelengths monitored were 659 (solid line) and 725 nm (dashed line).

the Zn hybrid dimer system as caused once again by excitation at 432 nm, it is apparent that there is a substantial increase in the intensity of fluorescence at 725 nm in the hybrid dimer due to energy transfer. This increase, after subtracting an expected emission due to some absorbance by the free base chromophore at 432 nm, also gives a value of 85% ($\pm 5\%$) for energy transfer from the zinc containing chromophore to the free base chromophore in the hybrid dimer.

Preliminary studies on a Zn hybrid dimer linked by a five carbon chain instead of a two carbon unit indicate that a decreased efficiency of energy transfer occurs. However, the five carbon analogue has not yet been fully characterized.

When Cu(II) or Ni(II) hybrid dimers were used, no transfer of excitation energy was observed, although fluorescence from the free base chromophore readily occurred when it was directly excited. This result is consistent with observation that less stable metalloporphyrins such as Zn(II), Cd(II), Pb(II), Mg(II), and Sn(II) show high fluorescence yields whereas the more stable and paramagnetic Co(II), Ni(II), Cu(II), Ag(II), Fe(II) and Fe(III) complexes do not (Falk, 1964; Hopf and Whitten, 1975). Thus, whatever the process is which competes with fluorescence for utilization of the excited singlet state in the Cu(II) and Ni(II) porphyrin complexes, it must occur appreciably faster than the transfer of the excited singlet state energy to the free porphyrin center in the dimer. This would seem to be a process which occurs at a much faster rate than is required for formation of a triplet state.

DISCUSSION

In our selection of a porphyrin dimer for measuring the effectiveness of transfer of energy in the excited singlet state, it was desirable to select covalently-linked porphyrin centers which had the following characteristics: (a) unique and substantially different absorbance spectra, (b) both with high fluorescence yields, (c) unique and substantially different fluorescence spectra (this usually follows if points (a) and (b) are met) and (d) good solubility properties in several solvent systems so that there is no intermolecular aggregation. The zinc and free base porphyrin centers covalently linked for this study nicely fulfill these conditions. Figure 10 shows the extent to which conditions (a) and (c) from above are met. In addition, they were selected such that the tolyl methyl hydrogens (free base porphyrin), carboxymethyl hydrogen (zinc porphyrin) and the ethylene hydrogens (bridge) would all have distinct locations when measured by NMR. Therefore, this spectroscopic tool could be used to both verify the composition of the dimer and also to substantiate that the rings were not interacting (for example, in a sandwich complex or by intermolecular aggregation) in the solvent systems used in this study.

The fluorescence emission and excitation data shown in Figs. 7, 8 and 9 clearly document a highly efficient transfer of the excited singlet state from the zinc porphyrin center in the covalently-linked dimer to the free base center, but not in the opposite direction. This result is as expected and is in agreement with theory as well as other experimental studies of

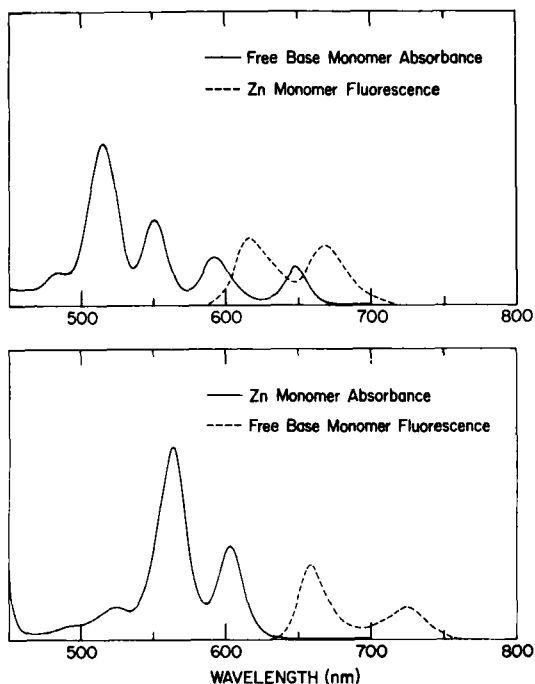


Figure 10. Relationship between the absorbance and emission spectra of the Zn(II) porphyrin and free base porphyrin monomers used in these studies. Solvents were as stated for Fig. 2.

excitation energy transfer using simpler fluorescing centers (Conrad and Brand, 1968; Birks, 1970; Burr *et al.*, 1975; Lee *et al.*, 1977).

Preliminary estimates of the fluorescence lifetimes, obtained in collaboration with K. Kaufmann, were $3 (\pm 1)$ ns for the Zn monomer (for all fluorescence > 610 nm, or at 670 nm), $20 (\pm 5)$ ns for the free base monomer (> 610 nm or at 725 nm), and $10 (\pm 3)$ ns for the hybrid dimer (> 610 nm, or at 670 or 725 nm).

The most probable mechanism for the observed energy transfer is the Förster dipole-dipole interaction (1959). Using the Förster equation a value for R (donor-acceptor distance) may be calculated and also the rate constant for energy transfer (k_{et}). The equations used are:

$$R = \left[(8.8 \times 10^{-28}) \frac{\kappa^2}{n^4} \Phi_f \Omega \left(\frac{1 - \Phi_{et}}{\Phi_{et}} \right) \right]^{1/6}$$

(Conrad and Brand, 1968)

$$k_{et} = \frac{\Phi_f k_f (1 - \Phi_{et})}{\Phi_{et}}$$

where Φ_f is the donor fluorescence quantum yield in the absence of energy transfer, Ω is the overlap integral for donor fluorescence and acceptor absorption, κ is the orientation factor for the donor and the acceptor, n is the refractive index of the medium, and Φ_{et} is the quantum efficiency of the energy transfer. Φ_f was taken to be 0.03 the same as reported for Zn TPP (Seybold and Gouterman, 1969). Assuming random orientation $\kappa^2 = 2/3$. The refractive index of the medium was taken to be 1.498 (benzene). Our measured value of 0.85 was used for Φ_{et} . The numerical value of the overlap integral was calculated by the procedure described by Conrad and Brand (1968). The value obtained was $2.139 \times 10^{-11} \text{ cm}^6 \text{ mol}^{-1}$. k_f is the intrinsic rate constant for donor fluorescence and was calculated to be $1 \times 10^7 \text{ s}^{-1}$ using our estimates of fluorescence lifetimes and the quantum yield measurement of Seybold and Gouterman (1969). Using the above values and equations an R value of 15 Å and a k_{et} of $1.9 \times 10^9 \text{ s}^{-1}$ were obtained. Assuming an extended configuration for the dimer linked by a two carbon bridge, the center to center distance between the porphyrins would be expected to be 22 Å, while the distance between the edges of the porphyrin ring systems would be about 14 Å. If complete alignment of the dipoles was assumed, the orientation factor κ would become 2 and the calculated donor-acceptor distance would be 21 Å.

From the data presented in this paper, light absorbed by the Zn chromophore of the Zn hybrid dimer is very efficiently transferred to the free base chromophore and is emitted from that center with a quantum yield that must be near that of the free base monomer. Thus, the energy transfer from the Zn chromophore to the free base chromophore in the dimer is sufficiently fast to compete very favorably with those processes in the Zn monomer that result

in a low fluorescence yield. In conclusion, the covalent attachment of two fluorescent porphyrin molecules with a resultant center to center distance of 22 Å (for an extended geometry) effectively doubled the antenna size for channeling light energy into the free base porphyrin chromophore.

The results reported in this communication underscore the value of examining the energy transfer properties of appropriate covalently linked porphyrin dimer and trimer complexes. We are presently extending this work to include the redox and photochemical properties of such model complexes.

Acknowledgements—We are grateful to Dr. C. A. Rebeiz for the use of the spectrofluorometer (used for obtaining data shown in Figs. 7–9) and to Drs. Charles Cohen, Susan McCarthy and Maarib Bazzaz for their help in these spectral measurements. We are also grateful to Dr. Ken Kaufmann for the preliminary measurements on the lifetimes of the excited states mentioned in the Discussion section. Absorbance spectra were recorded on a Cary 14R Recording Spectrophotometer at Argonne National Laboratory where the instrument was on line with a computer. We are grateful to Dr. J. R. Norris and Dr. Therese Cotton for their help in taking these spectra. We also wish to thank Dr. Chris Bull for his help in the computer simulations and Mr. Steve Jacobs for performing the gel permeation work.

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