

From the Executive Director

D.C. Neckers, Center for Photochemical Sciences

Frank Whittle died last summer. Who's Frank Whittle? Whittle invented the jet engine, but he never made a dime. As a 21-year-old graduate student at the RAF's college at Cranwell, he wrote a thesis entitled "Future Developments in Aircraft Design," and in 1930 he was awarded the first patents for a gas turbine jet engine that could fly a plane at 500 miles/hour. According to columnist Richard Reeves, whose article in the **Buffalo News** called this to my attention, "Thus began a wild tale of government stupidity, brilliance and risk that damn near cost the Allies victory in World War II". The British government did not classify Whittle's invention as crucial to national security while manufacturers of piston engines applauded. Soon enough, however, there was applause in Berlin as the Luftwaffe, using Whittle's calculations, developed the first jet plane much to Britain's horror.

Whittle raised no more than \$5,000 to develop his invention, and he moved to the United States shortly after the war. By the time jet planes became commercial, his 1930 patent was long since beyond the statute of limitations.

Science and technology is replete with examples of well-reasoned, conservative stupidity such as Reeves claimed, was the wont of the British government. It's also replete with examples of the well-reasoned being sold a technical bill of goods. The question is when is a good idea worth a serious investment of capital by private funds or the government's largesse?

First let's state the obvious. If I knew the answer, I'd be debating Ross Perot, rather than writing columns in a Bowling Green, Ohio newsletter. But besides that, there are probably some clues in the comparison of Edison and Carlson with Whittle, or for that matter Leo Szilard who held a patent on the atomic bomb.

Edison and Carlson were singled-minded about pursuing their inventions. Szilard pursued theoretical physics. A patent on atomic energy was an afterthought. Whittle was a pawn of his government. At the time of his invention, he was a government employee and, perhaps, too young. Brilliant though his invention might have been, the requirements for developing it as a commercial product, let alone selling it to anybody, were beyond him.

Therein lies the rub! How does one determine if an invention might be a salable product? How long does one wait? What is it worth? And what role does government play? Perhaps one way to tell is just how much is the inventor investing in the invention. Another is where is his government or his university?

Unfortunately, those who read of Edison's, Carlson's, or Ford's success forget their many years of failure. An invention/patent is but a hunting license. He who shoots the game stalks often the field and waits long.

In This Issue

From the Executive Director	1
Chlorosome Antennas from Green Photosynthetic Bacteria	2
Medical Applications of Stereolithography	8
Mimicking Charge Separation of the Bacterial Photosynthetic Reaction Center with Porphyrin Arrays	11
Students Available for Employment	14

Chlorosome Antennas from Green Photosynthetic Bacteria

Robert E. Blankenship

Department of Chemistry and Biochemistry, Arizona State University

Introduction

The vast majority of the pigments in a photosynthetic organism are not chemically active but function primarily as an antenna.^{1,2} The photosynthetic antenna system is organized to collect and deliver excited state energy by means of excitation transfer to the reaction center complexes where photochemistry takes place. The antenna system increases the effective cross section of photon absorption by increasing the number of pigments associated with each photochemical complex. The intensity of sunlight is sufficiently dilute that any given chlorophyll molecule only absorbs at most a few photons per second. By incorporating many pigments into a single unit, the biosynthetically expensive reaction center and electron transport chain can be used to maximum efficiency.

A remarkable variety of antenna complexes has been identified from various classes of photosynthetic organisms. There have probably been multiple evolutionary origins of antenna complexes, as there is no universal structural theme evident or single pigment type utilized. This diversity is in contrast to the situation with photosynthetic reaction centers. Two broad structural classes include all known reaction center complexes, and it is considered likely that all reaction centers derive from a common ancestor.³

In most cases, the pigments in both antenna and reaction center complexes are bound to specific sites on proteins, with the geometrical arrangements of the pigments largely determined by pigment-protein interactions. This "pigment protein" structural motif is now familiar from structural studies on a growing number of reaction centers and antenna complexes.

Antenna Systems in Green Photosynthetic Bacteria

The green photosynthetic bacteria⁴ are anoxygenic (non oxygen evolving) phototrophs that contain unique peripheral membrane antenna complexes known as chlorosomes.^{5,6} The chlorosome is unusual in that it contains a relatively small amount of protein compared to a very high pigment content. As described below, the available evidence favors a fundamentally different mode of pigment organization in chlorosomes from that found in other antenna complexes.

Chlorosomes are found in two rather different groups of photosynthetic bacteria. The green sulfur bacteria are strict anaerobes and contain a reaction center similar in many ways to Photosystem I of oxygenic photosynthetic organisms. Most of these organisms are adapted to live under extremely low irradiation levels, including the lowest known light intensity known to support photosynthesis.⁷ The other family is often called the green gliding or green nonsulfur bacteria. They are facultatively aerobic and contain a pheophytin-quinone type of reaction center similar to that found in Photosystem II and the purple photosynthetic bacteria. The only member of this family that has been well studied is the thermophilic organism *Chloroflexus aurantiacus*. The two families of green bacteria have very different metabolic lifestyles and appear to be very distantly related, based on 16S r-RNA analysis. Their principal common feature is the chlorosome.

Pigment Content and Organization

All green bacteria contain both bacteriochlorophyll (BChl) *a* and BChl *c* (*d* or *e*). The structures of the latter pigments are shown in Figure 1. BChls *c*, *d* and *e* (known collectively as chlorosome chlorophylls), unlike all other chlorophylls, are not single compounds but rather are groups of chemically related compounds, differing mainly in substituents at the 8 and 12 positions. In addition, the 3¹ carbon on ring A is asymmetric and both R and S diastereomers are often found in significant quantities.⁸ In most cases, a given cell culture contains a single main class of pigments, either BChl *c*, *d* or *e*, but within that pigment class there may be a large number of structurally distinct pigments present. The functional role of this extremely high degree of pigment heterogeneity is not known but may be involved in fine tuning the cell's absorption to fit the light available in a particular ecological niche.

The chlorosome chlorophylls function exclusively as antenna pigments and are found only in the chlorosomes. Evidence is now overwhelming that the chlorosome chlorophylls are organized into pigment oligomers, in which the

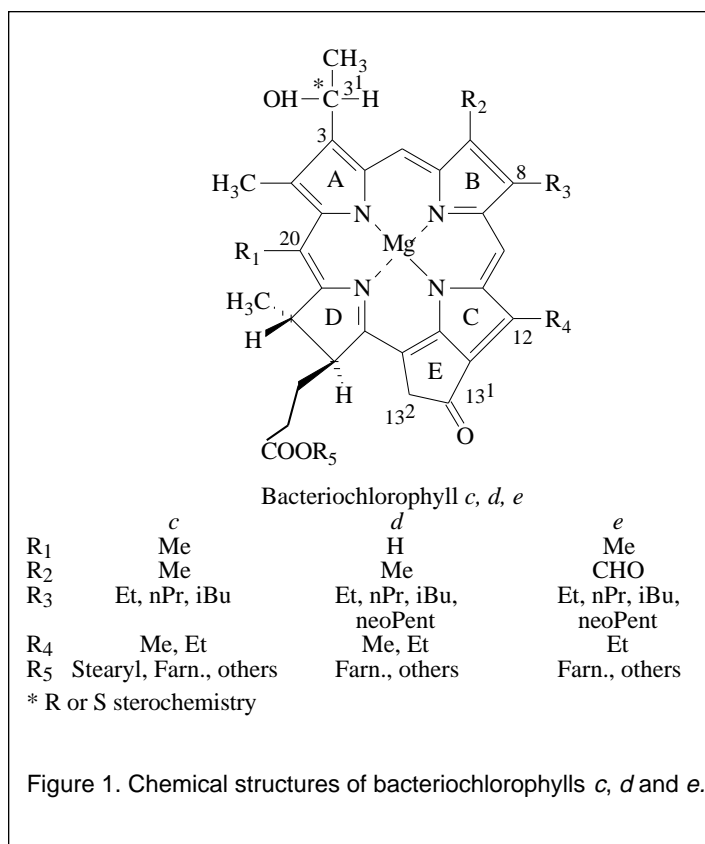


Figure 1. Chemical structures of bacteriochlorophylls *c, d* and *e*.

pigments are in direct van der Waals contact and proteins are of secondary importance in determining the pigment geometry. This organizational principle is in sharp contrast to the pigment protein motif described above for reaction centers and most other photosynthetic antenna complexes.

The structures of the chlorosome chlorophylls are programmed for self aggregation. The hydroxyl group at the 3¹ position on ring A and the carbonyl group at the 13¹ position on ring E have been implicated in the formation of a variety of aggregated species *in vitro*. These chlorophylls also lack the bulky carboxymethyl substituent at the 13² position on ring E that is found in all other chlorophyll type pigments, and therefore are able to pack together more closely than other chlorophylls or bacteriochlorophylls. There is a large literature on aggregation properties of BChl *c* and related pigments (reviewed in reference 6). The late A.A. Krasnovsky from Moscow pioneered this pigment oligomer view of the organization of the chlorosome chlorophylls.⁹ The overall correctness of this view is now accepted by most workers, although there continues to be a significant debate about the details of pigment oligomer structure and the possible functional roles of the proteins found in chlorosomes.

Many spectroscopic investigations have been carried out both on chlorosomes isolated from green bacteria and on oligomers formed *in vitro* from purified pigments. While it is not yet possible to give a definitive structure for the pigment oligomers present in either the *in vitro* aggregates or *in vivo* in chlorosomes, certain conclusions can be safely drawn.⁶ 1). Chlorosomes contain pigment oligomers in which the basic geometry of the oligomer is determined by pigment-pigment interactions. (The oligomers are possibly associated as a group with proteins, see below.) 2). The Mg atoms in the BChl *c* molecules in chlorosomes are essentially all pentacoordinate. 3). The 13¹-carbonyl of each BChl *c* interacts strongly with a functional group on another BChl *c*. 4). The 3¹-hydroxyethyl group is involved in oligomer formation and is most likely to be directly coordinated to a Mg atom and probably hydrogen bonded to the 13¹-carbonyl group. 5). The BChl *c* molecules are close together and oriented in such a way that they exhibit strong excitonic interactions and a significant red shift of the Q_y absorbance maximum in the red region, from 670 nm to 740 nm. 6). BChl *c* molecules show long range ordering with the Q_y transition moments aligned parallel to the long axis of the chlorosome. One of several possible local structural models that incorporates much of this information is shown in Figure 2.¹⁰

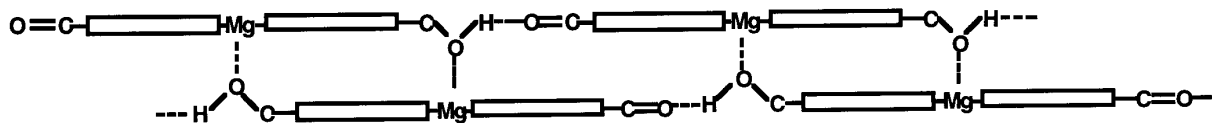


Figure 2. Local structural model for the interaction of BChl *c* pigments to form oligomers, from reference 10. For clarity, this is shown as a linear polymer, although a network structure in which additional layers are present is probably closer to the actual structure of the oligomer.

In many respects, the oligomeric pigments found in chlorosomes are similar to the J aggregates formed by certain dyes.¹¹ These systems have important applications in photography and have been extensively studied. They also exhibit long range orientational ordering and evidence for strong excitonic coupling.

Chlorosome Structure and Stoichiometry

Structural models of the chlorosomes and associated antenna and reaction center complexes are shown in Figure 3. The structures of chlorosomes from the two families of green bacteria are generally similar, with a flattened ellipsoidal shape of dimensions 100 to 200 nm long, 30 to 70 nm wide and 10 to 12 nm thick.¹² The smaller dimensions apply to the green nonsulfur bacteria, while the chlorosomes from the green sulfur bacteria are larger in all dimensions. Internal rodlike features 5-10 nm in diameter are observed by electron microscopy. It now seems likely that these rods are a direct visualization of the pigment oligomers found in chlorosomes. However, this has not been directly demonstrated and the precise geometrical arrangement of the pigments is still a matter of discussion. Several structural models have appeared that propose detailed molecular structures of the oligomers packing together to form these rods,¹³⁻¹⁶ (Figure 4). Each chlorosome contains roughly 10,000 molecules of BChl *c* and approximately 500 molecules of BChl *a*, with the precise values depending on the species and growth conditions.¹²

Chlorosome Antenna Complexes

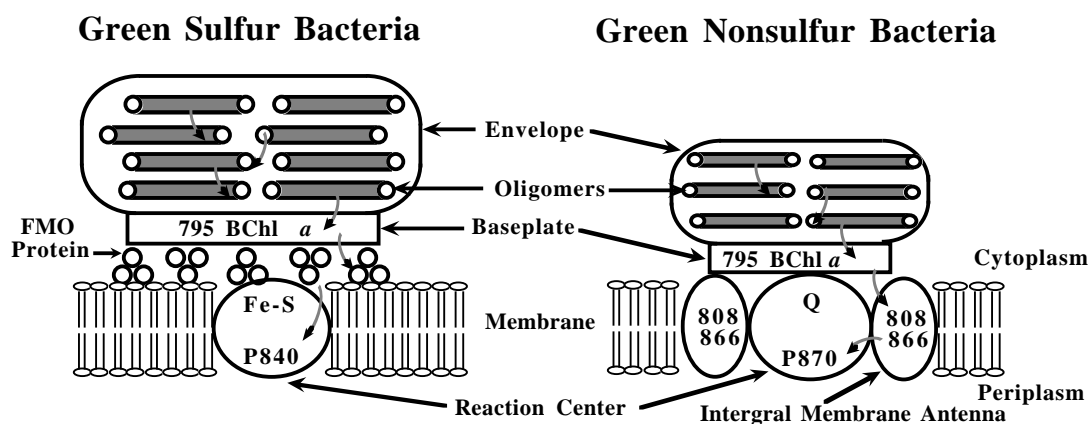


Figure 3. Schematic models for chlorosomes in the two families of green bacteria.

Purified chlorosomes from *Chloroflexus aurantiacus* contain three major protein components of molecular mass 11, 18 and 5.7 kDa, as well as a minor component of mass 5.8 kDa that has been proposed as the binding site of the 795 nm "baseplate" BChl *a* that forms the link between the chlorosome and the membrane-associated pigment-proteins.¹⁷ Most of the proteins are localized in the envelope that surrounds the chlorosome or at least are partly accessible to the

external surface of the envelope. Chlorosomes from green sulfur bacteria appear to be significantly more complicated in terms of protein composition than those from *Chloroflexus*.¹⁸

The function of the chlorosome proteins has been a subject of intense debate. The two extreme points of view are that the proteins play no role whatsoever in chlorosomes and that the proteins form the scaffolding for a classical pigment-protein complex. The former view has been most forcefully advocated by Holzwarth and coworkers.¹⁹ They have suggested that all the proteins can be removed from *Chloroflexus* chlorosomes without affecting their spectral properties or structure and some work confirms this view²⁰ (Y. Zhu and R. Blankenship, unpublished). However, the shape of the chlorosome is not retained

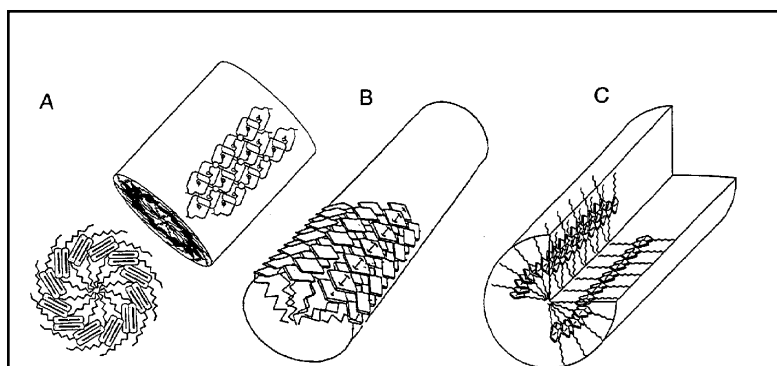


Figure 4. Proposed models for pigment oligomer formation into rodlike structures. Model A, from Reference (16); model B, from Reference (14); model C, from Reference (13).

and the interpretation that now seems most reasonable is that the LDS or SDS treatment used in the preparation has effectively extracted the pigment into micelles, rather than removing chlorosome proteins without changing the overall structure.

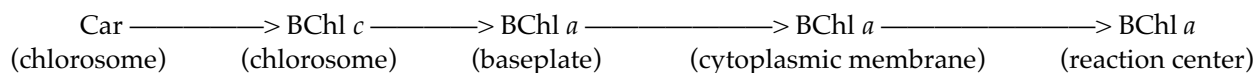
Other work has demonstrated that protease treatments of chlorosomes change the optical properties of the chlorosome, especially the circular dichroism spectrum.^{21,22} This has been interpreted in terms of a pigment protein complex.

Our view of the role of proteins in these systems is intermediate between the two extremes of “no proteins involved” and “classic pigment-protein”. The evidence for oligomers in chlorosomes is now so overwhelming that the second extreme is not tenable. However, we think the first view is too strong and ignores the important question of the assembly of the complex and a possible role of proteins in “tuning” the absorption of the pigments. We view the system as containing oligomers that are generally similar to those formed *in vitro*, but packaged and perhaps twisted or otherwise modulated by interactions with the proteins, with the 5.7 kDa protein appearing to be the most important in this regard.

The BChl *a* in green bacteria is mostly contained in membrane-bound antenna pigment-proteins and in the reaction centers, although a small amount is an integral part of the chlorosome. The best studied of these antenna pigment-proteins is a BChl *a* protein, commonly called the Fenna-Matthews-Olson or FMO protein. It is found only in the green sulfur bacteria. The structure of this protein is known,²³ and it has been studied intensely by spectroscopic and theoretical methods.

Kinetics and Pathways of Energy Transfer in Chlorosomes

The overall energy transfer pathway of green bacteria is described by the minimal scheme:



Each successive pigment species has progressively red-shifted absorption and fluorescence spectra. The descending energy levels thus provide a “funneling” of excitation into the reaction center. Absorption and fluorescence spectra and lifetimes, especially when coupled with careful biochemical resolution and separation procedures, can give some insight into the pathway and mechanism of excitation transfer and trapping. Several groups have carried out a number of studies of the kinetics of energy trapping using both steady-state and time-resolved fluorescence and transient absorption methods, with samples ranging from freshly isolated whole cells under physiological conditions to isolated complexes of various sorts at both room and low temperatures to purified oligomeric pigments. A generally consistent picture has emerged (reviewed in ref. 6). The data support a sequential energy transfer pathway from the BChl *c* (*d* or *e*) pigments in the body of the chlorosome to the baseplate to the membrane-bound antenna complexes and finally to the reaction centers. The strongest evidence for the sequential pathway is that the decay kinetics of the energy donor excited state match those of the rise of the acceptor; for example, in *Chloroflexus aurantiacus* the 10-15 ps decay of the BChl *c* emission is matched by a rise component in the baseplate BChl *a* 795.^{24,25} However, most of these studies did not have high enough time resolution to reveal ultrafast components that have been observed recently in chlorosomes from both *Chloroflexus* and *Chlorobium tepidum*.^{26,27} These components complicate the picture of the energy transfer system significantly and need to be further investigated using additional samples such as baseplate-free chlorosomes and alternative high time resolution techniques such as fluorescence upconversion.

Because the chlorosome antenna is so large, it seems likely that energy “tuning” of the pigment absorption might well be important in ensuring that the overall efficiency of energy collection is high. There are now some indications that this is the case, although overall the pigments in chlorosomes are dominated by homogeneous rather than inhomogeneous broadening.^{28,29} Femtosecond pump-probe experiments reveal little evidence for downhill energy transfers among spectrally distinct chromophores.^{26,27}

The overall framework of the energy transfer pathway in chlorosomes is now reasonably well established, although there is still much to learn about the details of this process. In particular, the mechanism of energy transfer in systems in with very strongly exciton coupled pigments is still very poorly understood.

Regulation of Photosynthetic Antenna Systems

Antenna systems have often been viewed as being “on” all the time, with the regulation of photosynthesis in response to different conditions such as excitation intensity, taking place primarily by adaptation on a slow time scale.

However, the modern view is of a much more actively regulated system at all stages of energy storage.³⁰ The advantages of “directional signals” or “volume controls” to control either the distribution between the photosystems or the number of excitations delivered by the entire antenna network are easy to appreciate. A variety of regulatory mechanisms appear to be functional in photosynthetic antennas, including reversible protein phosphorylation and excited state quenching possibly mediated by the carotenoid zeaxanthin. The green sulfur bacteria have a primitive regulatory mechanism that modulates the amount of energy reaching the reaction center in response to redox potential.^{31,32}

This redox-activated regulation of energy transfer in the green sulfur bacteria appears to involve a direct chemical titration of redox-active groups in the chlorosome antennas and was observed in whole cells, isolated membranes and purified chlorosomes. In the oxidized form, the redox-active groups efficiently quench excited states in the antenna system, reducing the overall energy transfer efficiency from nearly 100% to 10% or less. Additional work revealed that a similar redox modulation is present in the isolated Fenna-Matthews-Olson (FMO) protein that underlies the chlorosome.³³ The effect may therefore operate on at least two levels, within the chlorosome itself and in the FMO protein. Whether these two effects have similar molecular mechanisms is not yet clear.

Do these redox effects on the antenna system reflect a real cellular control mechanism? This is not yet clear and is the focus of much of our current research. Such an effect would serve to protect the cell from transient exposure to oxidizing conditions, in particular to oxygen. Green sulfur bacteria are obligate anaerobes and do not possess any respiratory activity. In nature they are found in a variety of environments, often just below the chemocline in stratified lakes.³⁴ Under these conditions they are likely to be exposed occasionally to moderate oxygen levels and a mechanism that provided even partial protection from oxidative damage would be of enormous adaptive advantage. The green sulfur bacteria appear to be especially vulnerable to oxidative damage. They contain a reaction center that has very low potential iron sulfur centers as early acceptors and reduces ferredoxin directly in a manner similar to Photosystem I. The reduced ferredoxin is freely diffusible in the cell cytoplasm. The reduced ferredoxins will readily react with oxygen to form superoxide, which leads to a variety of damaging photooxidative products. By preventing charge separation under oxygenic conditions by quenching excitations in the antenna system, green bacterial cells may avoid producing these toxic substances entirely. Thus, they may have a system that permits them to survive transient exposures to oxygen without incurring cellular damage.

Artificial Antennas Based on Pigment Organization in Chlorosomes

The field of artificial photosynthetic antennas is still in its infancy, compared to the sophisticated systems that have been reported that mimic reaction center function.³⁵ A few reports of artificial antennas have appeared,³⁶ including one consciously modeled on the chlorosome pigment organization.³⁷

Some of the features of chlorosome antennas make them attractive as models for artificial antenna complexes for photochemically based solar energy storage or for biosensor applications. The pigments are highly concentrated in the chlorosome, giving it an exceptionally high optical cross section (the effective molar extinction coefficient of a chlorosome at the peak of the red absorption is approximately $10^9 \text{ l mol}^{-1} \text{ cm}^{-1}$). The pigments can self-organize into very stable structures capable of efficient energy transfer. An attachment system is present that can serve to couple the complex to a receiver complex. The system can be modulated by redox potential. While no existing model system incorporates all these features, future work will hopefully incorporate many or all these attributes into a purely synthetic system that can be coupled with an artificial reaction center to give an efficient system that works over a wide range of light intensities.

Acknowledgments

The author gratefully acknowledges continuing support from the Energy Biosciences Program of the US Department of Energy for this work. This is publication #309 from the Arizona State University Center for the Study of Early Events in Photosynthesis.

References

1. van Grondelle, R.; Dekker, J.P.; Gillbro, T.; Sundstrom, W. *Biochim. Biophys. Acta* **1994**, *1187*, 1.
2. Pullerits, T.; Sundstrom, V. *Accts. Chem. Res.* **1996**, *29*, 381.
3. Blankenship, R.E. *Photosynth. Res.* **1992**, *33*, 91.
4. *Green Photosynthetic Bacteria.*; Olson, J.M.; Ormerod, J.G.; Amesz, J.; Stackebrandt, E.; Trüper, H.G., Eds.; Plenum: New York, 1988, 354.
5. Olson, J.M. *Biochim. Biophys. Acta* **1980**, *594*, 33.

6. Blankenship, R.E.; Olson, J.M.; Miller, M. In *Anoxygenic Photosynthetic Bacteria*; Blankenship, R.E.; Madigan, M.T.; Bauer, C.E., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995, 399.
7. Overmann, J.; Cypionka, H.; Pfennig, N. *Limnol. Oceanogr.* **1992**, *37*, 150.
8. Bober, F.W.; Pfennig, N.; Swanson, K.L.; Smith, K.M. *Biochemistry* **1990**, *29*, 4340.
9. Krasnovsky, A.A.; Bystrova, M.I. *BioSystems* **1980**, *12*, 181.
10. Brune, D.C.; King, G.H.; Blankenship, R.E. In *Photosynthetic Light-Harvesting Systems*; Scheer, H.; Schneider, S., Eds.; Walter de Gruyter: Berlin, 1988, 141.
11. Higgins, D.A.; Reid, P.J.; Barbara, P.F. *J. Phys. Chem.* **1996**, *100*, 1174.
12. Oelze, J.; Golecki, J.R. In *Anoxygenic Photosynthetic Bacteria*; Blankenship, R.E.; Madigan, M.T.; Bauer, C.E., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995, 259.
13. Nozawa, T.; Ohtomo, K.; Suzuki, M.; Nakagawa, H.; Shikama, Y.; Konami, H.; Wang, Z.Y. *Photosynth. Res.* **1994**, *41*, 211.
14. Matsuura, K.; Hirota, M.; Shimada, K.; Mimuro, M. *Photochem. Photobiol.* **1993**, *57*, 92.
15. Holzwarth, A.R.; Schaffner, K. *Photosynth. Res.* **1994**, *41*, 225.
16. Mimuro, M.; Matsuura, K.; Shimada, K.; Nishimura, Y.; Yamazaki, I.; Kobayashi, M.; Wang, Z.Y.; Nozawa, T. In *Photosynthesis: From Light to Biosphere*; Mathis, P., Ed.; Kluwer Academic Publishing: Dordrecht, The Netherlands, 1995, 41.
17. Feick, R.G.; Fuller, R.C. *Biochemistry* **1984**, *23*, 3693.
18. Chung, S.; Frank, G.; Zuber, H.; Bryant, D.A. *Photosynth. Res.* **1994**, *41*, 261.
19. Holzwarth, A.R.; Griebenow, K.; Schaffner, K. *J. Photochem. Photobiol.* **1992**, *65*, 61.
20. Miller, M.; Simpson, D.; Redlinger, T.E. *Photosynth. Res.* **1993**, *35*, 275.
21. Niedermeier, G.; Scheer, H.; Feick, R.G. *Eur. J. Biochem.* **1992**, *204*, 685.
22. Lehmann, R.P.; Brunisholz, R.A.; Zuber, H. *Photosynth. Res.* **1994**, *41*, 165.
23. Tronrud, D.E.; Schmid, M.F.; Matthews, B.W. *J. Mol. Biol.* **1986**, *188*, 443.
24. Holzwarth, A.R.; Müller, M.G.; Griebenow, K. *J. Photochem. Photobiol.* **1990**, *B5*, 457.
25. Causgrove, T.P.; Brune, D.C.; Wang, J.; Wittmershaus, B.P.; Blankenship, R.E. *Photosynth. Res.* **1990**, *26*, 39.
26. Savikhin, S.; van Noort, P.I.; Zhu, Y.; Lin, S.; Blankenship, R.E.; Struve, W.S. *Chem. Phys.* **1995**, *194*, 245.
27. Savikhin, S.; Zhu, Y.; Lin, S.; Blankenship, R.E.; Struve, W.S. *J. Phys. Chem.* **1994**, *98*, 10322.
28. Fetisova, Z.G.; Mairing, K. *FEBS Lett.* **1992**, *307*, 371.
29. Fetisova, Z.; Freiberg, A.; Mairing, K.; Novoderezhkin, V.; Taisova, A.; Timpmann, K. *Biophys. J.* **1996**, *71*, 995.
30. Allen, J.F. *Physiologia Plantarum* **1995**, *93*, 196.
31. Wang, J.; Brune, D.C.; Blankenship, R.E. *Biochim. Biophys. Acta* **1990**, *1015*, 457.
32. Blankenship, R.E.; Cheng, P.L.; Causgrove, T.P.; Brune, D.C.; Wang, S.H.; Choh, J.U.; Wang, J. *Photochem. Photobiol.* **1993**, *57*, 103.
33. Zhou, W.L.; Lobrutto, R.; Lin, S.; Blankenship, R.E. *Photosynth. Res.* **1994**, *41*, 89.
34. van Gemerden, H.; Mas, J. In *Anoxygenic Photosynthetic Bacteria*. Blankenship, R.E.; Madigan, M.T.; Bauer, C.E., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1995, 49.
35. Gust, D.; Moore, T.A.; Moore, A.L. *Accts. Chem. Res.* **1993**, *26*, 198.
36. Wagner, R.W.; Lindsey, J.S. *J. Am. Chem. Soc.* **1994**, *116*, 9759.
37. Tamiaki, H.; Miyatake, T.; Tanikaga, R.; Holzwarth, A.R.; Schaffner, K. *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 772.

About the Author

Dr. Blankenship received his B.S. in chemistry from Nebraska Wesleyan University in 1970 and Ph.D. in chemistry from the University of California, Berkeley in 1975. He is currently Professor of Chemistry and Biochemistry at Arizona State University.

The production of *The Spectrum*
is made possible through a donation from

Oriel Instruments
Stratford, Connecticut

Medical Applications of Stereolithography

Kathleen G. Specht, Spectra Group Limited, Inc.

Stereolithography is a rapid prototyping technique which has grown since the late 1980s to widespread use in the automobile and other industries for building engineering prototypes and models from CAD based files. It is a three-dimensional printing process which uses a moving laser beam to build parts by solidifying successive layers of a liquid plastic. In 1987, researchers in the laboratory of Dr. D.C. Neckers in the Center for Photochemical Sciences at Bowling Green State University realized that the use of stereolithography for medical applications held great potential. In 1988 the first medical data file was converted to a three-dimensional model. The file was a Magnetic Resonance Imaging (MRI) of a heart in a living patient.

A few groups in universities, medical schools and associated companies in the U.S. and Europe have developed the ability to produce three-dimensional medical models from patient specific data. There are now a few companies using the developed software to read and process Computed Tomography (CT) and MR data. They have commercialized this service to make plastic models for surgeons and prosthetic device manufacturers. However, only now are major companies such as 3D Systems and others moving in the direction of selling and marketing medical imaging stereolithography. It is expected that within a few years, once more physicians and patients are aware of medical imaging and insurance companies realize the cost savings in terms of surgical planning and operating room time, the use of stereolithography for medical applications will greatly expand. This article is a brief review of the status of medical imaging using stereolithography. For persons interested in more detailed information, the following rapid prototyping newsletters are available on the World Wide Web:

For Rapid Prototyping Report Website: <http://www.cadcamnet.com/circ>

For Rapid Prototyping Technologies in Manufacturing mailing list via World Wide Web:
<http://ltk.hut.fi/archives/>

The central concept that Spectra Group Limited, Inc. (SGL), a small company in Maumee, Ohio, has focused on is timely and easy availability of three-dimensional models of patient specific anatomy to referring physicians and prosthetic device manufacturers for surgical planning and prosthesis design. Three-dimensional models can enhance both the planning and the evaluation process. Three-dimensional models are easier to conceptualize than two-dimensional images and can be handled and viewed from any angle. They can be sliced for viewing internal structures and prosthetic devices can be removed during the printing process for more accurate surgical planning. Models can significantly reduce surgical time and associated expenses while enhancing patient care. The models are also useful for patient or student education and for permanent records.

The process depends on software that converts X-ray CT and MRI data to a format which can be recognized by rapid prototyping devices such as the stereolithography printing process which in turn generates anatomically correct three-dimensional models. Data from these scanners, which are already formatted in two-dimensional slices of known thickness along the z axis, are converted into a format recognized by the software. Gray-scaled data are then converted to a binary format after selecting a threshold which allows for differentiation between the anatomical feature of interest, such as differentiating bone from the surrounding tissue. The bone or tissue to be printed is then selected and the binary data is then manually evaluated, slice by slice, for extraneous spots and/or unwanted prosthetic devices which may be present and can be removed at this time. The external surface data may then be smoothed which helps to eliminate ridges which may form between layers. This data is then sliced further in the z dimension (.01 mm slices) to depths appropriate for building on the SLA.

At SGL an SLA 250 (3D Systems, Inc., Valencia, CA) is used to print the CT or MRI data forming an actual size three-dimensional model. This system uses a He/Cd, 40 mW, 324 nm laser beam that is directed across the surface of the polymerized monomer. The CT data, which is unique at every x, y, z point, is used to direct the beam, which is driven at a rate sufficient to form a gelled polymeric material as it scans the surface. The image is built from the

bottom up, layer by layer, until complete. This is followed by a thermal cure process, once the entire model has been built, that fixes and hardens the polymeric object.

A DuPont Somos 2110 prepolymer (triacrylate based) is currently used for building medical models. This resin forms a milky white non-toxic polymer which is somewhat flexible, but also durable. Its color resembles bone and the model made from it can be drilled or sawed as needed for template formation or to view the inside. We have found this polymer to be more appealing to physicians than the clear polyacrylates which tend to have unpleasant smells and occasionally tend to easily shatter.

A survey of the field shows that others have used similar approaches with all available literature indicating that the major (or only) emphasis has been on bones printed from CT scans. There are also several examples in the medical literature of three-dimensional models made by milling polystyrene or polyurethane foam.¹⁻³ These models were used for pre-surgical planning or cranio-facial surgery. The drawbacks to milling, include the facts that the highest resolution achieved is on the order of 1.6 mm and that the tools cannot perfectly reproduce objects which are hollow, such as the mastoid bone or canals such as the mandibular nerve canal. Stereolithography on the other hand can achieve resolution on the order of 0.1 mm with the best machines, internal configurations are no problem and there is no limit in the reproduction of shapes of various sizes.

Most of the medical stereolithography literature appears in the rapid prototyping literature with many of the case studies presented being similar to the cranio-facial surgery study described below. A general survey finds the following groups to be working in this area: researchers at Keio University in Japan;⁴ researchers at the University of Basel, Switzerland in collaboration with Proform AG, Fribourg, a subsidiary of CIBA, Fribourg;⁵ researchers at Katholieke Universiteit Leuven, Div. PMA, Belgium and Materialise NV, Belgium;⁶ researchers at the University of Queensland, Australia;⁷ a group of researchers at the Klinik für Radiologie und Diagnostik, RWTH Aachen, Germany;⁸ researchers at the University of Kentucky;⁹ and a group at Cyberform (Richardson, Texas) which has a CAD based software program called SurgiCAD. Only two of the above groups market software packages in the United States, Materialise and Cyberform.

Over the last five years SGL has built many different models for radiologists, surgeons and prosthetic device manufacturers which have been used for presurgical planning and prosthetic device sizing/evaluation. Printed parts include: a heart from MR data, whole heads from spiral CT data, skulls, hips and femurs, toes, spines, a wrist, and a sinus cavity. Two example case studies are described below.

Case 1: From Dr. Richard Nelson, Medical College of Ohio

A patient presented with a cancerous tumor in the sinus near the right eye. This patient had undergone a recent operation by a different neurosurgeon, but the operation was unsuccessful in removing the entire tumor. Because the tumor was located in such a delicate spot, which was very difficult to measure directly from the CT data, there was little chance for success in a second operation and most surgeons deemed it next to impossible.

SGL printed a model of the patient's skull from the CT data for Dr. Nelson. Using the model, the CT data and the MR data for presurgical planning, Dr. Nelson could determine exactly which section of the skull needed to be removed. This was outlined on the model, then the surgeon removed this section from the model and used it to make a metal template by vacuum melting the plastic to the metal. The template was sterilized and actually used during surgery as a cutting guide. This saved significant surgical time, since otherwise accurate measurements for incision would have had to be made from the data during the surgery. The same section of the model was also used to form a methacrylate prosthesis prior to surgery. The prosthesis was cut and shaped exactly to the model. Since the prosthesis was available prior to surgery it saved approximately 1.5 hours usually required during surgery to make and fit a prosthetic device. The patient is now disease free two years after surgery, which is amazing given the low probability of recovery prior to surgery.

Case Study 2: Hip

A second case study is typical of many cases in which the models are used. A patient presented with severe hip displacement and other related problems. This was a patient in his mid to late thirties who had been injured in a car accident in which there were fatalities. The patient had undergone several operations, the first to set the broken acetabula. The results were severe infection, several bone grafts and a poor fitting prosthesis by the time he arrived at this major medical center.

A model of his remaining acetabula was printed with the prosthesis, bone grafts and cement removed. This greatly aided the surgeon's ability to visualize the location and amount of actual remaining bone. The surgeon took the model into the operating room and referred to it as a guide during the surgery. Without the model it would have been very difficult to locate and remove all the infected cement and graft. The model also allowed her to fit a prosthesis prior to surgery and locate a supportive section of bone to attach the prosthetic device. Surgical time was significantly reduced and improved patient treatment could be administered because of the use of the medical model.

Medical stereolithography is a growing field with interest expected to increase over the next several years. Its acceptance has grown more slowly than originally anticipated due to the reticence of insurers to do anything in patient treatment which appears to increase cost. Though models can often be demonstrated to effect outcome, reduce the time of surgical procedures, and in other ways improve the final results, many more case studies need to be carried out to make the case convincing to the American medical community. Medical stereolithographic models of CT data are used much more commonly in Europe. The recent introduction of multicolor stereolithography based, in part, on patents assigned to SGL, is likely to increase the acceptability of the technique for complex surgical procedures in the immediate future.

The next step at SGL is to introduce work stations and medical imaging software in three major medical centers in our immediate vicinity. The CT/MRI data processing will be done at the site of data acquisition by the attending radiologist or radiological technician. The processed data will be forwarded to our sites, remote from the medical centers, where the models will be made.

References

1. Klein, H.M. et al. *Pediatric Radiology* **1992**, 22, 458-460.
2. Yab, K.; Tajima, S.; Imai, K. *J. of Cranio-Maxillo-Facial Surgery* **1993**, 21, 275-278.
3. Zonneveld, F.W. *Investigative Radiology* **1994**, 29, 716-724.
4. "Rapid Prototyping Report", CAD/CAM Publishing, Inc., July 1993.
5. Jacob, A.L.; Hammer, B.; Niegel, G.; Lambrecht, T.; Schiel, H.; Steinbrich, W.; Hunzicker, M. In Proc. 4th International Conference on Rapid Prototyping, Dayton, OH, June 1993.
6. Swaelens, B.; Kruth, J.P. In Proc. 4th International Conference on Rapid Prototyping, Dayton, OH, June 1993.
7. "Rapid Prototyping Report", CAD/CAM Publishing, Inc., June 1995.
8. Klein, H.M.; Schneider, W.; Alzen, G.; Voy, E.D.; Gunther, R.W. *Rof. Fortschritte auf dem Gebiete der Rongenstrahlen und der Neumen Bildgebenden Verfahren* **1992**, 156, 429-432.
9. "Rapid Prototyping Report", CAD/CAM Publishing, Inc., August 1992.

About the Author

Dr. Specht received her B.S. degree in biochemistry from Albright College, Reading, Pennsylvania, in 1983 and her Ph.D. in Environmental Health Chemistry from Johns Hopkins University School of Hygiene and Public Health, Baltimore, Maryland, in 1988. She is currently Director of Technical Development at Spectra Group Limited, Inc., Maumee, Ohio 43537.

The Spectrum on the World-Wide Web

The Spectrum is available on the Center's Web site: [Http://www.bgsu.edu/departments/photochem/](http://www.bgsu.edu/departments/photochem/). You can access via Acrobat Reader. There are instructions for downloading a free copy of Acrobat Reader from the Adobe Web site.

Please send an e-mail to:

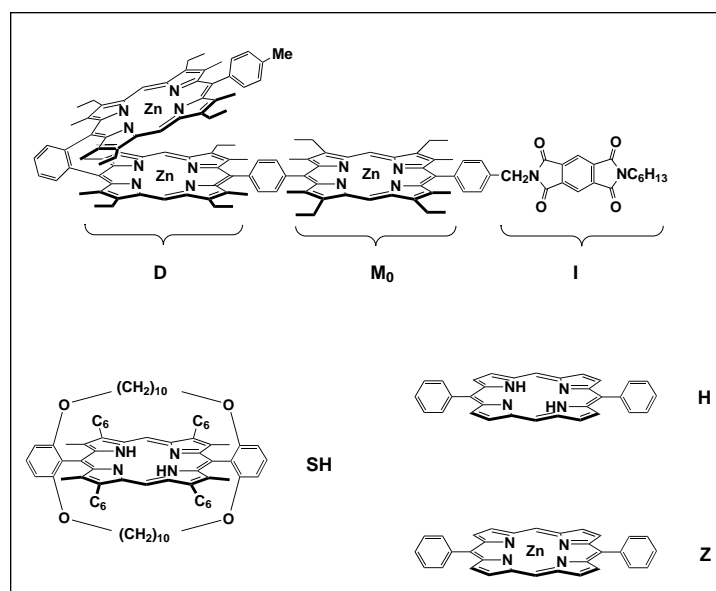
photochemical@listproc.bgsu.edu

if you plan to access *The Spectrum* electronically so we can remove you from our paper mailing list. Please browse our Web site for up-to-date information about the Center and its programs.

Mimicking Charge Separation of the Bacterial Photosynthetic Reaction Center with Porphyrin Arrays

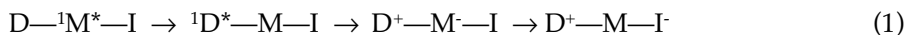
Atsuhiko Osuka, Kyoto University

During the last decade, structurally well-defined synthetic models have proven to be particularly effective in understanding the mechanism of the electron transfer (ET) reactions involved in photosynthesis.¹⁻³ One of longest used of these model studies may be the elucidation of key sequential photochemical events in RC, where light energy captured by photosynthetic pigments is effectively collected at the special pair (SP), giving $^1\text{SP}^*$ as the final energy sink as well as the first electron donor. A subsequent electron-transfer (ET) relay over cofactors such as bacteriochlorophyll, bacteriopheophytin, Q_a and Q_b results in a quantitative transmembrane charge separation (CS).



Here we present our recent efforts exploring synthetic triads D—M—I, where D, M, and I represent a 1,2-phenylene-bridged zinc porphyrin dimer, a porphyrin monomer, and a pyromellitimide electron-acceptor, respectively. The first goal we set is the achievement of the following photochemical reactions (equation 1); the singlet excitation energy captured by D and M is collected at D which is distal to the electron acceptor I, and the initial CS between $^1\text{D}^*$ and M followed by a charge shift reaction (CSH) gives $\text{D}^+—\text{M}—\text{I}^-$ as a secondary, long-lived ion-pair state. Functionally, D, M, and I may correspond to SP, bacteriopheophytin, and Q_a , respectively. Here it may be pointed out that the analysis and molecular design are quite simple but it has been very difficult to achieve all of these photochemical events in a single molecule. Although there

have been a lot of synthetic triads consisting of electron donor (ED)—porphyrin (P)—electron acceptor (EA) which provide long-lived charge separated states by a sequential ET relay of equation 2,¹⁻³ this sequence is different from that in the RC. In a few successful cases, Wasielewski *et al.* reported zinc pyropheophorbide—zinc porphyrin—quinone which undergoes a single step, long-distance ET within several ps even at 77K.⁴



In comparison to M_0 , D has a lower S_1 -energy by 0.19 eV and lower oxidation potential by 0.24 V.⁵ These differences are quite analogous to those found for a monomeric bacteriochlorophyll and SP, thereby encouraging the use of D as a functional model of SP. We used I as an electron acceptor, since it is chemically stable and has a pertinent reduction potential, and once reduced its anion radical exhibits a characteristic sharp absorption band around 715 nm which is very useful in tracing ET dynamics of complicated molecular systems.⁶ The D and I moieties are fixed in the series, and the central M moiety is changed from original zinc porphyrin monomer (M_0) to a doubly-strapped metal-free porphyrin (SH), a β-unsubstituted metal-free porphyrin (H), and a β-unsubstituted zinc porphyrin (Z) in pursuit of achieving a RC-type sequential ET relay in high efficiency.

D— M_0 —I Transient absorption measurements on D— M_0 —I show that two-step ET ($\text{D}—^1\text{M}^*—\text{I} \rightarrow \text{D}—\text{M}_0^+—\text{I}^- \rightarrow \text{D}^+—\text{M}_0—\text{I}^-$) provides $\text{D}^+—\text{M}_0—\text{I}^-$ with an overall quantum yield of 0.05 and a lifetime of 260 ns.⁶ $\text{D}^+—\text{M}_0—\text{I}^-$ was also detected by time-resolved ESR experiments.⁷ The initial CS competes with efficient energy transfer ($\text{D}—^1\text{M}_0^*—\text{I}$

→ ${}^1D^*—M_0—I$) but the resultant ${}^1D^*$ does not undergo ET. Thus, the D subunit in this model acts as an efficient singlet energy sink but as a poor electron donor towards the M_0 subunit, thereby reducing the overall CS quantum yield. Most probably, the lack of ET-reactivity in ${}^1D^*—M_0—I$ can be ascribed to an unfavorable energy diagram in that $D^+—M_0—I$ is higher in energy than ${}^1D^*—M_0—I$. The reaction sequence leading to the formation of $D^+—M_0—I$ is analogous to equation 2, being different from the reaction sequence in RC.

D—SH—I Usually metal-free porphyrin has a lower reduction potential compared with the corresponding zinc porphyrin. Thus, we attempted to prepare a D—metal free porphyrin—I triad the with intention to induce CS between D and a porphyrin monomer subunit. From the synthetic point of view, separation of desired partially metallated compounds from other metallated species was thought to be very difficult. These difficulties were overcome by introducing double straps over the metal-free porphyrin which prevented the metallation there.⁸ Since ${}^1D^*$ and ${}^1SH^*$ have similar excitation energies, an equilibrium of ${}^1D^*—SH—I \leftrightarrow D—{}^1SH^*—I$ is attained within *ca.* 50 ps. Transient absorption measurements show that an ET relay analogous to that of D— $M_0—I$ gives $D^+—SH—I$ with an overall quantum yield of 0.26. But in this model, it is interesting to note that $D^+—SH—I$ has a long lifetime (12 μ s), being *ca.* 50 times longer than that of $D^+—M_0—I$.

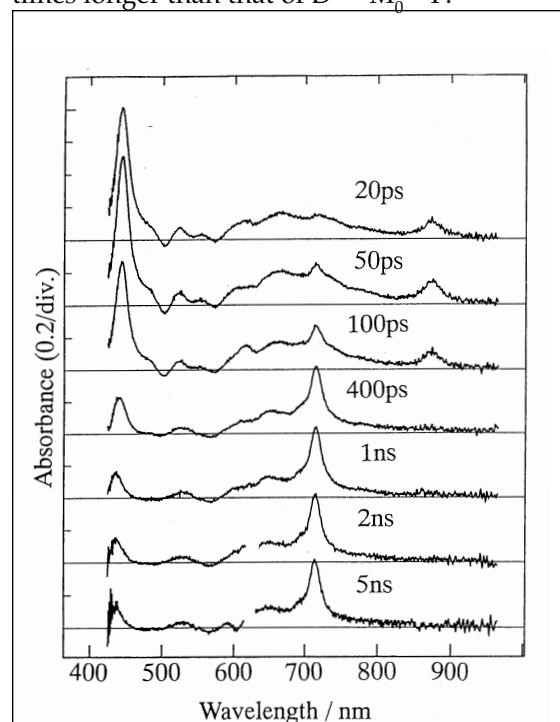
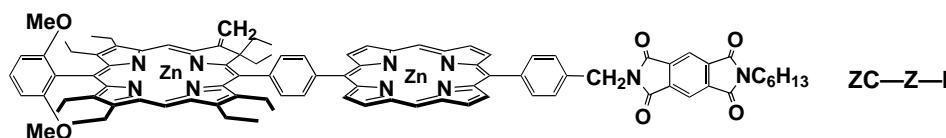


Figure 1. Transient absorption spectra of 1×10^{-4} M solution of D-H-I in the THF excited with 8 ps, 618 nm pulses.

D—H—I Here the central monomer subunit is a β -unsubstituted metal-free porphyrin (H), in which electron donating β -alkyl substituents are all omitted, thus making this subunit easier to be reduced and harder to be oxidized in comparison to M_0 and SH. Fortunately, this molecule was prepared by selective metallation only at the diporphyrin site. The energy levels of the key states are as follows; ${}^1D^*$ (1.97 eV), ${}^1H^*$ (1.95 eV), $D^+—H—I$ (1.59 eV), $D—H^+—I$ (2.05 eV), and $D^+—H—I$ (1.48 eV), allowing a RC-type sequential ET relay that has indeed been confirmed by the transient absorption measurements (Figure 1).⁹ Immediately after excitation, the absorption bands of D^+ (670 nm) and H^- (870 nm) rise and the decay of the H^- band is accompanied by the rise of I^- (715 nm). Eventually $D^+—H—I$ with a lifetime of 280 ns is produced with an overall quantum yield of 0.08.

D—Z—I In DMF, the energy levels are as follows; $D—{}^1Z^*—I$ (2.13 eV), ${}^1D^*—Z—I$ (1.93 eV), $D^+—Z—I$ (1.79 eV), and $D^+—Z—I$ (1.19 eV), being favorable for the sequential ET relay of ${}^1D^*—Z—I \rightarrow D^+—Z—I \rightarrow D^+—Z—I$. The ${}^1Z^*—I$ subunit can undergo CS to give $Z^+—I$ (1.75 eV) with a rate of 1.4×10^9 s⁻¹. However, the energy transfer from $D—{}^1Z^*—I$ to ${}^1D^*—Z$ is much faster (1.7×10^{11} s⁻¹) than this CS, thereby all the excitation energies absorbed by the D and Z subunits being preferentially collected at the D subunit. The subsequent ET relay of ${}^1D^*—Z—I \rightarrow D^+—Z—I \rightarrow D^+—Z—I$ proceeding with an overall quantum yield of 0.4 has been actually confirmed by the transient absorption measurements.

In less polar THF, the energy levels of the key states are as follows; $D—{}^1Z^*—I$ (2.13 eV), ${}^1D^*—Z—I$ (1.97 eV), $D^+—Z—I$ (1.99 eV), and $D^+—Z—I$ (1.48 eV). In contrast to the situation in DMF, the energy levels of ${}^1D^*—Z—I$ and $D^+—Z—I$ are nearly the same. The transient absorption measurements show that ${}^1D^*—Z$ decays in essentially the same manner as that of the reference ${}^1D^*$. We could not find any additional decaying pathway available for the ${}^1D^*—Z$ subunit. In particular, the charge separated species $D^+—Z^-$ was not detected. On the other hand, ${}^1D^*—Z—I$ provides $D^+—Z—I$ with a time constant of *ca.* 200 ps. It is interesting to note that Z^- species could not be detected in the ps transient absorption spectra of D—Z—I. A possible mechanism may be that there is an equilibrium between ${}^1D^*—ZI$ and $D^+—Z—I$, and the latter is effectively trapped by CSH



reaction to give $D^+—Z—I$ as reported for the related zinc chlorin (ZC)—Z—I triad in the same solvent.¹⁰ In this pre-equilibrium case, the decay of ${}^1ZC^*$ should be somehow accelerated through this equilibrium and its fluorescence decay becomes biexponential, reflecting the presence of re-generation of the excited state. However, this is not the case for $D—Z—I$. Alternatively, one may envision a direct, long-distance electron transfer via a superexchange mechanism. In this case, the intermediate ion-pair state can be used as a virtual state in the superexchange mechanism. According to the formalism developed for the superexchange mechanism,¹¹ the electronic matrix element, V_s , for the superexchange interaction between states i , m , and n , where i and n are the initial and final states and m is the virtual state, is given by equation 3,

$$V_s = V_{mi}V_{nm}/\Delta E_{mi} \quad (3)$$

where V_{mi} and V_{nm} are the respective electronic interaction matrix elements between the states i and m , and m and n , and ΔE_{mi} is the energy difference between the states i and m . In this case, $i = {}^1D^*—Z—I$, $m = D^+—Z—I$, and $n = D^+—Z—I$, respectively. In THF, the energy level of $D^+—Z—I$ is estimated to be slightly higher than that of ${}^1D^*—Z—I$ and small ΔE_{mi} may encourage the superexchange ET. But discrimination of the two mechanisms seems to be difficult as in the case of RC.

Through these studies, one may conclude that supramolecular porphyrin arrays appropriately designed with respects to geometries and energetics can operate as one expects. Rational molecular engineering, however, needs a very detailed knowledge of all the effects of structural perturbation on the rates of each energy and electron transfer and on the reaction mechanism as well. Environmental effects that are provided by the surrounding proteins and are considered to play key roles in biological ET should be incorporated into future more elaborate model systems.

References

1. Wasielewski, M.R. *Chem. Rev.* **1992**, 92, 435.
2. Gust, D.; Moore, T.A.; Moore, A.L. *Acc. Chem. Res.* **1993**, 26, 198.
3. Maruyama, K.; Osuka, A.; Mataga, N. *Pure Appl. Chem.* **1994**, 66, 867.
4. Wasielewski, M.R.; Gaines, III, G.L.; Wiederrecht, G.P.; Svec, W.A.; Niemczyk, M.P. *J. Am. Chem. Soc.* **1993**, 115, 10442.
5. Osuka, A.; Nakajima, S.; Nagata, T.; Maruyama, K.; Toriumi, K. *Angew. Chem. Int. Ed. Engl.* **1991**, 30, 582.
6. Osuka, A.; Nakajima, S.; Maruyama, K.; Mataga, N.; Asahi, T.; Yamazaki, I.; Nishimura, Y.; Ohno, T.; Nozaki, K. *J. Am. Chem. Soc.* **1993**, 115, 4577.
7. Nakamura, H.; Terazima, M.; Nirotta, N.; Nakajima, S.; Osuka, A. *Bull. Chem. Soc. Jpn.* **1995**, 68, 2193.
8. Osuka, A.; Okada, T.; Taniguchi, S.; Nozaki, K.; Ohno, T.; Mataga, N. *Tetrahedron Lett.* **1995**, 36, 5781.
9. Osuka, A.; Nakajima, S.; Okada, T.; Taniguchi, S.; Nozaki, K.; Ohno, T.; Yamazaki, I.; Nishimura, Y.; Mataga, N. *Angew. Chem., Int. Ed. Engl.* **1996**, 35, 92.
10. Osuka, A.; Marumo, S.; Mataga, N.; Taniguchi, S.; Okada, T.; Yamazaki, I.; Nishimura, Y.; Ohno, T.; Nozaki, K. *J. Am. Chem. Soc.* **1996**, 118, 155.
11. Won, Y.; Friesner, R.A. *Biochim. Biophys. Acta* **1988**, 935, 9.

Acknowledgments

The author acknowledges the contributions of his coworkers mentioned in the references. Work was supported by Grants-in-Aids for Scientific Research from the Ministry of Education, Science, Sports, and Culture of Japan.

About the Author

Dr. Atsuhiko Osuka received his Ph.D in chemistry in 1982 from Kyoto University. He is currently a professor of chemistry in the Graduate School of Science at Kyoto University. His address is Division of Chemistry, Graduate School of Science, Kyoto University, Sakyo-ku, Kyoto 606-01, Japan.

Center for Photochemical Sciences Students Available for Employment

The following students in the Center for Photochemical Sciences will be completing the Ph.D. degree in the Photochemical Sciences or a postdoctoral research fellowship within the next year. Please contact them if you have any positions available or can provide information about potential employment opportunities.

Ileana Balanescu

Phone: Work (419) 372-2089, Home (419) 352-3433

E-mail: ibalane@bgsuvax.bgsu.edu

Ph.D. in Photochemical Sciences expected in 1997, Dr. Kurt D. Deshayes, advisor

Concentration: Organic synthesis of macromolecular complexes (hemiarceplexes), isolation and purification (chromatography and NMR techniques), and photochemical studies of the complexes (absorption, fluorescence, phosphorescence spectroscopy, laser flash photolysis, energy and electron transfer, kinetics).

Andrei Fedorov

Phone: (419) 353-0383

E-mail: fedorov@bgnet.bgsu.edu

Ph.D. in Photochemical Sciences expected in 1997, Dr. Deanne Snavelly, advisor

My research interests involve physical, inorganic and organometallic chemistry. In particular, I am interested in vibrational spectroscopy of organometallic complexes. Along with experimental work my research activity covers some computational chemistry, namely, ab initio and semi-empirical methods.

Rupa Fernando

Phone: Work (419) 372-8520, Home (419) 354-2024

E-mail: rfernan@bgnet.bgsu.edu

Postdoctoral Fellow with Dr. Michael Ogawa

Multidisciplinary background in chemistry with specialization in physical measurements and synthesis of inorganic, metallo-organic and metallo-peptide complexes displaying novel photochemical and photophysical properties. Expertise in steady state emission, UV/Visible, NMR, FT-IR, CD, AA and time-resolved spectroscopic methods, HPLC, GC/MS, laser flash photolysis, quantum yield measurements and electrochemical techniques. On-line resume is available at <http://www.bgsu.edu/~rfernan>. Seeking a position in industry, government or an academic institution.

Bryan Fry

Phone: Home (419) 832-2405

E-mail: bfry@opie.bgsu.edu

Ph.D. in Photochemical Sciences expected December 1996, Dr. D.C. Neckers, advisor

Experience: Photopolymerization of carbosilane compounds, synthesis of ceramic precursor polymers, polymer characterization, three years employment as an engineer, M.S. in chemistry from Utah State University, B.S. in mechanical engineering from Purdue University.

Oleg Grinevich

Phone: Home (419) 353-1113

E-mail: ogrinev@opie.bgsu.edu

Ph.D. in Photochemical Sciences expected in 1997, Dr. Deanne Snavelly, advisor

My research interests are primarily in physical chemistry. I have been working on unimolecular reactions initiated by visible laser light for the past 2.5 years. These reactions include gas and liquid-phase processes. I am also involved in computational chemistry, namely, master equation simulation of unimolecular reactions.

Anton Guliaev

Phone: Work (419) 372-6964, Home (419) 354-6964

E-mail: aguliae@bgnet.bgsu.edu

Ph.D. in Photochemical Sciences expected in 1997, Dr. Neocles B. Leontis, advisor

NMR/molecular modeling studies of nucleic acids conformation; NMR/molecular modeling studies of binding modes of cationic porphyrins to nucleic acids: structural insights to site specific photosensitized cleavage; photochemical damage of DNA; thermodynamic characterization of nucleic acids and their complexes with photosensitizers.

Olaf Korth

Phone: Work (419) 372-6002

E-mail: korth@bgnet.bgsu.edu

Degree courses at Lomonossov University, Moscow, and Technical University, Berlin. Graduated in physics at Humboldt University, Berlin, 1994.

Currently conducting Ph.D. research at Humboldt University, Berlin, and Center for Photochemical Sciences, Dr. M.A.J. Rodgers' laboratory.

Knowledge and experience in optical steady-state and time resolved spectroscopy, laser physics, biophysics, molecular and chemical physics, and electronics. Languages: German, English, French, and Russian.

Adrian Lungu

Phone: Home (419) 354-6604

E-mail: alungu@bgnet.bgsu.edu

Ph.D. in Photochemical Sciences expected August 1997, Dr. D.C. Neckers, advisor

Looking for a position as a Polymer Chemist involved in research and development. Research background and interests include characterization of polymeric networks by solid-state NMR (1D and 2D) spectroscopy, analysis of polymers by fluorescence spectroscopy, stereolithography, studies of some ceramic precursors and reinforced photopolymers, polymer chemistry and photochemistry and photocurable coatings.

Victoria P. Manea

Phone: Home (419) 352-9551

E-mail: vmanea@bgnet.bgsu.edu

Ph.D. in Photochemical Sciences expected in December 1996, Dr. J. R. Cable, advisor

My research has been focused on the electronic spectroscopy of isolated molecules which are subjected to supersonic cooling in a molecular beam. Several aromatic amides and styrene derivatives have been studied, as well as some small molecular clusters with various solvents (argon, nitrogen, water, and ammonia). The structural characteristics of these systems are well understood from the observed spectra, in conjunction with ab initio/semi-empirical model calculations. I am interested in either industrial or academic positions in the areas of photochemistry, with an emphasis on analytical techniques of qualitative/quantitative analysis.

Alexander Mejiritski

Phone: Home (419) 352-0637

E-mail: amejiri@opie.bgsu.edu

Ph.D. in Photochemical Sciences expected in 1997, Dr. D. C. Neckers, advisor

Looking for a position at an industrial facility. Research background/interests include materials science in the area of polymers and semiconductors, surface chemistry and analysis of polymers and semiconductors via SEM, AFM, XPS, EDAX, microlithography, polymer chemistry and photochemistry, organic films, and polymer-surface interactions.

David W. Place

Phone: Work (419) 372-2089, Home (419) 352-3433

E-mail: dwplace@bgnet.bgsu.edu

Ph.D. in Photochemical Sciences expected in 1997, Dr. Kurt D. Deshayes, Advisor

Concentration: Organic synthesis of macromolecular complexes (hemicarceplexes), isolation and purification (chromatography and NMR techniques), and photochemical studies of the complexes (absorption, fluorescence, phosphorescence spectroscopy, laser flash photolysis, pulse radiolysis, and energy and electron transfer).

Applications Now Available for Ph.D. in Photochemical Sciences

A unique interdisciplinary program at the cutting edge of chemistry, biological sciences and materials science:

Photosynthesis; Transient Intermediate Spectroscopy; Fast Kinetics; Vibrational Overtone Spectroscopy; Photopolymerization; Optoelectronics; Photoelectron Microscopy; Organic Photochemistry; Multiphoton Spectroscopy; Molecular Recognition, Phototoxicity; Photochemical Viral Interaction; Photochemistry of Interfaces; Photoinitiation.

Students with undergraduate majors in chemistry, physics, biological or materials sciences may apply. Enhanced stipends and special fellowships available to outstanding students.

For application: E-mail: photochemical@listproc.bgsu.edu

Visit [Http://www.bgsu.edu/departments/photochem/](http://www.bgsu.edu/departments/photochem/)

© Copyright 1996 by the Center for Photochemical Sciences
The Spectrum is a quarterly publication of the Center for Photochemical Sciences, Bowling Green State University, Bowling Green, OH 43403.

Phone 419-372-2033 Fax 419-372-6069
Email photochemical@listproc.bgsu.edu
WWW <http://www.bgsu.edu/departments/photochem/>

Executive Director: D.C. Neckers
Administrative Director: Pat Green
Principal Faculty: G.S. Bullerjahn, J.R. Cable,
K.D. Deshayes, Y.J. Ding,
W.R. Midden, M.V. Munschau,
D.C. Neckers, M.Y. Ogawa,
M.A.J. Rodgers, D.L. Snavely,
V.S. Srinivasan

The Spectrum Editor: Pat Green
Production Editor: Alita Frater

COPYRIGHT PERMISSION

A person may make a single copy of any or all articles in this issue for personal use. Copying beyond that permitted by the U.S. Copyright law is allowed provided that the appropriate per copy fee is paid through the Copyright Clearance Center, Inc., 27 Congress St., Salem, MA 01970. For reprint permission, please write to the Center for Photochemical Sciences.

EDITORIAL POLICY

The Spectrum reserves the right to review and edit all submissions. The Spectrum is not responsible for contents of articles.

Articles submitted to The Spectrum will appear at the discretion of the editorial staff as space is available.