

1989 TECHNICAL PROGRESS REPORT

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Project Title: Photoinitiated Electron Transfer in Multi-chromophoric Species - Synthetic Tetrads and Pentads

Project Directors: J. Devens Gust, Jr. and Thomas A. Moore

Institution: Department of Chemistry, Arizona State University

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II. Technical Progress Report

A. Overall Research Goal. As discussed in detail in the original proposal document, this research project involves the design, synthesis and study of molecules which mimic many of the important aspects of photosynthetic electron and energy transfer. Solar energy conversion via photosynthesis is the ultimate energy source for essentially all life. In addition, most of mankind's energy needs are met by coal, oil, and other fossil fuels which are the result of ancient photosynthesis. Because photosynthesis is one of the most durable and, in its early steps, most efficient solar conversion "technologies", an understanding of the details of the process is crucial. This research project will lead to a better understanding of the energy conserving steps of photosynthesis via the study of synthetic model systems which abstract features of the natural photosynthetic apparatus. The knowledge gained from such studies could be used to design artificial photosynthetic systems which employ the basic physics and chemistry of photosynthesis to help meet mankind's energy needs.

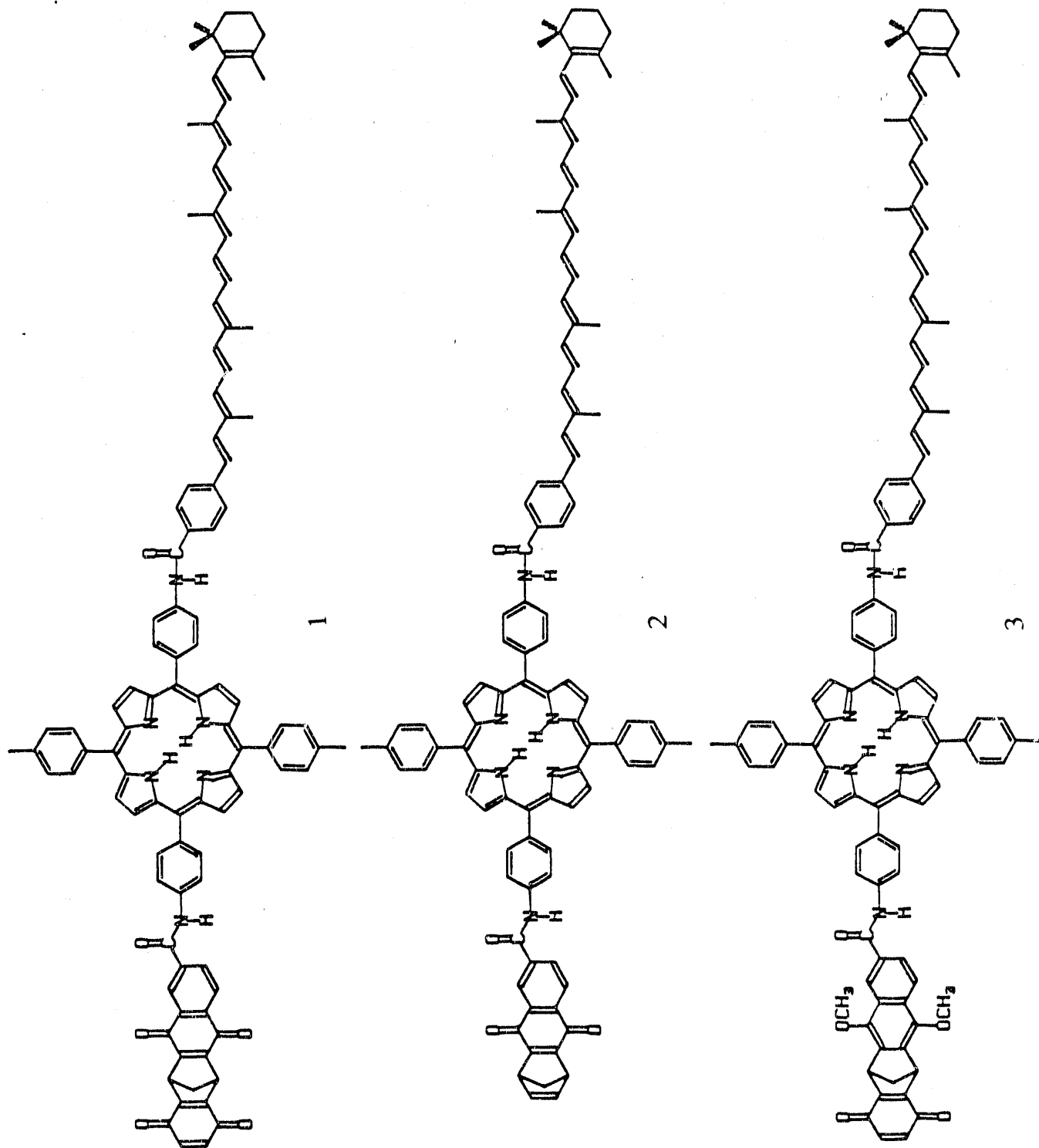
More specifically, the proposed models are designed to mimic the following aspects of natural photosynthetic multistep electron transfer: electron donation from a tetrapyrrole excited singlet state, electron transfer between tetrapyrroles, electron transfer from tetrapyrroles to quinones, and electron transfer between quinones with different redox properties. In addition, they will model carotenoid antenna function in photosynthesis

(singlet-singlet energy transfer from carotenoid polyenes to chlorophyll) and carotenoid photoprotection from singlet oxygen damage (triplet-triplet energy transfer from chlorophyll to carotenoids).

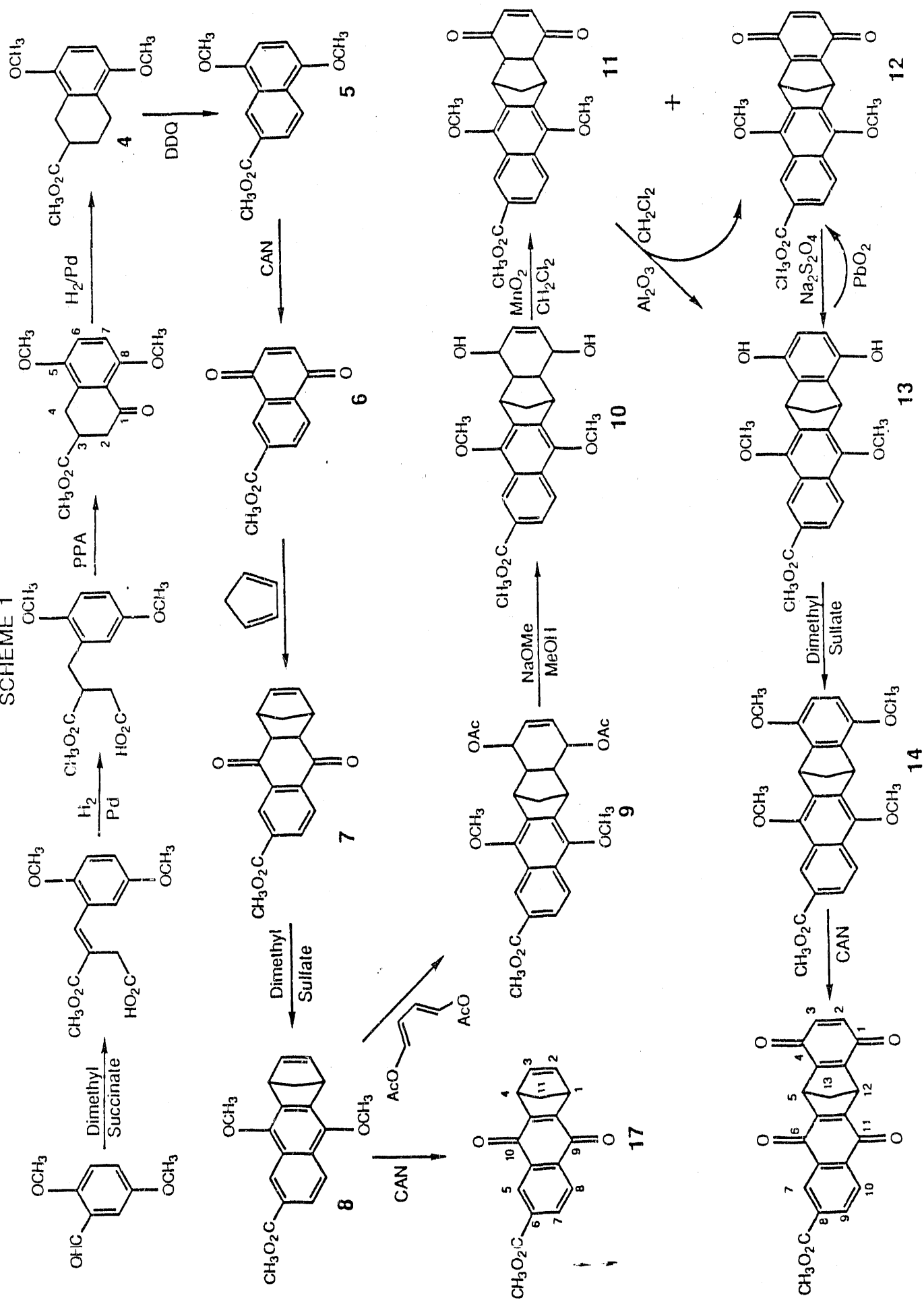
B. Progress To Date. The initial goal of the research was to prepare and study a molecular tetrad consisting of a porphyrin (P) linked to both a carotenoid polyene (C) and a diquinone moiety (Q_A-Q_B). This goal was achieved during the first year of the project with the synthesis of C-P- Q_A-Q_B species 1. Understanding the photophysics of 1 also required the preparation of model compounds 2 and 3. Preliminary photochemical studies of 1 - 3 were carried out last year, and were reported in a communication to the Journal of the American Chemical Society.¹

During the second year of the project, work performed included development of a higher-yield synthetic route to the key diquinone precursor of 1, new photophysical studies of 1 - 3 and some related molecules including a zinc derivative of 1, initiation of synthetic routes to several new tetrad and pentad molecules, and initiation of photoelectrochemical studies of 1 in Langmuir-Blodgett films. Each of these areas will be discussed briefly.

Improved synthetic scheme for preparation of the diquinone precursor. In last year's progress report, it was noted that preparation of new tetrad and pentad molecules required relatively large quantities of diquinone precursor 14 (see Scheme 1), and that this in turn required even larger amounts of dimethoxynaphthoic acid 6. Our original route to this material



SCHEME 1



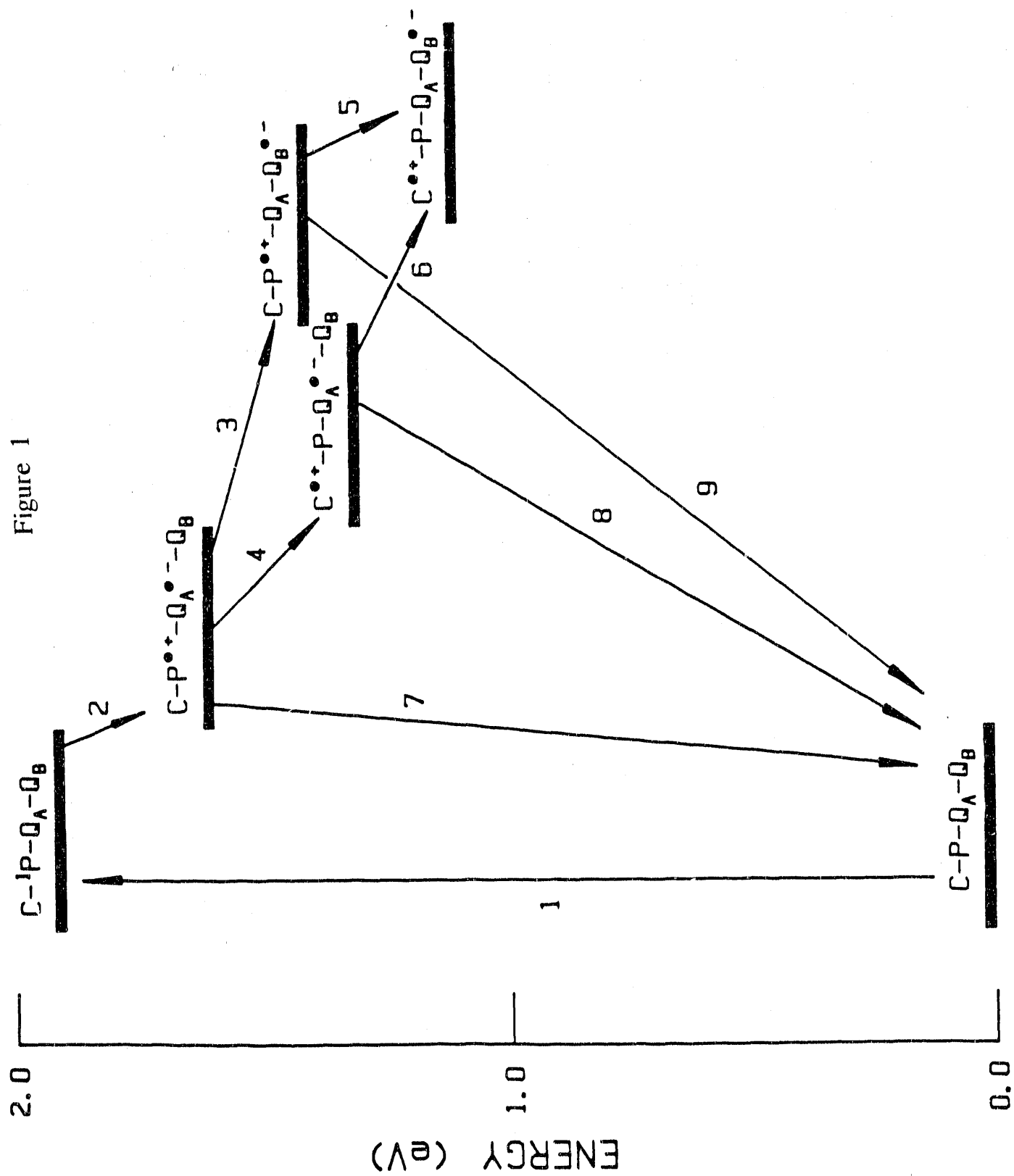
was complex, and the overall yield was not high. We have now developed a new synthetic route to 14 which incorporates a much more direct, higher-yield synthesis of 6. The new scheme is outlined in Scheme 1; using it, we have prepared ≈ 750 mg of 14. This is enough material to allow us to proceed with new tetrad and pentad syntheses, as outlined below. The preparation of molecules 1 - 3 and related model compounds and precursors, including 14, have been written up for a special Tetrahedron Symposium in Print issue which is now in press.²

New photophysical studies of tetrad 1, its zinc analog, and related materials. The photophysical and photochemical events following excitation of tetrad 1 are depicted in Figure 1. Excitation of the porphyrin generates the first excited singlet state, which donates an electron to the naphthoquinone to yield $C-P^{+}\cdots Q_A^{-}\cdots Q_B$ (step 2). By analogy with the triad systems previously studied in our laboratories, $C-P^{+}\cdots Q_A^{-}\cdots Q_B$ may go on to produce a second charge-separated state $C^{+}\cdots P-Q_A^{-}\cdots Q_B$ (step 4), which in turn undergoes a third electron transfer to yield the final $C^{+}\cdots P-Q_A-Q_B^{-}$ species. The $C-P^{+}\cdots Q_A^{-}\cdots Q_B$ state may undergo an additional reaction in which an electron is transferred between quinones to yield $C-P^{+}\cdots Q_A-Q_B^{-}$ (step 3). This species may also go on to give $C^{+}\cdots P-Q_A-Q_B^{-}$.

The rate constant for the photodriven electron transfer step 2 may be determined by using the relationship:

$$k_2 = (1/\tau) - (1/\tau_0) \quad \text{eq. 1}$$

where τ is the measured fluorescence lifetime of 1 and τ_0 is the lifetime of a model compound which has essentially the same



photophysics as 1, but which lacks the electron transfer step. Our initial attempts to determine k_2 yielded only a lower limit because the electron transfer was too fast to measure using the equipment which was available to us.¹ We have now completed the construction of a picosecond time correlated single photon counting fluorescence spectrometer with support from the DOE University Instrumentation Program. This state-of-the-art instrument uses an ultrafast Hamamatsu R2809U-01 microchannel-plate photomultiplier tube as the detector, and has an overall instrument response function of about 35 ps. Thus, fluorescence decays of less than 10 ps may be reliably deconvoluted from the response function.

Using this instrumentation, we measured the fluorescence decay for a solution of tetrad 1 in dichloromethane solution. The results are shown in Figure 2, which indicates that the significant component of the decay (>99%) was exponential with a lifetime of 15 ps. Suitable model systems lacking electron transfer to the quinone have lifetimes of 3.4 ns. Therefore, eq. 1 yields a value of $6.6 \times 10^{10} \text{ s}^{-1}$ for k_2 .

The quantum yield of the initial $\text{C-P}^+-\text{Q}_\text{A}^{\cdot-}-\text{Q}_\text{B}$ charge-separated state (Φ_a) may be calculated from:

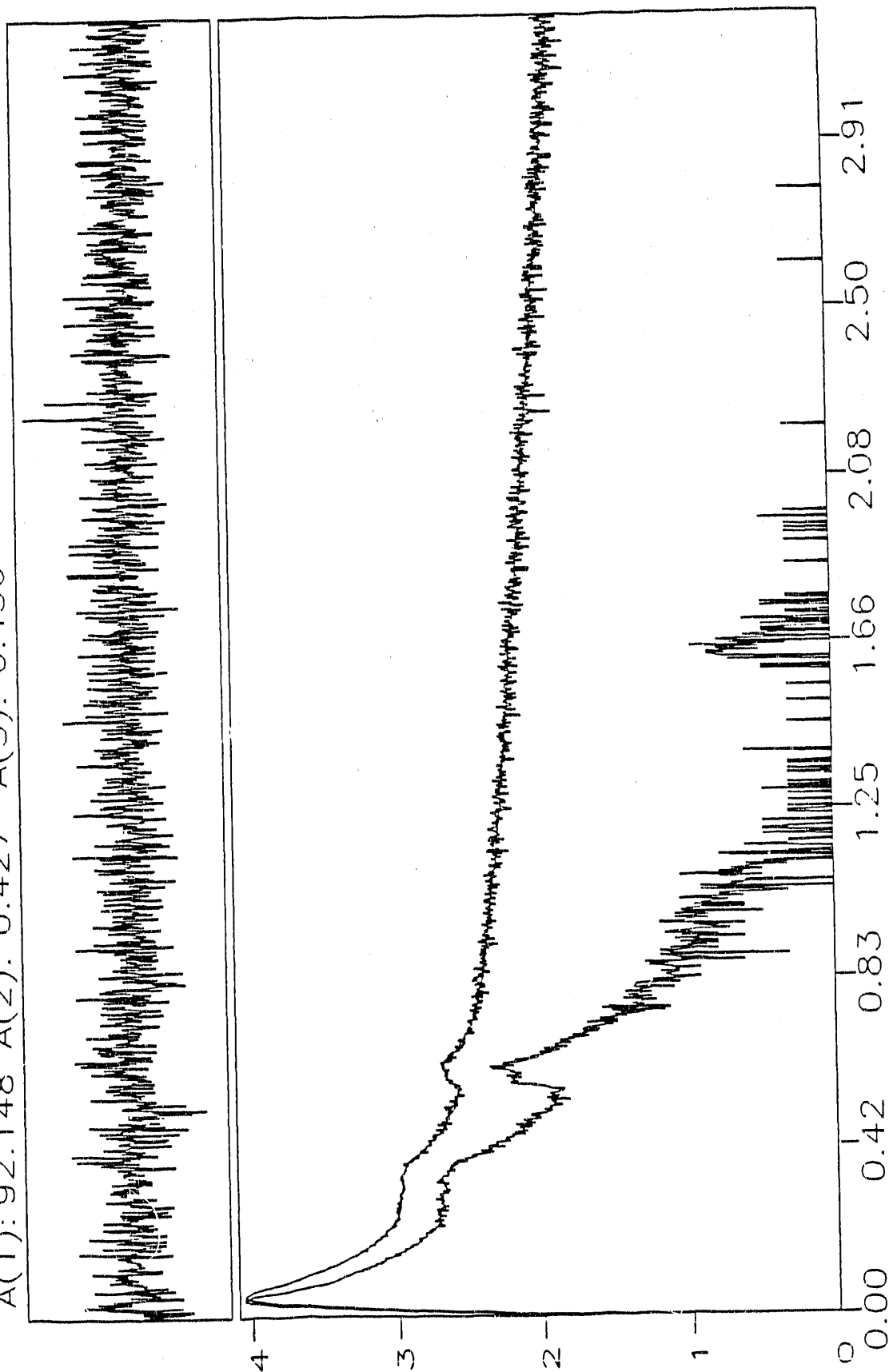
$$\Phi_\text{a} = k_2 \times \tau$$

Given that τ equals 15 ps for 1, Φ_a is 0.99. Thus, the photoinitiated electron transfer step is extremely efficient.

The zinc analog of 1 was recently prepared, and an investigation of its photochemistry has begun. A fluorescence lifetime for the $\text{C-}^1\text{ZnP-Q}_\text{A}-\text{Q}_\text{B}$ state of 5 ps was determined. This

Figure 2

Spectrum no.: 1888 Prompt no.: 1889 Date: 3-FEB-89
Subst.: CPQQ Shift: -1.777
Excitation: 590.0 nm Emission: 652.0 nm
X2glob: 1.035 X2: 1.035 Time/channel: 0.0021 ns
T(1): 0.015 T(2): 0.138 T(3): 1.998
A(1): 92.148 A(2): 0.427 A(3): 0.456



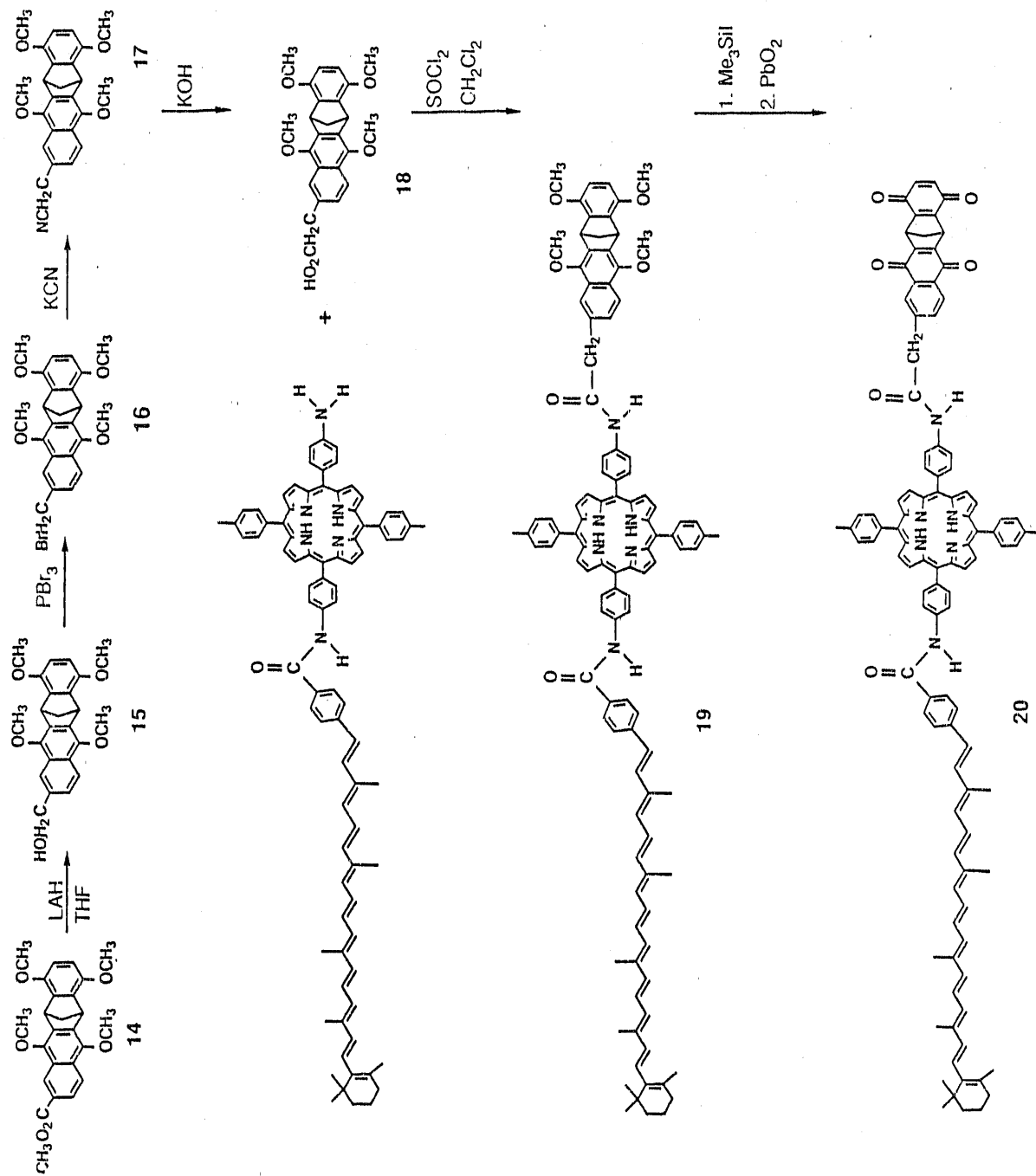
corresponds to an electron transfer rate constant of $2.0 \times 10^{11} \text{ s}^{-1}$ as calculated using eq. 1 and appropriate model compounds. The quantum yield of $\text{C-ZnP}^{++}\text{-Q}_\text{A}^{\cdot-}\text{-Q}_\text{B}$ is again essentially quantitative. The enhanced photoinitiated electron transfer rate constant for the zinc tetrad results from the fact that zinc substitution in the porphyrin not only raises the energy of the first excited singlet state to $\approx 2.1 \text{ eV}$ (vs. 1.9 eV for the free base), but would also be expected to lower the energy of P^{+} by about 300 meV relative to the free base porphyrin. Thus the thermodynamic driving force for the electron transfer is greatly increased, relative to 1.

The quantum yield of the final $\text{C}^+\text{-ZnP-Q}_\text{A}\text{-Q}_\text{B}^{\cdot-}$ state is only 70% that for the free base analog. This result is also reasonable. Lowering the energy of P^{+} will lower the thermodynamic driving force for steps 4 and 5 in Scheme 1, and therefore slow down these steps. The driving force for charge recombination reactions 7 and 9 will also be decreased, but as these reactions likely fall in the Marcus inverted region, this may well lead to an increase in the rates of these reactions. The net result of all of these effects can only be an overall decrease in the quantum yield of the final charge separated state, as is observed. This net negative effect of zinc substitution on quantum yield in spite of an overall increase in driving force for charge separation is an excellent example of the subtle interplay of competing and sequential electron transfer steps which make these complex molecular devices both interesting and challenging to study.

Synthesis of new C-P-Q_A-Q_B tetrads. As mentioned above, the very rapid electron transfer from the porphyrin first excited singlet state to yield C-P^{•+}-Q_A^{•-}-Q_B assures a quantum yield of essentially one for this step. The rapid transfer is a consequence of the relatively strong electronic coupling between the porphyrin and quinone moieties provided by the amide linkage. However, this strong coupling also must enhance the rates of charge recombination reactions 7, 8 and 9 in Figure 1, and this in turn leads to an overall quantum yield of less than one for the final C^{•+}-P-Q_A-Q_B^{•-} species (0.23 at ambient temperatures in dichloromethane). Decreasing the degree of coupling would slow down electron transfers 2, 7, 8 and 9, but should leave the rates of steps 3, 4, 5 and 6 virtually unchanged, because these steps do not involve electron transfer between the porphyrin and the quinone moieties. Decreasing the rate of step 2 by a factor of 10 would still give a quantum yield of 0.96 for the initial photoinitiated charge separation. On the other hand, a similar decrease by a factor of 10 in the rates of the charge recombination reactions should dramatically increase the quantum yield of the final state, and a quantum yield near one for that state should be possible.

In order to achieve this goal, we have begun the synthesis of tetrad 20 (see Scheme 2), which is identical to 1 with the exception of the insertion of a methylene group into the porphyrin-naphthoquinone linkage. As shown in the Scheme, the synthesis begins with the protected diquinone 14. Reduction of 14 to the alcohol 15 with lithium aluminum hydride is followed by

Scheme 2



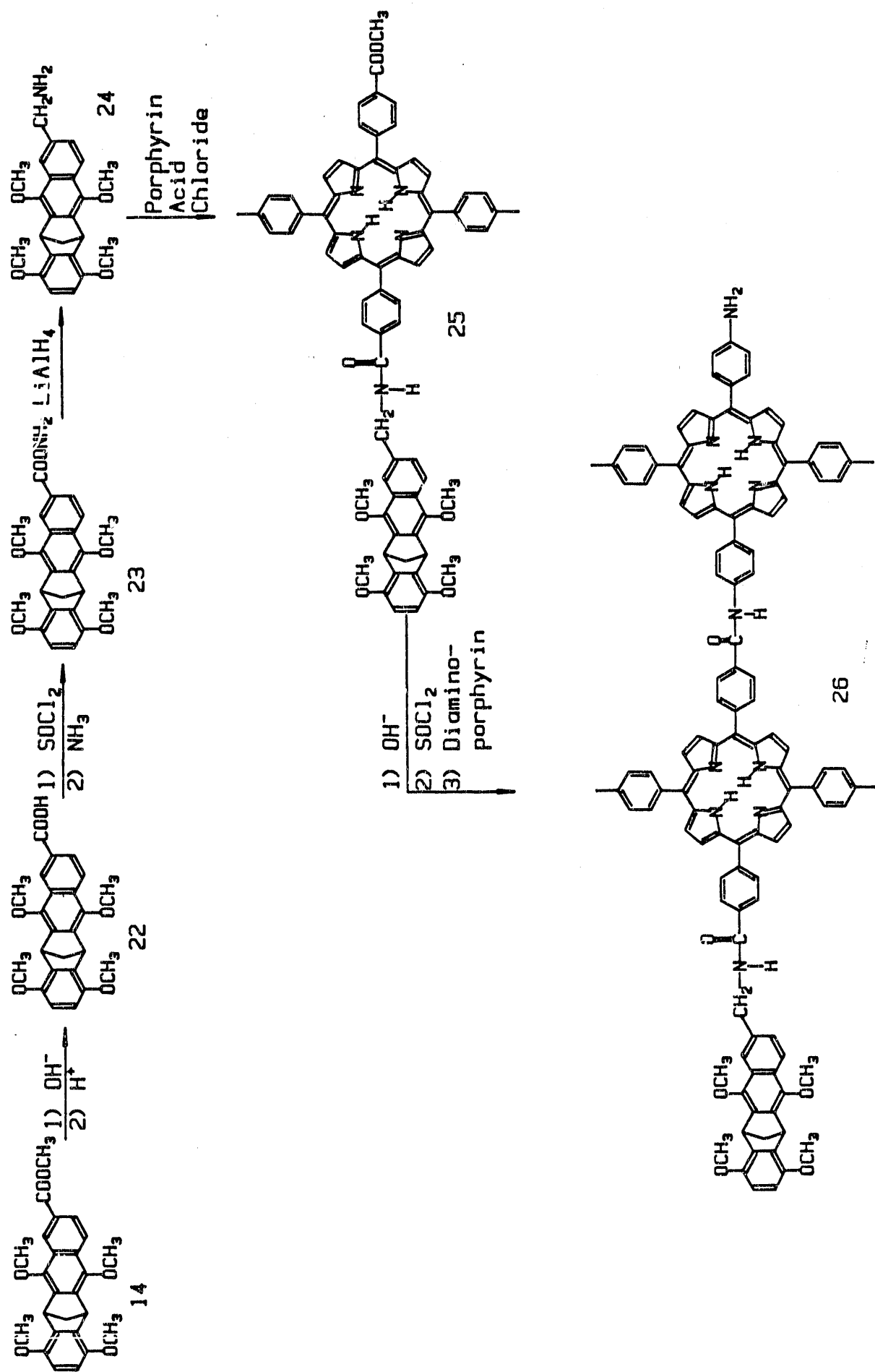
bromination with PBr_3 to yield benzyl bromide 16. The bromide is substituted by cyanide ion to yield 17, which is then hydrolyzed with aqueous sodium hydroxide to give a new acid 18. Thus far, 18 has been prepared and linked to the carotenoporphyrin moiety to yield the new tetrad in protected form (19). The final step will be removal of the methoxy groups using the methods developed during the synthesis of 1.

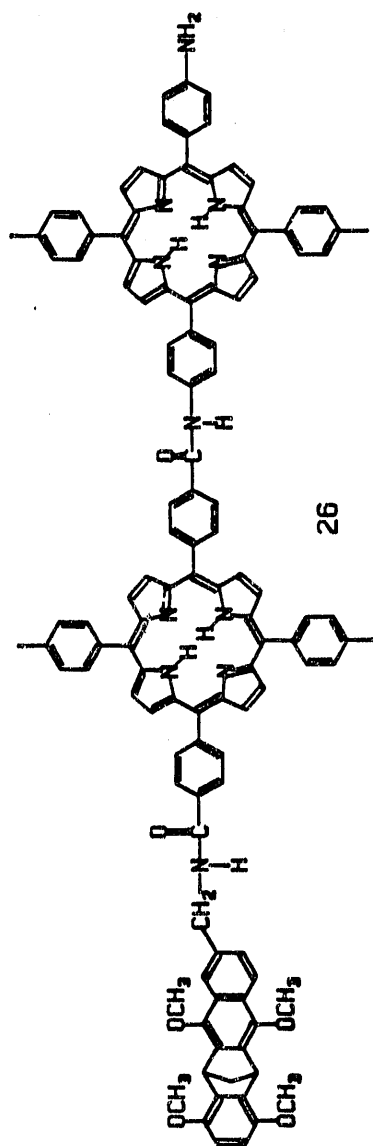
When the synthesis is complete, the photochemistry of the new tetrad will be investigated using the techniques which have been employed for 1 - 3.

Preparation of a C-P_A-P_B-Q_A-Q_B molecular pentad. The synthesis of the first of a planned series of pentad molecules (21, see Scheme 3) has also begun. The proposed route, diagrammed in the Scheme, begins with the preparation of the amide of protected diquinone acid 22. The amide (23) is reduced to the amine (24), which is then linked to a porphyrin to form amide 25. The methyl ester moiety of 25 is hydrolyzed with aqueous potassium hydroxide, and the resulting acid is linked to 5,15-(4-aminophenyl)-10,20-(4-methylphenyl)porphyrin via the acid chloride. The protecting methoxy groups are then removed from the quinones using trimethylsilyl iodide to yield 27, which is subsequently linked to a carotenoid acid to give the final pentad 21. At present, intermediate 25 has been prepared, and the synthesis is proceeding as expected. We anticipate completing it within the next few months.

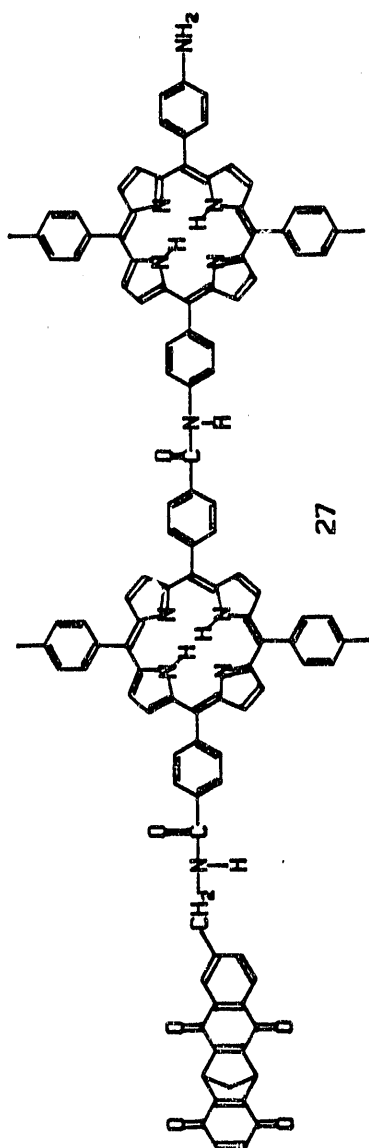
Photoelectrochemical studies of tetrads in monolayer films. Tetrad 1 undergoes relatively efficient photoinitiated electron

SCHEME 3



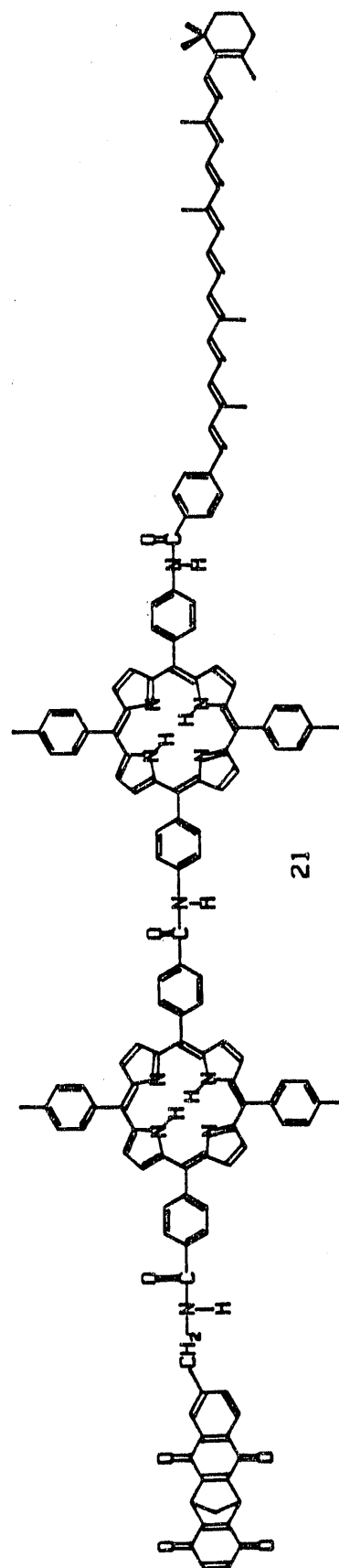


26



27

Carotenoid Acid Chloride



21

transfer to yield an energetic charge-separated state with a long lifetime. However, from a practical point of view, such charge separation is useless if the final state simply undergoes charge recombination to generate heat. Thus, the incorporation of molecular photovoltaic devices such as 1 into electronic or chemical circuits will be necessary if they are to be technologically useful. We have therefore begun some preliminary investigations of the behavior of 1 in monolayer films.

It is well known that certain materials form ordered monolayer films on the surface of water which may be deposited onto solid substrates to form layered structures (Langmuir-Blodgett films).³⁻⁷ The monolayers are stable and have a large surface area, which makes them amenable to a wide variety of spectroscopic and electrical measurements. In addition, there have been many proposals for the incorporation of such films into electronic devices. Because the nature of the various monolayers making up a multilayer array need not be identical, one may envision relatively complex devices consisting of stacked layers of chromophores, electron donors, acceptors, etc. Several systems of this type have been studied, especially by Kuhn, Mobius and coworkers.⁶ Chlorophylls, porphyrins, quinones and carotenoids may be incorporated into these monolayers, where they show a variety of photoelectrochemical effects.

Most of the monolayer-based devices prepared to date are limited in that the monolayer imposes order in one dimension, but not in the other two. For example, a monolayer containing an electron donor in some matrix material may be deposited onto a

second monolayer containing an acceptor in a similar matrix. Although this arrangement constrains the donor-acceptor separation normal to the plane of the monolayers, it does not limit the separation in the lateral dimensions; a donor in one layer may be very far from an acceptor in the other, even though the layers are in contact. In order to circumvent this problem, most workers use pure monolayers or very high concentrations of the active species. This in turn favors aggregation and/or domination of the observed properties by intermolecular effects including energy migration and the quenching of excited states or charge-separated states. Multicomponent molecular devices such as tetrad 1 ensure the desired relative relationships of chromophores, donors, acceptors, etc. by virtue of the covalent linkages, but the orientation of these devices in solution is isotropic. Incorporation of these devices into monolayer films should allow one to study monomolecular properties in an ordered environment, and in addition will allow the electrical contacts necessary for investigation of the tetrads as components of electrical circuits.

Some very preliminary work has been performed with 1. Monolayers of pure 1 were prepared in a Nima "Langmuir-Blodgett Trough" by depositing a chloroform solution of the tetrad on the surface of deionized water, and compressing the resulting film. The associated pressure-area isotherm is shown in Figure 3. The monolayer at 37 mN/m was deposited onto a clean glass slide by dipping. The UV-VIS spectrum of this monolayer (Figure 4) shows

Figure 3

Pressure-Area Isotherm for Tetrad I

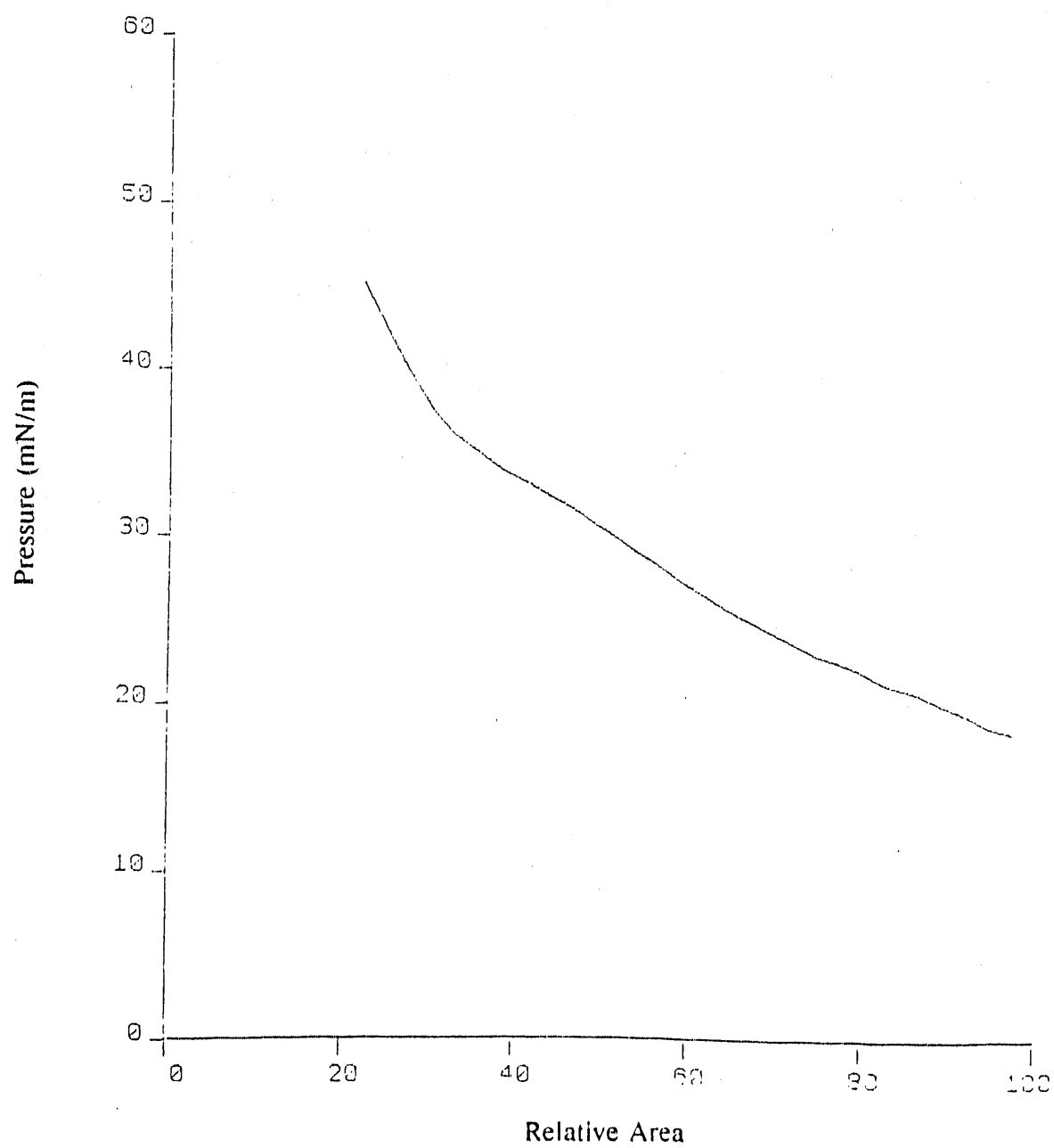
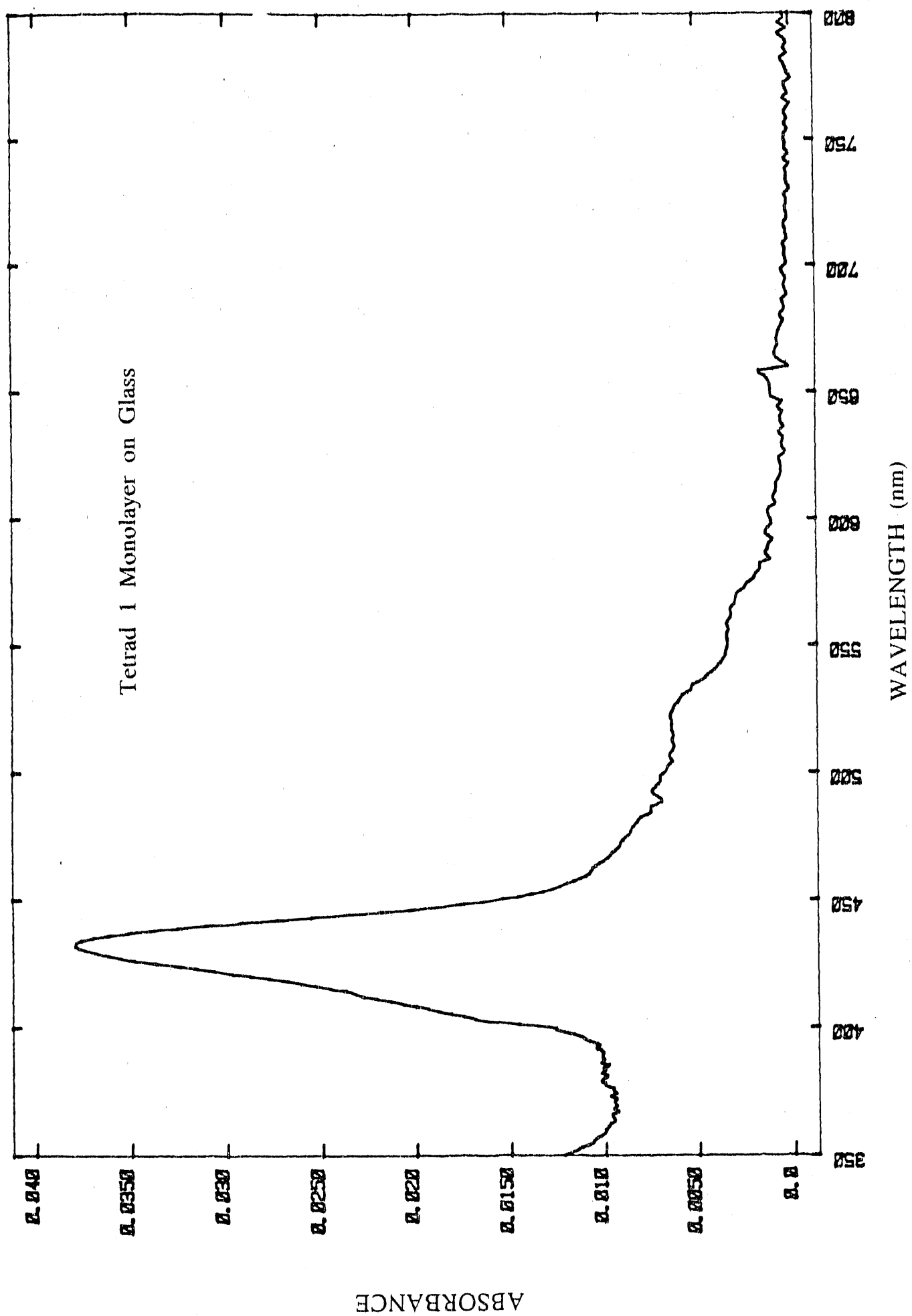


Figure 4



characteristic absorptions, although some broadening of the bands (especially those of the carotenoid) is evident.

The tetrad monolayer has also been deposited on a transparent (~ 200 Å) gold film which serves as the bottom electrode of an electrochemical circuit. A mercury drop placed on top of the monolayer serves as the other electrode. In an initial experiment, illumination of the monolayer through the gold film with visible light resulted in the observation of a photovoltage, but many more experiments must be done before this result can be confirmed and the nature of the photovoltage can be determined.

This report has provided a brief summary of the results obtained thus far in the project. The publications listed on pp. 21-22 of this report should be consulted for details. A general review of the project is included in an article by Gust and Moore which appeared in Science magazine in April, 1989.⁸

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III. Publications and Presentations Resulting From This Work: 1988-89

1. "Photoinitiated Charge Separation in a Carotenoid-Porphyrin-Diquinone Tetrad: Enhanced Quantum Yields via Multistep Electron Transfers," Devens Gust, Thomas A. Moore, Ana L. Moore, Donna Barrett, Larry O. Harding, Lewis R. Makings, Paul A. Liddell, F. C. De Schryver, M. Van der Auweraer, René V. Bensasson and Michel Rougée, J. Am. Chem. Soc. 1988, 110, 321-323.
2. "Carotenoporphyrin Quinone Triads and Tetrads as Reaction Center Mimics: Strategies for Control of Electron Transfer Rates," Devens Gust and Thomas A. Moore, Japan-US Information Exchange Seminar: Chemical Approach to the Photosynthetic Reaction Center, held in Lake Biwa, Japan, January 10-14, 1988.
3. "Enhanced Quantum Yields in Reaction Center Models via Multistep Electron Transfers," Devens Gust, International Minisymposium on Synthetic Model Approach to Photosynthetic Reaction Center, ISIR, Osaka University, January 16, 1988.
4. "Mimicry of Photosynthetic Charge Separation in a Carotenoid-Porphyrin-Diquinone Molecular Tetrad," Devens Gust, Thomas A. Moore, Ana L. Moore, Donna Barrett, Larry O. Harding, Lewis R. Makings and Paul A. Liddell, Biophysical Journal 1988, 53, 271a.
5. "Mimicry of Photosynthetic Charge Separation - Multistep Electron Transfer Reactions in a Carotenoid-Porphyrin-Diquinone Molecular Tetrad," Larry O. Harding, Ana L. Moore, Donna Barrett, Lewis R. Makings, Paul A. Liddell, Devens Gust and Thomas A. Moore, Photochem. Photobiol. 1988, 47S, 17S.
6. "Long-Lived, Photoinitiated Charge Separation in a Carotenoid-Porphyrin-Quinone Molecular Tetrad," Devens Gust, Thomas A. Moore, Ana L. Moore, Donna Barrett, Larry O. Harding, Lewis R. Makings and P. A. Liddell, Twelfth DOE Solar Photochemistry Research Conference, Airlie, VA, May, 1988.
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10. "A Carotenoid-Porphyrin-Diquinone Tetrad: Synthesis, Electrochemistry and Photoinitiated Electron Transfer," Devens Gust, Thomas A. Moore, Ana L. Moore, Gilbert Seely, Paul A. Liddell, Donna Barrett, Larry O. Harding, Xiaochun C. Ma, Seung-Joo Lee and Feng Gao, Tetrahedron, in press.
11. "Mimicking Photosynthesis," Devens Gust and Thomas A. Moore, Science 1989, 244, 35-41.

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