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Artificial Photosynthesis Using Chlorophyll Based Carotenoid Quinone Triads

A Brief Synopsis of Research Progress as of 31 Dec 1986 for DOE SOLERAS Grant No. DE-FG02-84CH10198

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Devens Gust

Devens Gust Date

A. Moore

Thomas A. Moore Date

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DISCLAIMER

A major aspect of the proposed research has been the design, synthesis and study of a series of carotenoid-chlorophyll-quinone triad molecules which mimic some of the basic photochemistry and photophysics of natural photosynthesis. The first members of this series have now been prepared, and have been found to mimic photosynthetic charge separation, carotenoid antenna function, and carotenoid photoprotection from singlet oxygen damage. The results have recently appeared in press (J. Am. Chem. Soc. 1986 108, 5350 and Nature 1986 322, 570, see enclosed reprints).

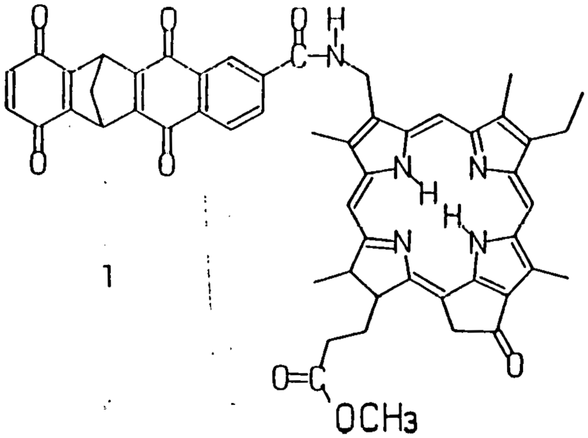
Although the triad molecules mimic the general principle of multistep electron transfer which is found in natural photosynthesis, the details of photosynthetic electron transfer differ in some respects from those of the model systems. For example, in the triads, the first electron transfer step involves electron donation from the excited state donor, followed by reduction of the resulting donor radical cation by the carotenoid. In photosynthesis, the electron is moved through several acceptors before the chlorophyll radical cation is reduced. Therefore, our recent work has concentrated on the design and synthesis of new model systems which better mimic certain aspects of natural photosynthesis.

As mentioned in this year's grant proposal, a potentially more exact mimic of photosynthetic electron transfer might be a P-Q-Q' system wherein the porphyrin donor is linked covalently to a quinone acceptor Q, which in turn is attached to a second acceptor quinone Q' which is more easily reduced:

$$\text{P-Q-Q} \xrightarrow{h\nu} {}^{1}\text{P-Q-Q} \longrightarrow \text{P}^{+\cdot}\text{-Q}^{-\cdot}\text{-Q} \longrightarrow \text{P}^{+\cdot}\text{-Q-Q}^{-\cdot}$$

Sakata, Mataga and coworkers (J. Am. Chem. Soc. 1983 105, 7771) have prepared and studied a system of this type. The synthetic approach was quite elegant, but the photophysical studies revealed that no significant enhancement of the lifetime of the charge separated state had been achieved. Examination of the structure of this molecule suggests that the reason for the failure is quite likely the utilization of flexible polymethylene bridges between the various moieties involved. These bridges allow the last quinone moiety (Q′) to fold back across the porphyrin. This in turn would result in rapid charge recombination, and possibly in elimination of the first electron transfer step as well (i.e. direct photodriven electron transfer from P to Q′).

We are now engaged in a new attempt to mimic this aspect of photosynthetic electron transfer by preparing and studying 1 and 2. Triad 1 features a pyropheophorbide linked through an amide bond to a rigid moiety which bears two quinones. The one closest to the tetrapyrrole is a naphthoquinone, whereas the second is a benzoquinone analog. The second quinone is a much better



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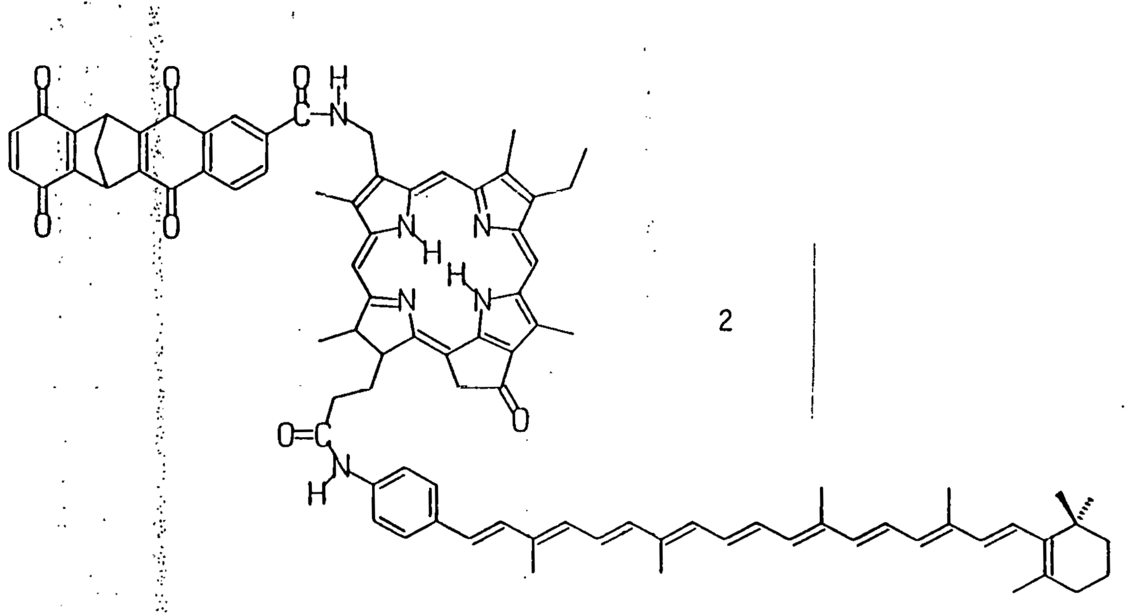

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electron acceptor than the naphthoquinone, and this should ensure that the two-step electron transfer outlined above will occur. The rigid linkage will prevent the quinones from folding back under the tetrapyrrole. Tetrad 2 features the same quinone system, but includes a carotenoid moiety. This structure would in theory permit the following electron transfer sequence:

$$\mathrm{C{-}P{-}Q{-}Q} \dashrightarrow \mathrm{C{-}{}^{1}P{-}Q{-}Q}$$

$$\mathrm{C{-}{}^{1}P{-}Q{-}Q} \dashrightarrow \mathrm{C{-}P^{+\cdot}{-}Q^{-\cdot}{-}Q}$$

$$\mathrm{C{-}P^{+\cdot}{-}Q^{-\cdot}{-}Q} \dashrightarrow \mathrm{C{-}P^{+\cdot}{-}Q{-}Q^{-\cdot}}$$

$$\mathrm{C{-}P^{+\cdot}{-}Q{-}Q^{-\cdot}} \dashrightarrow \mathrm{C^{+\cdot}{-}P{-}Q{-}Q^{-\cdot}}$$

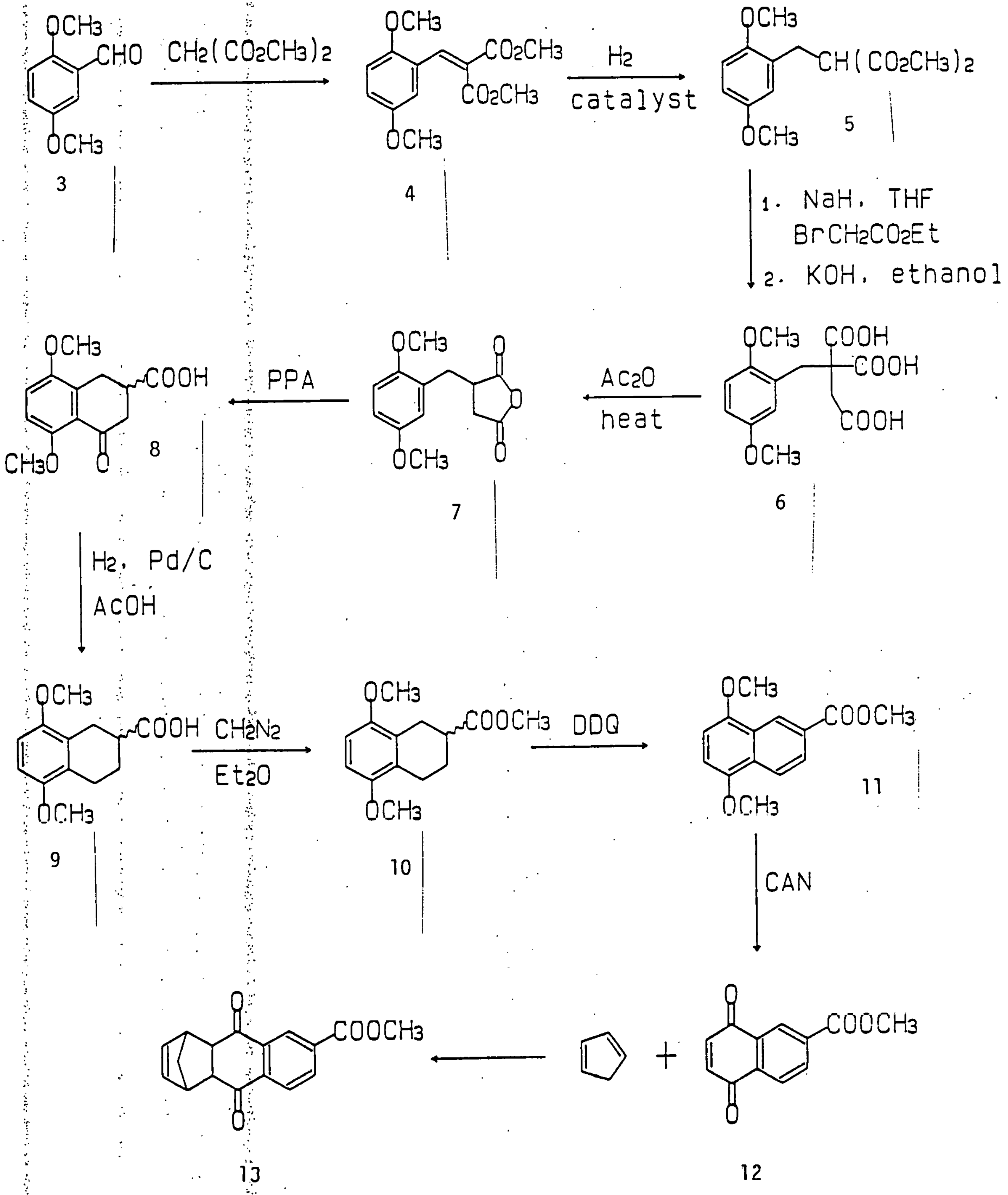
The linkages chosen for the quinone portion of the molecule should allow the first two electron transfer steps to occur quickly. The resulting state should then have a long lifetime, and this should ensure that the carotenoid will have plenty of time to reduce the pyropheophorbide radical cation in spite of its rather long linkage.

The main synthetic challenge in the preparation of 1 and 2 has proven to be the preparation of the rigid quinone moiety. However, as of December, 1986, the synthesis of this structure is nearly complete. The route employed is shown in Figure 1. Condensation of 2,5-dimethoxybenzaldehyde 3 with dimethyl malonate yielded 4, which was catalytically hydrogenated to 5. Treatment of 5 with sodium hydride and ethyl bromoacetate followed by saponification yielded triacid 6, which was decarboxylated and dehydrated by heating with acetic anhydride. The resulting anhydride 7 was cyclized with polyphosphoric acid to yield 8 as a pair of enantiomers. Reduction of the keto group gave 9, whose methyl ester was oxidized to the protected naphthoquinone 11. Treatment with ceric ammonium nitrate yielded quinone 12 which underwent the Diels-Alder reaction with cyclopentadiene to yield 13. Methylation of 13 followed by a second Diels-Alder reaction gave 15 as a mixture of diastereomers, which could be deacetylated and then oxidized to 16 with manganese dioxide. Molecule 16 rearranged smoothly with alumina to yield 17 as a pair of enantiomers. The final step in the synthesis, treatment of 17 with trimethylsilyl iodide to yield diquinone 18, has not as yet been carried out, but this should be accomplished within the next few weeks. After 18 is prepared, it will be coupled to pyropheophorbides or carotenopyropheophorbides to yield 1, 2 and/or related triads and tetrads.

As with the compounds which we have previously studied, ^{1}H NMR will be used to determine the solution conformations of the new triads and tetrads. The main photophysical tools for the study of these molecules will be nanosecond laser flash photolysis and nanosecond or picosecond fluorescence lifetime measurements. Picosecond absorption studies may well be necessary, and if this is the case, collaborative arrangements to carry them out will be made.

We expect that the synthesis of at least some of these new triads and tetrads will be completed before the expiration of the grant period. Funds for the continuation of this work are currently being sought from other sources.

Figure 1



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OCH3
3
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CO2CH3
CO2CH3
OCH3
4
H2
catalyst
OCH3
CH(CO2CH3)2
OCH3
5
1. NaH, THF
BrCH2CO2Et
2. KOH, ethanol
OCH3
COOH
COOH
COOH
OCH3
6
Ac2O
heat
OCH3
O
O
O
OCH3
7
PPA
OCH3
COOH
CH3O
O
8
H2, Pd/C
AcOH
OCH3
COOH
OCH3
9
CH2N2
Et2O
OCH3
COOCH3
OCH3
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CAN
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+
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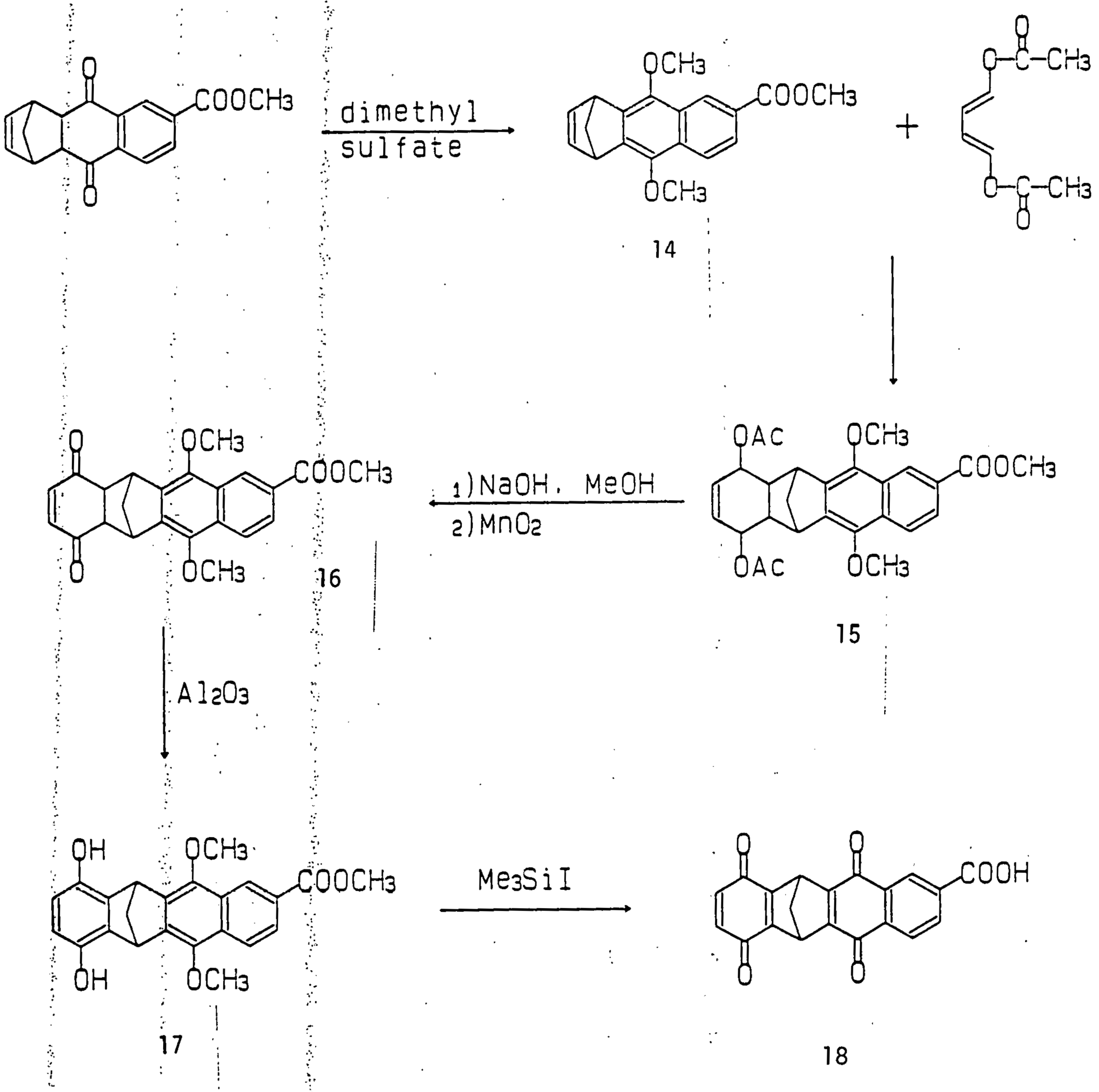
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O-C-CH3
OAc
OCH3
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OAc
OCH3
15
1) NaOH, MeOH
2) MnO2
OCH3
COOCH3
OCH3
16
Al2O3
OH
OCH3
COOCH3
OH
OCH3
17
Me3SiI
COOH
18