Energy Transfer between Covalently Linked Metal Porphyrins

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ABSTRACT

A zinc porphyrin is linked covalently to either a copper or a cobalt porphyrin by a peptide linkage containing either a p-phenylene or an ethylene group. These double porphyrins were prepared by reacting the acid chloride of 2-carboxyl-12,17-diethyl-3,7,8,13,18-pentamethylporphyrin with either p-phenylenediamine or ethylenediamine and subsequent reaction with a second acid chloride porphyrin. In rigid solutions of 2-methyltetrahydrofuran at 77°K intramolecular energy transfer from the zinc triplet state to that of the copper tripledoublet is manifested in a shortening of the zinc porphyrin triplet state lifetime from 46 ± 1 to 34 ± 1 msec in the ethylene bridged dimers. In the cobalt-zinc ethylene bridged dimers triplet energy transfer from the zinc chromophore is more efficient as manifested in the complete quenching of the zinc phosphorescence. Calculations suggest that in the copper-zinc case energy transfer proceeds by a triplet-triplet exchange mechanism whereas in the cobalt-zinc case, quenching of the zinc triplet proceeds by the formation of a charge transfer complex. There is no evidence for triplet-triplet energy transfer in the phenylene bridged double porphyrins. Singlet-singlet energy transfer is not observed in any of the above systems.

INTRODUCTION

Electronic energy transfer between nonconjugated covalently linked chromophores has been demonstrated in a variety of cases [1]. The problem is intermediate between studies of intermolecular energy transfer between
noncovalently linked molecules and studies of electronic relaxation within a single molecule. A covalent linkage has several inherent advantages: (1) The distance between the chromophores can be known and varied from several to many Ångstroms. (2) The orientation of one chromophore with respect to the other may sometimes be rigidly fixed whereas intermolecular energy transfer in solutions involves randomly oriented molecules. (3) Since the energy is transferred within the molecule, the role of the environment is minimal. The only limitation of this technique is the availability of such molecules.

In this study we investigate intramolecular energy transfer in a series of double porphyrin molecules. Two metalloporphyrins are linked via amide groups, CO—NH—R—NH—CO, where R is either an ethylene or p-phenylene group, as shown:

The two 12,17-diethyl-3,7,8,13,18-pentamethylporphyrin carboxamide molecules are structurally identical except for the metals M and M'. We shall refer to molecules (I) as M ~ R ~ M'. Thus we use ~ to refer to the porphyrin macrocycle with the CO·NH side chain. For the free base porphyrin we shall use H₂ for M.

Our choice of metals was based on the energy levels, which are indicated in Fig. 1, and luminescence characteristics. We see that Zn fluoresces and phosphoresces [2], Cu luminescences from the tripdoublet or quartet [3], while Co has no emission [4]. The Cu phosphorescence has a far shorter lifetime than the Zn [5]. Energy transfer can easily be studied in double porphyrins whose moieties show different emission properties. Moreover we can see how this is affected by the ethylene or phenylene linkages. Our reason for undertaking this study is its biological relevance. The initial step of photosynthesis involves energy transfer among chlorophyll units [6], which are magnesium dihydroporphin systems. The systems we report on here are closely related.
EXPERIMENTAL SECTION

A. Apparatus

All melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. Thin-layer chromatography was carried out on alumina plates using chloroform:ethyl acetate (8:1) as eluent. High resolution mass spectra were recorded on an AEI mass spectrometer operating at 70 eV with an emission current of 300–400 μA and a resolution of 7,000 to 10,000. The internal standard in the high resolution mass spectra was either heptacosafluorotributylamine or a μ-oxo dimer of scandium octaethylporphyrin [7]. Nuclear magnetic resonance spectra were run on a Varian Associates Model HA-100 spectrometer, chemical shifts are given in δ values with tetramethylsilane as internal standard.

The room temperature absorption spectra were recorded on a Cary 14 spectrophotometer. Low temperature and room temperature excitation and emission spectra were detected by a Bausch and Lomb 33-86-45 monochromator and a RCA 7102 photomultiplier cooled to near dry ice temperature. The light emission was viewed at right angles to the excitation light. Monochromatic excitation was provided by light from a 250-W Osram xenon lamp which was passed through a Bausch and Lomb No. 33-86-40 monochromator. Slit widths of this monochromator were 13.3 nm and those of the emission measuring monochromator were 6.6 nm. The excitation

![Energy Level Diagram](image)

Fig. 1. Energy level diagram and the emission characteristics of the copper, zinc, and cobalt chromophores. The tripdoublet and quartet levels of the cobalt chromophore are from Ref. 3. Solid arrows indicate radiative transitions and the wavy arrows, radiationless transitions. Primed triplet decay lifetimes are p-aminophenylene amide lifetimes and the unprimed are those of the aminoethylene amides.
spectra were corrected for variation in the exciting light intensity by use of a Rhodamine B quantum counter. The Rhodamine B absorbs light from 220 to 600 nm and emits a red fluorescence with a constant quantum yield to within ±5% error which is detected by a RCA 1P28 photomultiplier. Output from the 1P28, operated at 750 V, is fed along with the output from the RCA 7102 operated at 1500 V and amplified by a Keithley 417 Picoammeter, into a ratio recording device. This device utilizes the servo-mechanism in a Honeywell Electronik 19 Recorder to give a recording of the ratio of the above two signals. At the low optical densities used in these experiments, this ratio is proportional to $\Phi_e$ where $\Phi$ is the quantum yield of the detected emission excited by light being absorbed with an extinction coefficient $e$.

The room temperature quantum yields were measured with an additional instrument. Simultaneously with the emission and excitation intensity measurements, both of which were measured separately, the optical density of the sample of the excitation wavelength was also determined. This was done by placing a probe from an Optics Technology Model 610 Power Meter behind the cell and measuring the intensity of the transmitted light. From a previous measurement of a blank, the optical density was determined.

Lifetime measurements of the long lived luminescences at 77°K were made by flash excitation from a General Radio Strobotac type 1531-AB electronic stroboscope whose light was passed through a Corning No. 5-58 filter. The RCA 7102 was replaced by a RCA 7265 photomultiplier whose output was fed through a preamp, several X10 amplifiers, and into a PAR Model TDH-9 Waveform Eductor. After a sufficient number of flashes, which were approximately one per second, the output of the Eductor was recorded by either a Monsanto digital printer or a Heathkit recorder. In addition a Corning #3-72 filter was used in the detection system when measuring the triplet lifetimes of Zn porphyrins.

At very low luminescence levels a modified lifetime measuring procedure was used. The photomultiplier was gated so that it detected the decay sometime after the exciting flash. We were thus able to measure very small phosphorescence decays in wavelength regions where interfering fluorescences were very strong.

Transient changes in the absorption spectra of the samples resulting from flash excitation were measured by inserting the sample in between a dc 1000-W tungsten lamp and the detecting monochromator–RCA 7265 photomultiplier combination. Intense flash excitation of the sample was applied perpendicular to the dc light beam and provided by a stroboscope operated in the free run mode. Before the flash excitation, the large PM anode current resulting from the dc light penetrating the sample was nulled.
by a scaling summer circuit consisting of a 44J-Analog-Devices operational amplifier. The circuit was designed to null an anode current of $\sim 10^{-4}$ A which was obtained by adjusting the PM voltage and slit openings of the monochromator. Small transient changes on the order of 0.1% in the dc light level resulting from flash excitation of the sample were detected and amplified by the X10 amplifiers. The amplified signal was fed into the eductor and after a sufficient number of flashes the output of the eductor was recorded on the Honeywell recorder.

B. Synthesis

**Diethyl 2-formyl-4-methylpyrrole-3,5-dicarboxylate**

Diethyl 2,4-dimethylpyrrole-3,5-dicarboxylate (100 g) and acetic acid (500 ml) were heated to 50°, and sulfuryl chloride (71 ml) in 140 ml of acetic acid was added to the stirred solution at such a rate as to maintain the temperature between 50-60°. When the addition was complete the solution was maintained at this temperature for a further ½ hr, cooled to room temperature, diluted with water and allowed to stand overnight. The product was collected by filtration, washed with water, and upon air drying gave 96 g (90%) of a white powder m.p. 124–125° (lit [8] 124–125°). It was used without further purification.

**Ethyl 2-formyl-4-methylpyrrole-3-carboxylate**

Ethyl 2-iodo-5-formyl-3-methylpyrrole-4-carboxylate [8] (15 g) in methanol (200 ml) was reduced under 1 atm of hydrogen in the presence of 10% Pd/C (2.5 g) and sodium acetate (10 g). When no further hydrogen was absorbed the solution was filtered into a flask containing a few drops of 0.1-N Na$_2$SO$_4$. The solvent was removed at room temperature and the residue triturated with water. The brown crystalline solid was collected by filtration, washed with water and air dried to give 66 g (70%) m.p. 144° (lit [9] m.p. 143–144°).

**3-Ethoxycarbonyl-2',4,4',5'-tetramethyl-2-2'-dipyrrromethene hydrobromide**

Ethyl 2-formyl-4-methylpyrrole-3-carboxylate (4.53 g) and 2,3,4-trimethylpyrrole (2.73 g) were dissolved in 120 ml of ethanol. The solution was cooled in an ice bath and 48% hydrobromic acid (12 ml) was added in one portion. An orange precipitate formed immediately. The mixture was allowed to stand at room temperature for two hours. The product was collected by filtration, washed with ethanol and air dried to give 7.58 g (86%) of the dipyrrromethene as deep orange needles (m.p. 193–194°);
nmr (CF$_3$CO$_2$H) 1.55 (3H, $t$, $J = 7.0$ Hz, CH$_3$) 2.14 (3H, s, CH$_3$), 2.4 (3H, s, CH$_3$), 2.7 (6H, s, 2CH$_3$), 4.56 (2H, $q$, $J = 7$ Hz, CH$_2$) 7.41 (1H, mult.), 8.46 (1H, s), 11.7 (2H, br., NH).

*Anal.* Calculated for C$_{32}$H$_{33}$BrN$_4$O$_2$: C, 44.19; H, 5.94; N, 22.67; found: C, 43.83; H, 6.82; N, 23.11.

1-Bromo-1,19-dideoxy-13-ethoxycarbonyl-8,8-diethyl-2,7,12,17,18,19-hexamethylbiladiene-ac dihydrobromide

5-Bromo-5'-bromomethyl-3,4-diethyl-3',4-dimethyl-2,2'-dipyrrormethene hydrobromide [10] (3.37 g) and 3-ethoxycarbonyl-3',4,4',5'-tetramethyl-2,2'-dipyrrromethene hydrobromide (2.47 g) were dissolved in dry methylene dichloride (350 ml). Stannic chloride (7 ml) was added and the solution kept at room temperature for two hours. The solvent was removed under vacuum, and the thick oily residue cooled in an ice bath. A mixture of ethanol (175 ml) and 48% HBr (175 ml) was slowly added and the mixture was stirred at room temperature until the oil had solidified. The brown solid was collected by filtration, washed with ethanol and dried under vacuum to give 4.14 g (80%) of the biladiene dihydrobromide, m.p. $> 250^\circ$, m/e 590.2361, C$_{32}$H$_{33}$BrN$_4$O$_2$ (the free base) required m/e 590.2256.

**Ethyl 1,17-diethyl-8,7,8,13,18-pentamethylporphyrin-2-carboxylate**

The biladiene dihydrobromide (2.1 g) was suspended in dimethylsulfoxide (300 ml) and 7 ml of pyridine was added. The mixture stirred until the biladiene had dissolved. The reaction was then allowed to stand at room temperature for 48 hr, filtered, and washed with methanol to give 1 g (69%) of the porphyrin as shining purple plates m.p. $> 250^\circ$, nmr (CF$_3$CO$_2$H) 1.67 (6H, $t$, $J = 7.5$ Hz, 2CH$_3$), 1.81 (3H, $t$, $J = 6.5$ Hz, CH$_3$), 3.65 (12H, s, 4CH$_3$), 4.05 (3H, s, CH$_3$), 4.16 (4H, $q$, $J = 6.5$ Hz, 2CH$_2$), 5.02 (2H, $q$, $J = 6.5$ Hz, CH$_2$), 10.78 (1H, s), 10.84 (1H, s), 11.06 (1H, s), 11.70 (1H, s); MS, 508 (100), 493 (27), 465 (27), 254 (18).

*Anal.* Calculated for C$_{32}$H$_{36}$N$_4$O$_2$: C, 75.56; H, 7.13; N, 11.01; found: C, 75.55; H, 7.39; N, 10.85.

2-Carboxyl-12,17-diethyl-8,7,8,13,18-pentamethylporphyrin

To a suspension of the porphyrin ethyl ester (2 g) in pyridine (400 ml) was added a solution of potassium hydroxide (10 g) in methanol (50 ml). The mixture was heated in an oil bath (90–100$^\circ$), and the hydrolysis was followed by t.l.c. After 5 hr the reaction was complete and the mixture cooled to room temperature. Acetic acid (50 ml) was added, and the solvent removed under vacuum. The residue was triturated with methanol, filtered
and washed with methanol and then water. The product, crystallized from pyridine/methanol, was collected by filtration, washed with methanol, and then water. The product recrystallized from pyridine/methanol was collected by filtration, washed with methanol, and air dried to give 1.6 g (85%) of the porphyrin, m.p. 325–326°, nmr (CF₃CO₂H) 1.77 (6H, J = 7.0 Hz, 2CH₃), 3.68 (12H, s, 4CH₃), 4.1 (3H, s, CH₃), 4.21 (2H, q, J = 7.0 Hz, CH₂), 10.78 (1H, s), 10.82 (1H, s), 11.09 (1H, s), 11.57 (1H, s). MS 480 (100), 465 (28), 436 (25), 240 (14), uv λmax [solvent:2-Methyltetrahydrofuran (2MeTHF) (ε X 10⁻¹/l/M cm)] 407 nm (17.2), 507 nm (0.920), 545 nm (1.32), 574 nm (0.674), and 630 nm (0.205) (10% error in all ε determinations).

Anal. Calculated for C₃₀H₂₆N₄O₂:C, 74.97; H, 6.11; N, 11.66; found: C, 75.37; H, 6.93; N, 11.46.

Copper 2-Carboxyl-12,17-diethyl-3,7,8,13,18-pentamethylporphyrin

The porphyrin carboxylic acid (50 mg) and cupric acetate (50 mg) were heated in dry dimethylformamide (DMF) under nitrogen at 100°. The reaction was complete within 30 min. This was evident by the transformation of the four visible bands of the free base into the two Q bands of the Cu complex. The solution was cooled, diluted with water. The product was collected by filtration under vacuum, washed with water and methanol and dried under vacuum for 24 hr, to give 47 mg (83%) of the copper complex; m.p. > 300°. An analytical sample was recrystallized from chloroform. uv λmax (solvent:2MeTHF) 403 nm (18.7), 538 nm (0.704), and 577 nm (1.57).

Anal. Calculated for C₃₀H₂₆N₄O₂Cu:C, 66.46; H, 5.58; N, 10.34; found: C, 66.52; H, 5.41; N, 10.37.

Cobalt 2-Carboxyl-12,17-diethyl-3,7,8,13,18-pentamethylporphyrin

The porphyrin carboxylic acid (150 mg) and cobalt acetate (150 mg) were heated in DMF at 160° for four hr. The reaction mixture was worked up in the same manner as the copper complex above to give 47 mg (88%); m.p. > 300°. An analytical sample was crystallized from chloroform.

Anal. Calculated for C₃₀H₃₀N₄O₂Co:C, 67.01; H, 5.63; N, 10.42; found: C, 67.09; H, 5.72; N, 10.56.

2-Chlorocarboxyl-12,17-diethyl-3,7,8,13,18-pentamethylporphyrin

Oxalyl chloride (1 ml) was added dropwise to a vigorously stirred solution of the porphyrin carboxylic acid (150 mg) suspended in dry benzene (13 ml). The mixture immediately turned green. Stirring was continued for four hours under dry nitrogen. Solvent and excess oxalyl
chloride were removed under reduced pressure, and the residue was redisolved in dry benzene and again taken down to dryness under vacuum to remove the last traces of oxalyl chloride. The product was immediately used without further purification.

**Copper and Cobalt 2-Chlorocarbonyl-12,17-diethyl-8,7,8,13,18-penta-methylporphyrins**

Both were prepared by the same method used for the free base and were immediately used without further purification.

**2-(β-Aminoethylaminocarbonyl)-12,17-diethyl-8,7,13,18-pentamethylporphyrin**

To a gently refluxing solution of the acid chloride (freshly prepared from 150 mg of the free base porphyrin) in dry benzene (25 ml) was added dry ethylenediamine (0.4 ml). The mixture was refluxed for six hr under dry nitrogen, and cooled to room temperature. The product was collected by filtration, washed with benzene and methanol and dried under vacuum to give 134 mg (82%) m.p. >300°. uv λ<sub>max</sub> (solvent: CH<sub>2</sub>Cl<sub>2</sub>) 403 nm (12.5), 507 nm (0.788), 543 nm (0.846), 570 nm (0.579), and 625 nm (0.099). An analytical sample was recrystallized from chloroform.

Anal. Calculated for C<sub>32</sub>H<sub>38</sub>N<sub>6</sub>O: C, 73.53; H, 7.33; N, 16.08; found: C, 73.46; H, 7.51; N, 15.91.

**Copper 2-(β-Aminoethylaminocarbonyl)-12,17-diethyl-8,7,13,18-pentamethylporphyrin**

The free-base β-aminoethylaminocarbonylporphyrin (35 mg) and cupric acetate (35 mg) were heated in pyridine (15 ml) for 30 minutes. The solvent was removed under reduced pressure and the residue washed with methanol and water and dried under vacuum to give 29 mg (74%). An analytical sample was recrystallized from chloroform. uv λ<sub>max</sub> (solvent: 2MeTHF) 404 nm (∼11.0 (15% error)), 535 nm (0.5), 577 nm (0.7).


**Zinc 2-(β-Aminoethylaminocarbonyl)-12,17-diethyl-8,7,13,18-pentamethylporphyrin**

The free base β-aminoethylaminocarbonylporphyrin (30 mg), zinc acetate (30 mg) and sodium acetate (30 mg) were refluxed in DMF (15 ml) for one hr. The solvent was removed under reduced pressure, the residue washed with methanol and water and dried under vacuum to give 29 mg
(86.5%) m.p. >300°. uv $\lambda_{\text{max}}$ (solvent:CH$_2$Cl$_2$) 417 nm (18.5), 547 nm (0.990), and 590 nm (1.02). An analytical sample was recrystallized from chloroform.

*Anal.* Calculated for C$_{32}$H$_{37}$N$_5$OZn: C, 65.58; H, 6.19; N, 14.34; found: C, 65.73; H, 6.31; N, 14.27.

2-(p-Aminophenylaminocarbonyl)-12, 17-diethyl-7, 8, 13, 18-pentamethylporphyrin

p-Phenylenediamine (130 mg) in dry pyridine (15 ml) was added to the acid chloride freshly prepared from 50 mg of the free-base porphyrin. The mixture was refluxed for six hours under dry nitrogen. The solvent was removed under reduced pressure; and the product was washed with benzene and methanol. Drying under vacuum gave 42 mg (71%) of the product m.p. >300°. uv $\lambda_{\text{max}}$ (solvent:2 MeTHF) 405 nm (18.0), 507 nm (0.94), 543 nm (1.27), 570 nm (0.79), and 625 nm (0.124). An analytical sample was recrystallized from chloroform.

*Anal.* Calculated for C$_{36}$H$_{39}$N$_6$: C, 75.76; H, 6.71; N, 14.73; found: C, 75.82; H, 6.87; N, 14.93.

Copper 2-(p-Aminophenylaminocarbonyl)-12, 17-diethyl-7, 8, 13, 18-pentamethylporphyrin

The free-base p-aminophenylaminocarbonylporphyrin (35 mg) and cupric acetate (35 mg) were heated at 80° in pyridine (15 ml). When the absorption spectrum showed that the reaction had gone to completion the solvent was removed under vacuum and the product washed with methanol and water. Drying under vacuum gave 31 mg (80%) of product, m.p. >300°. uv $\lambda_{\text{max}}$ (solvent:2 MeTHF) 404 nm (14.7), 530 nm (0.510), and 575 nm (1.08). An analytical sample was recrystallized from chloroform.

*Anal.* Calculated for C$_{38}$H$_{38}$N$_6$OCu: C, 68.39; H, 5.74; N, 13.29; found: C, 68.17; H, 5.78; N, 13.54.

Zinc 2-(p-Aminophenylaminocarbonyl)-12, 17-diethyl-7, 8, 13, 18-pentamethylporphyrin

The free-base p-aminophenylaminocarbonylporphyrin (30 mg) and zinc acetate (50 mg) were refluxed in pyridine (15 ml) for six hours. The solvent was removed under vacuum and the product washed with methanol and water. Drying under vacuum gave 27 mg (81%) of product m.p. >300°. uv $\lambda_{\text{max}}$ (solvent:2 MeTHF) 413 nm (15.9), 543 nm (0.722), and 587 nm (0.902). An analytical sample was recrystallized from chloroform.

*Anal.* Calculated for C$_{38}$H$_{38}$N$_6$OZn: C, 68.19; H, 5.72; N, 13.25; found: C, 68.30; H, 5.64; N, 13.57.
Cu $\sim$ C$_2$H$_4$ $\sim$ H$_2$ double porphyrin

The $\beta$-aminoethylaminocarbonyl free-base porphyrin (5.2 mg) and the acid chloride of the copper porphyrin freshly prepared from 5.4 mg of the copper complex of porphyrin acid were suspended in dry pyridine (10 ml) and heated at 90° for two hr, until the absorption spectrum of the solution (the product is soluble in pyridine) remained unchanged. The mixture was then filtered and the filtrate taken down to dryness under reduced pressure. The residue was washed with methanol and air dried to give 8.7 mg (83%) of the product. T.l.c. showed that only one complex (free from starting materials) was present, m.p. $>$300°, m/e 1045.4508 C$_{62}$H$_{66}$N$_{10}$O$_2$Cu requires m/e 1045.4668 (for Cu = 62.9298).

Cu $\sim$ C$_2$H$_4$ $\sim$ Zn double porphyrin.

The Cu $\sim$ C$_2$H$_4$ $\sim$ H$_2$ double porphyrin (41 mg) sodium acetate (29 mg), and zinc acetate (29 mg) were heated at 90° for three hours in pyridine (10 ml). At this time the four Q bands of the Cu $\sim$ C$_2$H$_5$ $\sim$ H$_2$ complex had transformed in the two Q bands of the Cu $\sim$ C$_2$H$_4$ $\sim$ Zn complex. The pyridine was removed under reduced pressure and the product washed with water and methanol. Drying under vacuum gave 40 mg of the product. T.l.c. showed that only one complex (free of any starting material) was present, m.p. $>$300°, m/e 1107.3798, C$_{62}$H$_{64}$N$_{10}$O$_2$CuZn requires m/e 1107.3802 (for Cu = 62.9298 and Zn = 63.9291).

Co $\sim$ C$_2$H$_4$ $\sim$ H$_2$ double porphyrin

The same procedure was followed as was used in the preparation of the corresponding Cu $\sim$ C$_2$H$_4$ $\sim$ H$_2$ double porphyrin, except that the reaction was carried out at 70° to give an 80% yield of product, m.p. $>$300°. uv $\lambda_{max}$ (solvent:CH$_2$Cl$_2$) 405 nm (17.1), 417 nm (15.9), 495 nm (0.647), 545 nm (0.975), 573 nm (0.856), and 630 nm (0.073). m/e 1041.4725, C$_{62}$H$_{66}$N$_{10}$O$_2$Co requires m/e 1041.4703 (for Co = 58.9332).

Co $\sim$ C$_2$H$_4$ $\sim$ Zn double porphyrin

A similar procedure as that employed for the corresponding Cu $\sim$ C$_2$H$_4$ $\sim$ Zn double porphyrin was used. T.l.c. showed only one product, however the electronic absorption spectrum $\lambda_{max}$ (solvent:CH$_2$Cl$_2$) 407 nm (14.2), 543 nm (0.833), and 587 nm (1.16) is very similar to that of the zinc 2-(beta-Aminoethylaminocarbonyl)-12, 17 diethyl-3, 7, 8, 13, 18-pentamethylporphyrin so that apparently there is an excess of zinc over that of cobalt. We have observed that zinc displaces cobalt from the cobalt complex of the monomeric porphyrin acid. The high resolution mass spectrum was
consistent with mixture of the Co ~ C₂H₄ ~ Zn and the Zn ~ C₂H₂ ~ Zn complexes.

Cu ~ C₆H₄ ~ H₂ double porphyrin

The preparation was the same as that used to prepare the Cu ~ C₂H₄ ~ H₂ complex, using the p-aminophenylaminocarboxylporphyrin. A 50% yield of the product, m.p. >300° was obtained. uv λ_max (solvent:2MeTHF) 403 nm (34.8), 510 nm (0.980), 540 nm (1.46), 577 nm (2.50), and 630 nm (0.122). m/e 1093.4684, C₆₆H₆₆N₁₀CuO₂ requires m/e 1093.4668 (for Cu = 62.9298).

Cu ~ C₆H₄ ~ Zn double porphyrin

The procedure was identical to that used for the preparation of the Cu ~ C₂H₄ ~ Zn complex. Using zinc acetate (55 mg) and Cu ~ C₆H₄ ~ H₂ (45 mg) a yield of 38 mg (79%) was obtained, m.p. >300°. uv λ_max (solvent:2MeTHF) 403 nm (37.8), 538 nm (1.40), and 577 nm (2.58). m/e 1155.3802, C₆₆H₆₄CuN₁₀O₂Zn requires m/e 1155.3792 (for Cu = 62.9298 and Zn = 63.9291).

Co ~ C₆H₄ ~ H₂ double porphyrin

The p-aminophenylaminocarboxylporphyrin (60 mg) in dry pyridine (15 ml) was added to a suspension of the freshly prepared acid chloride of the cobalt porphyrin, prepared from the cobalt porphyrin acid (55 mg), in dry pyridine (15 ml). The mixture was heated at 90°, under dry nitrogen, for three hours by which time no further spectral changes took place. The mixture was filtered, the solvent removed from the filtrate under reduced pressure and the product washed with methanol. Drying under vacuum gave 78 mg of product, m.p. >300°. uv λ_max (solvent:2MeTHF) 403 nm (30.7), 505 nm (1.66), 538 nm (1.99), 572 nm (1.18), and 630 nm (0.288). m/e 1089.4673, C₆₆H₆₄N₁₀O₂Co requires m/e 1089.4692 for Co = 58.9332).

Co ~ C₆H₄ ~ Zn double porphyrin

A solution of Co ~ C₆H₄ ~ H₂ (36 mg) and zinc acetate (44 mg) was refluxed in pyridine (25 ml) until the spectrum of the free base disappeared. The solvent was removed under reduced pressure and the product washed with water and methanol. Drying under vacuum gave 30 mg of the product m.p. >300°. Mass spectra revealed that as in the case of the Co ~ C₂H₄ ~ Zn, some of the zinc had displaced the cobalt. uv λ_max (solvent:2MeTHF) 412 nm (43.0), 533 nm (2.12), and 587 nm (2.76).
C. Spectral Solvents

The 2MeTHF was MCB chromatoquality reagent grade and used without any further purification. The concentrations of the solutions were on the order of $10^{-5}$ M and were not degassed. The triethylamine was triply distilled.

RESULTS

Cu $\sim C_2H_4 \sim$ Zn

This compound shows three distinct luminescences. A fluorescence is observable at room temperature with peaks at 590 and 640 nm. At $77^\circ$ K an additional luminescence appears at 710 nm. Flash excitation shows that it has two decay lifetimes: 70 $\mu$s and $35 \pm 1$ msec. Excitation spectra of these luminescences are presented in Fig. 2. The excitation spectra of the copper and zinc porphyrin monomers are presented in Fig. 3. The excitation spectra clearly show that the fluorescence arises from excitation of the zinc moiety and that the low temperature emission at 710 nm arises essentially from excitation into the copper moiety. A measurement of the fluorescence quantum yield and its comparison with the fluorescence quantum yield of

Fig. 2. Excitation spectra of the 640-nm (---) and the 710-nm (-----) emissions of Cu $\sim C_2H_4 \sim$ Zn in 2MeTHF at $77^\circ$K.
Fig. 3. Excitation spectra of the aminoethyleneamide-ZnCDP and the p-amino-phenyleneamide-ZnCDP 640-nm fluorences (---) and of the aminoethyleneamide-CuCDP and the p-aminophenyleneamide-CuCDP 710-nm phosphoresces (---) in 2MeTHF at 77°K.

the zinc 2-(β-aminoethylaminocarbonyl)-12, 17-diethyl-3, 7, 8, 13, 18-pentamethylporphin (hereafter referred to as aminoethyleneamide-ZnCDP) (see Appendix I) shows that there is no singlet-singlet energy transfer between the chromophores.

There is some interaction, however, between the copper moiety and the zinc porphyrin triplet states. This is manifest in a shortening of the zinc triplet lifetime from 45 ± 1 msec in aminoethyleneamide-ZnCDP to 35 ± 1 msec in Cu ~ C₂H₄ ~ Zn. The 70 μsec decay lifetime is, however, identical to the 710 nm phosphorescence decay lifetime of aminoethyleneamide-CuCDP. It will be shown that this quenching of the zinc moiety's triplet state is due to a small amount of triplet transfer to the Cu porphyrin.

Almost any triplet transfer mechanism as discussed below, requires overlap of the wavefunctions of the two moieties. This suggested that addition of a zinc complexing agent such as triethylamine (TEA) to the Cu ~ C₂H₄ ~ Zn-2MeTHF solution would reduce overlap and thus restore the natural lifetime of the zinc phosphorescence. With the addition of 0.05 ml of TEA to 2 ml of a Cu ~ C₂H₄ ~ Zn—2MeTHF solution, the zinc phosphorescence lifetime is 43 ± 1 msec which compares favorably with the 40 ± 2 msec phosphorescence lifetime of the aminoethyleneamide-ZnCDP in a similar solvent mixture. Furthermore addition of TEA produces a
change in the intensity ratio of the zinc chromophore $Q(0, 1)/Q(0, 0)$ bands in fluorescence and the mirror image $Q(1, 0)/Q(0, 0)$ bands in absorption. An identical change is observed in the zinc monomer.

**Co $\sim$ C$_2$H$_4$ $\sim$ Zn**

This compound shows three distinct luminescences. A fluorescence with peaks at 590 and 640 nm is observable at room temperature. At 77°K an additional, very weak luminescence with a decay lifetime of 51 ± 8 msec appears at 720 nm. An excitation spectrum of the fluorescence is presented in Fig. 4 and it shows that the fluorescence arises from excitation of the zinc moiety. A comparison of the fluorescence quantum yield with the fluorescence quantum yield of the aminoethyleneamide-ZnCDP shows that there is no difference in the two quantum yields and thus, there is no singlet-singlet energy transfer.

A comparison of the low temperature luminescence spectrum with that of the aminoethyleneamide-ZnCDP in Fig. 5 shows, however, that the zinc phosphorescence is quenched > 90% in the Co $\sim$ C$_2$H$_4$ $\sim$ Zn double porphyrin. Since the lifetime of the 720 nm luminescence agrees with that of the aminoethyleneamide-ZnCDP, the 720 nm luminescence may be attributed to the Zn $\sim$ C$_2$H$_4$ $\sim$ Zn impurity observed in the mass spectrum.

![Fig. 4. Excitation spectrum of the 640-nm emission of Co $\sim$ C$_2$H$_4$ $\sim$ Zn in 2MeTHF at 77°K.](image-url)
Fig. 5. Emission spectra of Co $\sim C_2H_4 \sim Zn$ (---) and of aminoethyleneamine-ZnCDP (-----) in 2MeTHF at $77^\circ$K excited by 541-nm light.

of the Co $\sim C_2H_4 \sim Zn$ (see synthetic section). However, the presence of this impurity does not affect our conclusions regarding energy transfer.

As in the case of Cu $\sim C_2H_4 \sim Zn$, the lack of triplet luminescence of the zinc moiety can be explained by triplet energy transfer to the cobalt porphyrin. Addition of TEA to the Co $\sim C_2H_4 \sim Zn$--2MeTHF solution restores the zinc phosphorescence as shown in Fig. 6. The zinc porphyrin absorption and fluorescence bands also undergo changes similar to the corresponding Cu $\sim C_2H_4 \sim Zn$ absorption and fluorescence bands upon addition of TEA to the Co $\sim C_2H_4 \sim Zn$--2MeTHF solution.

Since the efficient quenching of the Zn moiety triplet state might be due to the formation of the charge transfer state Co$^{3+} \sim C_2H_4 \sim Zn^{-1}$, as discussed below, an attempt was made to detect this species spectroscopically.

Absorption changes in the optical density of the Co $\sim C_2H_4 \sim Zn$--2MeTHF sample upon an intense flash excitation were investigated. The apparatus was able to detect transient changes in the range of 40 $\mu$sec and on the order of 0.1% in the optical density of various test samples. All attempts to detect transient changes in the sample optical density were unsuccessful from 380 to 650 nm, where the zinc anion porphyrin has an absorption band [11]. Transient bleachings of the cobalt or zinc moiety's Soret bands due to the formation of the charge transfer complex were also not observed.
Fig. 6. (a) Emission spectrum of Co ∼ C₃H₅ ∼ Zn in a solution of TEA and 2MeTHF at 77°K excited by 541-nm light. (b) Emission spectra of aminoethyleneamide-ZnCDP in a solution of TEA and 2MeTHF at 77°K excited by 541-nm light.
Fig. 7. Excitation spectra of the 640-nm (—) and the 710-nm (---) emissions of 
Cu \(\sim\) C\(_6\)H\(_4\) \(\sim\) Zn in 2MeTHF at 77°K.

\textbf{Cu \(\sim\) C\(_6\)H\(_4\) \(\sim\) Zn Double Porphyrin}

This compound shows three luminescences identical to those observed in 
the Cu \(\sim\) C\(_6\)H\(_4\) \(\sim\) Zn double porphyrin. Flash excitation of the 710 nm 
luminescence reveals the presence of two decay lifetimes; 85 \(\mu\)sec and 
46 ± 2 msec. The excitation spectra of these luminescences are presented in 
Fig. 7 along with the excitation spectra of the Cu and the Zn \(p\)-amino-
phenyleneamid-CDP metal complexes. As in the Cu \(\sim\) C\(_6\)H\(_4\) \(\sim\) Zn double 
porphyrin, the excitation spectra show that the two chromophores appear 
to be acting essentially independently. A comparison of the fluorescence 
quantum yield with that of the \(p\)-aminophenyleneamide-ZnCDP shows 
that there is no energy transfer from the Zn porphyrin singlet excited state 
to the copper porphyrin. Unlike the Cu \(\sim\) C\(_6\)H\(_4\) \(\sim\) Zn double porphyrin, 
the Zn phosphorescence lifetime of 46 ± 1 msec is approximately equal to 
lifetime of the \(p\)-aminophenyleneamid-ZnCDP phosphorescence. The 85 
\(\mu\)sec decay lifetime is also identical to the decay lifetime of the \(p\)-amino-
phenyleneamide—CuCDP phosphorescence.

\textbf{Co \(\sim\) C\(_6\)H\(_4\) \(\sim\) Zn Double Porphyrin}

This compound shows two distinct luminescences. A fluorescence is 
observed at room temperature with peaks at 590 and 640 nm. At 77°K an
additional luminescence appears at 740 nm. The emission spectrum at 77°K appears to be identical to the emission of the pure Zn p-aminophenyleneamide-CDP metal complex as shown in Fig. 8. Flash excitation shows that the decay time of the 740-nm luminescence is 48 ± 1 msec. The emission characteristics are, thus, identical to that of the pure p-aminophenyleneamide-ZnCDP. Excitation spectra of the 640- and 740-nm emissions are
identical to the 640- and the 740-nm excitation spectra of the pure p-aminophenyleneamide-ZnCDP.

DISCUSSION

A. Summary of Results

Experimentally we find that only the Zn moiety’s triplet state is affected by the presence of the Cu or Co chromophore. Furthermore this effect appears only in the ethylene-linked dimers. From fluorescence quantum yield measurements and excitation spectra we find that the zinc fluoresces as if the Cu or Co were not present. In the phenylene-linked dimers the zinc phosphoresces as if the Cu or Co were not present. In the ethylene linked Cu, Zn dimer the Zn phosphorescence lifetime is slightly shortened. In the ethylene-linked Co, Zn dimer the Zn phosphorescence disappears. Both of these effects disappear in the presence of TEA.

The shortening of the zinc phosphorescence lifetime in Cu ~ C₂H₄ ~ Zn must be due to the presence of a triplet decay mechanism. This mechanism could be a paramagnetic effect by the Cu which would, however, also reduce the Zn fluorescence quantum yield by enhancing the intersystem crossing rate, an effect that is not observed. Similarly, in Co ~ C₂H₄ ~ Zn the quenching of the Zn phosphorescence must be due to a triplet transfer mechanism, far more efficient than the mechanism present in Cu ~ C₂H₄ ~ Zn. This difference is due to either differences between the cobalt and copper metals or, as explained shortly, different geometries of the two dimers. One basic difference between Co porphyrin and Cu porphyrin is their electron transfer properties. Wolberg and Manassen have shown that oxidation of Cu tetraphenylporphin (TPP) proceeds with a potential of 0.99 eV and by abstraction of an electron from the ring [12]. However oxidation of CoTPP proceeds with a potential of 0.52 eV and by abstraction of an electron from the metal [12]. If we assume their geometries to be the same, the more efficient quenching in Co ~ C₂H₄ ~ Zn could be explained by formation of a charge transfer state followed by fast radiationless decay. In Cu ~ C₂H₄ ~ Zn, the triplet decay mechanism could be triplet exciton transfer by an exchange interaction or a dipole-dipole coupling; both of which will be shown to be less efficient in quenching the Zn triplet.

Unfortunately our attempts to verify spectroscopically a charge transfer state, Co⁺ ~ C₂H₄ ~ Zn⁻, were unsuccessful. If this state had a lifetime greater than 10 μsec our apparatus would detect it. From the quantum yield of φₑ = 0.04 and a natural radiative decay rate of 60 nsec, we obtain a singlet state lifetime of 2.4 nsec for Zn porphyrin. Thus our results can be
explained if the charge transfer state \( \text{Co}^+ \sim \text{C}_2\text{H}_4 \sim \text{Zn}^- \) lives in the time range \( 10^{-9} - 10^{-5} \) sec only, a result that seems quite possible.

If triplet exciton transfer were the mechanism in \( \text{Cu} \sim \text{C}_2\text{H}_4 \sim \text{Zn} \), we must, however, explain why we were unable to detect the zinc moiety's absorption bands in the excitation spectrum of the Cu phosphorescence. This may be due to the following factors: (1) Strong similarity between the two absorptions would make a difference hard to detect, especially with the high experimental error of \( \sim 5\% \). (2) The yield of triplet exciton transfer to the Cu is very low. At low optical densities the phosphorescence intensity of the aminoethyleneamide-CuCDP is similar to the Zn fluorescence expression derived in Appendix I:

\[
P = \Phi_p \Phi_{st} \text{ O.D. (Cu) } I_0 ;
\]

\( \Phi_p \) is the number of phosphorescing triplets per number of triplet states. \( \Phi_{st} \) has been shown to be approximately \( \sim 1.0 \) [13]. In the dimer, Eq. (1) has an additional term due to triplet exciton transfer from the Zn;

\[
P(\text{dimer}) = \Phi_p I_0 [\Phi_{st} \text{ O.D. (Cu)} + \phi_{tt} \Phi_{st} (\text{Zn}) \text{ O.D. (Zn)}],
\]

where \( \phi_{tt} \) is the triplet exciton yield. \( \phi_{tt} (\text{Zn}) \) can be estimated to be approximately \( \sim 0.2 \) [14]. \( \phi_{tt} \) is calculated from the magnitude of the triplet decay lifetime shortening to be 0.22. Therefore the relative change in the excitation spectrum of the Cu phosphorescence in the dimer is approximately \( 0.04 \) O.D. (Zn)/O.D.(Cu). From the TFA method described in Appendix I, the maximum ratio of the optical densities was found to be \( \sim 2.0 \) so that the maximum change in the spectrum would be approximately 8\%, very close to the experimental error of 5\%.

Both electron transfer and exchange interaction require overlap of the wavefunctions while dipole-dipole coupling falls off as \( R^{-3} \), where \( R \) is the intermolecular distance. TEA coordinates with zinc as shown by its effect on the relative intensity of the two visible bands. It would act to separate the Zn moiety from its partner and reduce the rate for all three mechanisms. The fact that TEA completely prevents quenching suggests that the quenching mechanisms are dependent on overlap mechanisms rather than dipole-dipole coupling. This conclusion is further supported by our estimate, given below, that triplet exciton transfer by dipole-dipole coupling is too slow to be of any importance.

**B. Geometrical Considerations**

The lack of any interaction between the porphyrin moieties in the phenylene linked dimers can be explained by geometrical considerations.
Fig. 9. (a) Spaced filling model of an ethylene-bridged double porphyrin. (b) Spaced filling model of a phenylene-bridged double porphyrin.
Space-filled molecular models of the double porphyrins were made and compared. The configurations of closest approach between the chromophores of both the ethylene and phenylene linked dimers are shown in Fig. 9. The only constraints were those imposed by the models. In the ethylene-bridged double porphyrins, the configuration of closest approach is one where the molecular planes overlap. The average distance between the metals of the chromophores is \( \sim 5 \) Å. In the phenylene-bridged double porphyrins, the configuration of closest approach is one where there is no overlap and the centers of the chromophores are separated by \( \sim 10 \) Å. The lack of interaction between the porphyrin moieties in the phenylene-linked dimers is readily explained if the triplet quenching mechanisms are dependent on overlap and if, at 77°K, the dimers assume the configuration of closest approach.

Closer inspection of the space-filling model for the ethylene bridged dimers suggests that the metal orbitals of one moiety overlap the porphyrin ring nitrogen orbitals of its partner. In crystals of Cu phthalocyanine which are similar in structure to the porphyrins a geometry of metal over nitrogen is found and seems somewhat more likely than metal over metal [15]. As will be shown below, such a geometry enhances electron transfer from the Co to the Zn porphyrin ring but decreases triplet exciton transfer. By assuming such a twisting of the porphyrin planes in the ethylene-linked dimers we can nicely account for our three observed phenomena: (1) Lack of any evidence for chromophore interaction in the phenylene-linked porphyrins is due to low overlap. (2) A slight reduction of the triplet lifetime in Cu \( \sim \) C\textsubscript{2}H\textsubscript{4} \( \sim \) Zn is due to triplet transfer by exchange coupling. (3) In Co \( \sim \) C\textsubscript{2}H\textsubscript{4} \( \sim \) Zn the fast quenching is due to charge transfer.

C. Estimate of Singlet Transfer Rate by Dipole-Dipole Coupling

From studies of the fluorescence spectrum, fluorescence yield, and the fluorescence excitation spectrum of the Zn moiety in the various dimers, we could find no evidence for any singlet energy transfer, which must be slow compared to the singlet lifetime of 2.4 nsec. Furthermore the lack of singlet energy transfer over distances where triplet exciton transfer is fairly efficient is itself a curiosity. Let us consider theoretical estimates for such rates based on dipole-dipole coupling.

The rate of energy transfer from state \( i \) to state \( f \) can be calculated from time dependent perturbation theory [16] to be:

\[
P_{i \rightarrow f} = (2\pi/\hbar) \rho(E) | V_{fi} |^2.
\]

In this expression \( \rho(E) \) is the density of states involved in the transfer and
$V_{fi}$ is the matrix element between final and initial states. For single-$e$ energy transfer the interaction matrix element is

$$V_{fi} = \left( \frac{e^2}{\epsilon R_{DA}} \right) [r_D r_A - 3(r_A \hat{r}_{DA} (r_A \hat{r}_{DA})].$$

Here $e r_D$ is the transition dipole for the first excited state of zinc porphyrin and $e r_A$ that for either the copper or the cobalt porphyrin acceptor; $\hat{r}_{DA}$ is a unit vector pointing from one dipole to the other; and $\epsilon$ is the dielectric constant.

Calculation of $P_{i \rightarrow f}$ by Eqs. (3) and (4) for nondegenerate initial and final states can give quite variable results depending on the relative orientation of $r_A$ and $r_D$, for we can have

$$0 \leq |V_{fi}|^2 \leq 4e^4 |r_A|^2 |r_D|^2/\epsilon^2 R_{DA}^6.$$

The average value of $|V_{fi}|^2$ for randomly oriented dipoles is

$$\overline{|V_{fi}|^2} = (2/3)e^4 |r_A|^2 |r_D|^2/\epsilon^2 R_{DA}^6.$$

In the case of porphyrin the initial and final states are doubly degenerate, so the rates $P_{i \rightarrow f}$ must be summed over final states and averaged over initial states to obtain the effective transition rate. The same result can be obtained by defining $|V_{fi}|^2_{\text{eff}}$ for use in Eq. (3) to calculate the effective transition rate. It is quite apparent that $|V_{fi}|^2_{\text{eff}}$ cannot vanish for the interaction of two degenerate pairs of states. Thus for the interaction of planar degenerate oscillators we do not risk an order of magnitude error if we set

$$|V_{fi}|^2_{\text{eff}} \sim 2 \overline{|V_{fi}|^2} = (4/3)e^4 |r_A|^2 |r_D|^2/\epsilon^2 R_{DA}^6.$$

We might note that for parallel porphyrin planes, with the center-center axis perpendicular to the planes, $|V_{fi}|^2_{\text{eff}} = 2e^4 |r_A|^2 |r_D|^2/\epsilon^2 R_{DA}^6$.

To calculate a value for Eq. (7) we note that $|r_A| \approx |r_D|$. These can be estimated from the observed oscillator strength $f \approx 0.04$ as

$$2e^2 |r_A|^2 = 2.13 \times 10^{-30} \nu^{-1} f \approx (2.2 \times 10^{-18} \text{ esu})^2.$$

(Note: $\nu \approx 1.82 \times 10^4 \text{ cm}^{-1}$ for the Zn 0, 0 absorption.) The distance between the chromophores $R_{DA}$ is $\sim 5 \text{ Å}$ in the ethylene linked dimer and $\sim 10 \text{ Å}$ in the phenylene linked dimer. The dielectric constant $\epsilon$ can be replaced by the square of the refractive index $n$ of 2 MeTHF. We found $n = 1.406$ at 25°C and for $\lambda = 589 \text{ nm}$. Using these estimates we obtain

$$|V_{fi}|^2_{\text{eff}} = (4/3n^4) [98 \text{ cm}^{-1}]^2$$

for ethylene linkage and for phenylene linkage

$$|V_{fi}|^2_{\text{eff}} = (4/3n^4)[12 \text{ cm}^{-1}]^2.$$

The density of states $\rho_E$ is determined from the spectral overlap between the donor $0,0$ emission band and the acceptor $0,0$ absorption band. We find $\rho_E \sim 7.4 \times 10^{-4}$ cm for a half width of 540 cm$^{-1}$ and a separation of the maxima of 323 cm$^{-1}$. (See Appendix II.)

Using this method we find a rate for singlet energy transfer of $P_{se} \sim 2 \times 10^{12}$ sec$^{-1}$ for the ethylene-bridged double porphyrin and $\sim 3 \times 10^{11}$ sec$^{-1}$ for the phenylene-bridged. The singlet decay rate is $4 \times 10^8$ sec$^{-1}$. Both of these rates are far higher than that of the singlet decay rate. We might well imagine errors in our various approximate quantities that might lower the energy transfer rate. However, these do not seem sufficient to lower it to the point where singlet energy transfer would be negligible compared to singlet decay. We therefore must assume the general formula is in error for these close distances.

There are other cases where singlet energy transfer rates calculated by a dipole model do not agree with experiment. Lamola et al. [17] found that the observed rate of intramolecular singlet energy transfer between 1-methylnaphthalene and 4-methyl benzophenone in, for example, 1-(1-napthyl)-2-(4-benzoylphenyl) ethane is slower than the rate calculated by the Förster equation which is based on a dipole-dipole interaction. In the case of 2-(4-p-terphenylyl methyl)-triphenylene, Brinen et al. [18] found, however, that the observed rate of intramolecular singlet-singlet energy transfer to be greater than the rate calculated from the Förster equation. Filipescu et al. [19] have observed efficient intramolecular triplet transfer between tetralin-1, 4-dione and fluorene chromophores. However they were unable to explain the lack of intramolecular singlet transfer between these chromophores.

**D. Estimate of the Triplet Transfer Rate by Dipole Coupling**

Triplet exciton transfer can also proceed by dipole-dipole coupling. Although a pure triplet excited state has no transition dipole to the ground state, the triplet contains some singlet component which by perturbation theory is:

$$\psi = \psi^0 + \sum_i \frac{\langle \psi_i^0 | H_{so} | \psi^0 \rangle}{(\psi_i^0 - \psi^0)} \psi_i^0.$$  \hspace{1cm} (5)

$H_{so}$ is the spin-orbit Hamiltonian that couples the pure singlet state $\psi^0$ into the pure triplet $\psi_i^0$. Ake and Gouterman [3] calculated a natural radiative lifetime of 3 sec for Zn octalkylporphin, which was reasonable in comparison with the luminescence data. From the absorption spectrum, the singlet radiative lifetime was found to be 60 nsec [2]. From this data we can deduce
for the ratio of the transition dipole of the triplet to that of the singlet:

$$[\mu(^3E_u)/\mu(^1E_u)]^2 = [\lambda_s/\lambda_t]^3 [\tau_s/\tau_t] \approx 4 \times 10^{-8}. \quad (6)$$

Here $\lambda_s$, $\tau_s$ and $\lambda_t$, $\tau_t$ are the singlet and triplet wavelengths and their natural radiative lifetimes.

For dipole-dipole transfer, the final state in either Cu or Co porphyrin will be the tripdoublet, which has a far larger transition dipole to the ground state than the quartet. Again Ake and Gouterman estimated the natural radiative lifetime for the tripdoublet in these molecules to be $\sim 70 \mu$sec, a result consistent with the observed luminescence lifetime of Cu porphyrin. Thus the transition dipole for the tripdoublet can be estimated by Eq. (6) to be

$$[\mu(^2T')/\mu(^2E_u)]^2 \approx 1.7 \times 10^{-3}, \quad (7)$$

where $^2T_1$ is the lowest energy tripdoublet and $^2E_u$ is the singdoublet.

Now the experimental singlet lifetime for the $^1E_u (Zn)$ excited state is $\sim 2.4 \times 10^{-9}$ sec. Singlet energy transfer by a dipole-dipole mechanism must be slow compared to this value. The triplet to tripdoublet energy transfer rate can be estimated to be slower by a factor of $(4 \times 10^{-8}) (1.7 \times 10^{-3}) = 6.8 \times 10^{-11}$. Thus the lifetime for such transfer should be long compared to $2.4 \times 10^{-9}$ sec $6.8 \times 10^{-11} = 35$ sec. Thus it would be far too slow to complete with triplet phosphorescence from Zn porphyrin, which has a lifetime of 45 msec.

E. Estimate of Triplet Transfer Rate by Exchange Coupling

For triplet exciton transfer the initial states can be represented by $^3E_u (Zn), ^3B_{1g} (Cu)$, which has a sixfold spin degeneracy. The final states are $^1A_{1g} (Zn)$- $^2E_u (Cu)$ and $^1A_{1g} (Zn)$- $^4E_u (Cu)$, where $^2E_u$ and $^4E_u$ are the tripdoublet and quartet states of the Cu moiety.

Exchange interaction is determined by the $e^2/r_{12}$ operator, which conserves spin. For all spin conserving transitions we find

$$V_{fi} = - \langle e(1)a'(2) | e^2/r_{12} | e'(1)a(2) \rangle \langle \chi' | \chi' \rangle \quad (8)$$

in Eq. (4) where $(a, e)$ are the $(\pi, \pi^*)$ orbitals of the Zn triplet, $(a', e')$ are those of the Cu triplet, and $\langle \chi' | \chi' \rangle$ is the Franck-Condon factor. We omit the dielectric constant of the solvent because exchange transfer occurs over very short dimensions. Note that the unpaired electron plays no role.

In Appendix II we describe in some detail how we estimate $\rho(E)$ and $V_{fi}$. Assuming that the Franck-Condon factor in $V_{fi}$ is unity and that the
molecule assumes the closest approach configuration for the ethylene bridged double porphyrin, we estimate \( P_{TT} \sim 2 \times 10^7 \text{ sec}^{-1} \).

This is much faster than the rate of 6 sec\(^{-1}\) observed for \( \text{Cu} \sim \text{C}_2\text{H}_4 \sim \text{Zn} \). However, \( P_{TT} \) depends on the fourth power both of the orbital overlap and of the Franck-Condon factor. The Franck-Condon factor might be such as to reduce \( P_{TT} \) by perhaps a power of ten; the rest of the reduction must come from unfavorable orbital overlap as discussed in Appendix II. In any case we see that theoretical estimates of maximum triplet transfer due to exchange coupling can easily account for the shortened lifetime of the Zn moiety in \( \text{Cu} \sim \text{C}_2\text{H}_4 \sim \text{Zn} \) and even for the quenching of the Zn moiety phosphorescence in \( \text{Co} \sim \text{C}_2\text{H}_4 \sim \text{Zn} \). The difference between the two can be explained by appeal to different orbital overlap.

### F. Triplet Quenching by Charge Transfer

As seen from Sec. E above, triplet exciton transfer is a mechanism that could lead to very fast triplet deactivation depending on the overlap of the porphyrin moieties. However, in view of the similarity of the two dimers, it is appealing to believe that the triplet transfer rate by exchange coupling is similar in both cases and that another mechanism accounts for the phosphorescence quenching in \( \text{Co} \sim \text{C}_2\text{H}_4 \sim \text{Zn} \). This mechanism would be

\[
{^2A_1}_g(\text{Co}) \cdot {^3E_u}(\text{Zn}) \rightarrow {^1A_1}_g(\text{Co}^+) \cdot {^2E_g}(\text{Zn}^-),
\]

with the complex decaying radiationlessly through rather different paths.

The formation of the state \( {^1A_1}_g(\text{Co}^+) \cdot {^2E_g}(\text{Zn}^-) \) involves the transfer of one electron from the \( d_{z^2} \) orbital on Co to the hole orbital of the Zn(\( \pi, \pi^* \)). The \( V_{fi} \) matrix element is

\[
V_{fi} = \langle {^1A_1}_g(\text{Co}^+) \cdot {^2E_g}(\text{Zn}^-) | H | {^2A_1}_g(\text{Co}) \cdot {^3E_u}(\text{Zn}) \rangle. \tag{9}
\]

There are six spin states for the initial state, corresponding to a tripdoublet and a quartet. The final state is a doublet. If \( H \) consists of the main spin independent terms, only the tripdoublet states can undergo charge transfer. If we take \( H \) as a sum of one electron kinetic and potential energy terms, we obtain for the tripdoublet coupling:

\[
| V_{fi} |^2 = (3/2) | \langle d_{z^2}(\text{Co}) | h | \pi(\text{Zn}) \rangle |^2, \tag{10}
\]

where \( h \) is the one electron operator and \( \pi \) is the Zn porphyrin hole orbital. We can assume that most of the two electron interaction is subsumed in the effective Coulomb potential of \( h \) so that the direct two electron coupling terms can be neglected. (We might note that the rate obtained from substitution of Eq. (10) into Eq. (4) would have to be divided by 3, for
among the six initial spin states two undergo transition by a rate set by Eq. (9) but four do not undergo transition.)

We can roughly compare the rate for electron transfer with the rate for triplet transfer by comparing $V_{ij}$, in Eqs. (8) and (10). We see that charge transfer depends on a one electron integral, which is linear in orbital overlap, while triplet transfer depends on a two electron integral, which is quadratic in orbital overlap. Both integrals will be quite dependent on the detailed dimer geometry. The matrix element of Eq. (8), as discussed in Appendix II, will be largest and give a triplet transfer rate greater than the observed rate if the orbitals of corresponding atoms are in positions of favorable overlap, i.e. metal-metal, nitrogen-nitrogen, etc. Such a geometry would tend to make the matrix element of Eq. (10) small, since the $d_{2z}$ of the Co atom would not overlap a very large $\pi$ density of the Zn porphyrin ring. The matrix element of Eq. (10) would be large if the metal of the Co porphyrin overlaps the nitrogen of the Zn moiety, which seems like a reasonable structure. Therefore in Cu $\sim \text{C}_{2}\text{H}_{4} \sim \text{Zn}$ triplet exciton transfer due to exchange coupling would explain the slow quenching of the Zn triplet while in Co $\sim \text{C}_{2}\text{H}_{4} \sim \text{Zn}$ the fast quenching would be attributed to charge transfer.

H. Biological Relevance

We undertook the study of double porphyrins since energy transfer in these systems is similar to, but far simpler than, that postulated to occur in photosynthesis [6]. In green plants light absorbed by chlorophyll, a magnesium dihydroporphin henceforth abbreviated Chl, is believed to be transferred from one “antenna” Chl to another until it reaches an active site termed $P_{700}$.

It is thought that this transfer takes place by inductive resonance processes, i.e., the Förster mechanism. Studies of energy transfer in model systems of monomolecular films containing Chl molecules indicate, however, show that energy transfer could also proceed by free or local exciton migration [20, 21]. Although the organization of Chl in the chloroplast is not well characterized, it is thought that they are in a planar array with parallel faces [22].

In view of the singlet energy transfer that is known to occur between Chl molecules [20, 21], the lack of singlet energy transfer between linked porphyrins is quite surprising. This is especially so since our studies suggest that in the ethylene-linked dimers the porphyrin planes are at the close-approach geometry of Fig. 9, a configuration similar to that proposed by Calvin for Chl in chloroplasts [22]. We can reconcile the lack of singlet
energy transfer between porphyrins found here with fast singlet energy transfer between Chl molecules as follows: Since the absorption intensity of Chl is \( \sim \) five times higher than in porphyrins, by Eqs. (4) and (7) we might expect singlet energy transfer to proceed \( \sim 25 \) times faster. On the other hand from the absorption intensity and fluorescence quantum yield, we expect that Chl and zinc porphyrin have comparable singlet excited state lifetimes. Thus fast singlet energy transfer between Chl units and slow transfer between metalloporphyrins are not contradictory.

With this in mind, our results give rise to several interesting suggestions concerning biological systems. It becomes clear why in the evolutionary process Chl molecules were favored over metalloporphyrins as energy transfer agents in chloroplasts and why metalloporphyrins have never been used even in the role of accessory pigments. They just would not adequately transfer energy. Our results also suggest that even between Chl molecules, singlet energy transfer by intermolecular hopping is not so fast as might have been supposed. Thus for efficient transfer from the "antenna" Chl to the active site an exciton mechanism involving the array may be necessary.

The partial quenching of the zinc porphyrin triplet in Cu \( \sim \) C\(_2\)H\(_4\) \( \sim \) Zn and its total quenching in Co \( \sim C_2H_4 \sim Zn \) also give some interesting possibilities. The former process occurs with a rate of \( \sim 10 \text{ sec}^{-1} \), and we have proposed it occurs by triplet transfer through exchange coupling. The latter process occurs faster than \( 10^5 \text{ sec}^{-1} \), which we have proposed occurs by electron transfer. Our results show that an almost overlapping configuration of the chromophores is needed for these processes to occur. The electron transfer mechanism postulated for the deactivation of the zinc triplet in Co \( \sim C_2H_4 \sim Zn \) has considerable resemblance to the following two steps that occur in bacterial photosynthesis [23]: (i) After energy is transferred to the active site an electron is ejected from bacteriochlorophyll with a rate of \( 10^4 \sim 10^{11} \text{ sec}^{-1} \). (ii) Subsequently, at a rate of perhaps \( 10^4 \sim 10^6 \text{ sec}^{-1} \), the oxidized bacteriochlorophyll is reduced by an adjacent cytochrome, whose active component is a ferrous porphyrin. Thus both in the quenching of the zinc porphyrin triplet reported here and in the photosynthetic processes a \( (\pi, \pi^*) \) excited state is degraded through the participation of a transition metal porphyrin. It is perhaps no accident that the quenching rate caused by the more readily oxidized Co porphyrin approaches that of the biological system containing readily oxidized ferrous porphyrin, while that caused by the Cu porphyrin is several orders of magnitude slower. Our results suggest the great importance of highly favorable overlap for such processes.

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APPENDIX I

For low total optical density (O.D.) it is easy to show that the fluorescence of a sample in a square cuvette is

\[ F_1 = 2.3 \Phi_1 \text{O.D.}_1 I_0 A, \quad (A.1) \]

where \( \Phi_1 \) is the quantum yield of the fluorescent species, O.D., is the optical density of this species, \( I_0 \) is the beam intensity (photons cm\(^{-2}\) sec\(^{-1}\)), and \( A \) is the beam area. In the case of the zinc monomer we measured O.D. directly whereas we had to calculate it in the double porphyrins.

We employed two methods to calculate the zinc chromophore's optical density. In the case of the Cu \( \sim \) C\(_6\)H\(_4\) \( \sim \) Zn and Co \( \sim \) C\(_2\)H\(_4\) \( \sim \) Zn, we determined O.D., from the zinc monomer extinction coefficients and from, resp., the extinction coefficients of the Cu \( \sim \) C\(_6\)H\(_4\) \( \sim \) Zn and Co \( \sim \) C\(_2\)H\(_4\) \( \sim \) Zn double porphyrins. Since the Cu \( \sim \) C\(_2\)H\(_4\) \( \sim \) Zn extinction coefficients are unknown, we used another method to calculate O.D.\(_1\) of this double porphyrin.

When a few drops of trifluoroacetic acid (TFA) are added to a solution of a zinc porphyrin in DCM, the zinc is displaced by protons resulting in a protonated free base porphyrin. Copper porphyrins are, however, stable to the TFA. Therefore addition of TFA to Cu \( \sim \) C\(_2\)H\(_4\) \( \sim \) Zn in DCM yields Cu \( \sim \) C\(_2\)H\(_4\) \( \sim \) H\(_4\). To compute the optical density of the zinc chromophore, we compared the optical changes of a Cu \( \sim \) C\(_3\)H\(_4\) \( \sim \) Zn—DCM solution upon addition of the TFA to the corresponding changes of the known optical density of an aminoethylene amide-ZnCDP—DCM solution. More specifically the percent absorption by the zinc chromophore was determined by the following:

\[ \text{O.D.}_1\% = \text{O.D.}_1/\text{O.D.}(\text{Cu } \sim \text{ C}_2\text{H}_4 \sim \text{ Zn}) = (1 - b)/(1 - a), \quad (A.2) \]

where \( b = \text{O.D.}(\text{Cu } \sim \text{ C}_2\text{H}_4 \sim \text{ H}_4)/\text{O.D.}(\text{Cu } \sim \text{ C}_2\text{H}_4 \sim \text{ Zn}) \) and \( a = \text{O.D.}_1 \) (monomer)/\( O.D. \) (aminoethylene amide-H\(_4\)CDP) with the condition that the concentrations and the cell depths are equal in each ratio. All optical densities are measured at the fluorescence excitation wavelength. Since the extinction coefficients of the zinc moiety vary with the solvent, we had to convert the \( \%\text{O.D.}_1 \) in DCM to the \( \%\text{O.D.}_1 \) in 2MeTHF. The following equation was used for this conversion:

\[ \text{O.D.}_1\%(2\text{MeTHF}) = cd \text{O.D.}_1\%(\text{DCM}), \quad (A.3) \]

\( c \) is the ratio of the zinc monomer extinction coefficient in 2MeTHF to that...
in DCM. \( d \) is the ratio of the extinction coefficient of Cu \( \sim C_2H_4 \sim Zn \) in DCM to that in 2MeTHF. We determined \( d \) by the following sequence of steps: (1) The O.D. of the dimer in DCM was measured. (2) The DCM was removed by evaporation and an equal volume of 2MeTHF was added to redissolve the Cu \( \sim C_2H_4 \sim Zn \) residue. (3) The O.D. of this solution was compared to the O.D. measured in step (1). Once the O.D. was determined in 2MeTHF it was but a simple matter to obtain the O.D. (Cu \( \sim C_2H_4 \sim Zn \)). To check this method we applied it the determination of O.D. in the Co \( \sim C_2H_4 \sim Zn \) double porphyrin. The cobalt chromophore was also observed to be stable to the TFA.

APPENDIX II

To evaluate the triplet transfer rate we need to know the density of states \( \rho_B \). This is given by [23]:

\[
\rho_B = \int_0^\infty F(E)f(E)dE, \tag{A.4}
\]

where \( F(E) \) is the band shape for the emission spectrum of the state donating excitation and \( f(E) \) is the band shape of the absorption spectrum of the state receiving the excitation. Both \( F(E) \) and \( f(E) \) are normalized to unity. If we assume both of these are gaussian with the same halfwidth \( \Delta \) and that the peaks of \( F(E) \) and \( f(E) \) are separated by energy \( \delta \), then it is easily shown that

\[
\rho_B = \frac{1}{\Delta} \left( \frac{1.38}{\pi} \right)^{1/2} \exp \left[ -1.38 \frac{\delta^2}{\Delta^2} \right]. \tag{A.5}
\]

For the case of triplet energy transfer from Zn to Cu we have \( \Delta = 173 \text{ cm}^{-1} \) and \( \delta/\Delta = 0.33 \), giving \( \rho_B = 1.6 \times 10^{-3} \text{ cm} \). For singlet energy transfer between these chromophores we have \( \Delta = 540 \text{ cm}^{-1} \) and \( \delta/\delta = 0.6 \), giving \( \rho_B = 7.4 \times 10^{-4} \text{ cm} \).

To estimate the electronic part of the triplet transfer matrix element of Eq. (5), we expand the wave functions:

\[
e = \sum_i c_i \phi_i, \tag{A.6}
\]

\[
a = \sum_j a_j \phi_j .
\]

Here \( c_i \)s, \( a_j \)s are MO coefficients, and \( \phi_i \), \( \phi_j \) are atomic orbitals on the Zn porphyrin moiety. The same expansion will hold for the Cu moiety.
Assuming a geometry so aligned that the orbitals of corresponding atoms overlap favorably, we obtain for the exchange integral

\[ K \equiv \langle e(1)a'(2) | e^2/r_{12} | e'(1)a(2) \rangle \]
\[ \approx \sum_i \sum_j c_i^2 a_i^2 \langle \phi_i(1)\phi_i'(2) | e^2/r_{12} | \phi_i'(1)\phi_i(2) \rangle. \]  (A.7)

Now the average value of \( c_i^2 \) and \( a_i^2 \) is \( N^{-1} \), where \( N \) is the number of atoms. If we keep only those cases where \( i = j \) (an underestimate), we estimate for the exchange integral

\[ K \sim (24)^{-1} \langle \phi_i(1)\phi_i'(2) | e^2/r_{12} | \phi_i'(1)\phi_i(2) \rangle. \]  (A.8)

For this basic two center, two electron integral, Jortner et al. [25] calculate a value of \( \sim 2 \text{ cm}^{-1} \) for orbitals separated by \( \sim 5 \text{ Å} \). Using this value in Eq. (A.8) we very crudely estimate \( K \sim 0.1 \text{ cm}^{-1} \). With this value for \( K \) and \( \rho_2 \approx 1.6 \times 10^{-3} \) we obtain \( P_{TT} \sim 2 \times 10^7 \text{ sec}^{-1} \) for the rate of triplet energy transfer by exchange interaction. Of course if the molecules are misaligned the simple sum of squares Eq. (A.7) would not hold and \( K \) would be greatly reduced. Another way \( K \) could be reduced is if the distance between the chromophores is larger. An increase from 5 to 6 Å reduces the integral by a factor of \( \sim 20 \) [23]. We tend to think our estimate for \( P_{TT} \) is an upper limit and a considerably smaller value is possible.

REFERENCES AND FOOTNOTES

7. Treatment of octaethylporphyrin (OEP) with pyridine and scandium trichloride gives the \( \mu \)-oxo dimer of Sc(III)OEP. Since scandium has only one naturally occurring isotope, the dimer is particularly useful as a standard when measuring high \( m/e \) values.
12. A. Wolberg and J. Manassen, J. Am. Chem. Soc. 92, 2982 (1970). The same oxidation of the ring of copper octaethylporphyrin (CuOEP) and the metal of CoOEP have also been observed. (D. Dolphin, R. H. Felton, D. Borg, and J. Fager, unpublished results.).
13. This assumption is based on the observations that there is no copper porphyrin fluorescence and the \( \phi_P\phi_{ST} \) of similar Cu porphyrins are \( \sim 0.6 \) [5].
14. J. B. Callis, Ph.D. thesis, University of Washington, Seattle, Washington 1970 has measured $\phi_{ST}$ in Zn etioporphyrin to be 0.7. The triplet decay lifetime of the Zn chromophore is 1.5 times faster than that of the Zn etioporphyrin whereas its phosphorescence quantum yield is quenched by a factor of five. Since it is reasonable to suppose that both Zn compounds have the same natural radiative lifetime, the additional decrease of phosphorescence must be due to a reduction of $\phi_{ST}$ by a factor of 0.3 in the aminoethyleneamide-ZnCDP and thus $\phi_{ST}(\text{Zn}) \sim 0.2$ in Eq. (2).