

Investigations of Photocatalytic Surface Chemistry Using *In Situ* Solid-State NMR

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Introduction

Photocatalysis provides a promising solution to the problem of widespread use and release of volatile organic compounds (VOCs), many of which pose serious environmental threats.¹⁻⁵ The most common photocatalysts in use today are TiO₂ and ZnO because of their activity and stability compared with other semiconductors. The detailed mechanisms that describe the observed multiple-step surface reactions are complex and are not fully understood. However, what is generally known is that the absorption of UV light by the semiconductor material photo-excites electrons from the valence band to the conduction band producing electron-hole pairs within the semiconductor. These electrons and holes can then either recombine, producing heat, or migrate to the surface and initiate redox reactions with adsorbed species through electron transfer. Surface OH groups can be converted to highly reactive OH radicals by acting as hole scavengers. OH radicals can then abstract hydrogen to start the degradation process. It has also been proposed that adsorbed O₂ can act as an electron trapping agent and combines with the electron to form superoxide radical, which can also initiate degradations.^{6,7} These steps are shown in Figure 1.

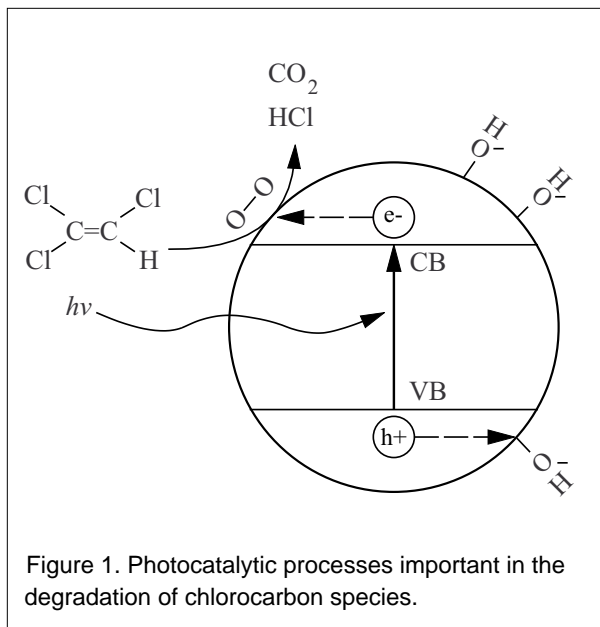


Figure 1. Photocatalytic processes important in the degradation of chlorocarbon species.

The complexity inherent in photocatalytic oxidations is demonstrated by the degradation of trichloroethylene (TCE). A number of recent studies have focused on the photocatalysis of TCE due to its importance in industry and its role as an environmental hazard.⁸⁻¹² Complete mineralization to CO₂ and HCl occurs for a number of organochlorine photocatalytic reactions, however, a recent study of TCE photodegradation indicated a number of intermediates and by-products were formed, including CO, Cl₂, dichloroacetyl chloride (CHCl₂CClO, DCAC) and phosgene (COCl₂).¹⁰ There is still considerable debate regarding the identity of the major initiator in the reactions.^{11,12}

Despite recent progress towards the understanding of photocatalytic processes, a number of important questions remain. Mechanistic studies are still at an early stage, and systematic studies of a broad range of compounds is currently lacking. In particular, the formation (and ultimate elimination) of undesirable intermediates is an important concern. The identities, distributions and concentrations of these species may be modified by reactor conditions such as oxygen or humidity levels, light intensity and throughput. The relative importance of gas-phase versus surface reactions remains an important issue that will have considerable impact on

From the Executive Director

D.C. Neckers, Center for Photochemical Sciences, Bowling Green State University

Paul D. Bartlett (P.D.) turns 90 years old in August. In celebration of the occasion, some of his former collaborators are hoping to arrange to deluge him with birthday cards. P.D. has a large connection to the Center for Photochemical Sciences. George Hammond, McMaster Distinguished Visiting Professor, took his Ph.D. under P.D.'s direction in 1947, and I did postdoctoral work with him. His connections in the photochemical sciences extend to many students and research associates who became intrigued with light as a reagent, tool, initiator, and probe.

Louis Hammett, in his acceptance address for the James Flack Norris Award of the American Chemical Society, described Bartlett's work on halonium ions, first published in 1934, as the most important of all in the beginning days of physical organic chemistry. Hammett was, I think, the first winner of the Norris Award in physical organic chemistry for the work which formed the underlying relationships of structure to reactivity.

It would be impossible, in so short a space, to do justice to Bartlett's fundamental physical organic studies that led to carbonium theory, free radical reactivity, understanding the mechanisms of cycloadditions, radical chain reactions and polymerization, structure reactivity in carbanions, oxygen chemistry and oxidation, and the many other areas which now form the basis of mechanistic theory in organic chemistry.

I would like to describe his ability to work with, and mentor, students and postdoctorals. He was a master at leading, cajoling and developing young talent which contributed to his enormous productivity. When I was a postdoc, P.D. divided his group into smaller ones based on similar areas of research. We met with him once a week to discuss the results. I don't remember much, if anything, of significance that I contributed to these meetings, but do remember the excitement when Steve Nelson synthesized the first tertiary aliphatic azo compound, when Larry Singer finally figured out the structures of his 2 + 2 adducts of fluorenone to olefins, and Nick Turro finally figured out that the photodecarbonylation of tetramethylcyclobutanedione probably first involved the formation of tetramethylcyclopropanone. These meetings, and other informal, group events engendered a spirit of collaboration and cooperation. Competitive environments were fostered in other groups in chemistry departments those days, but Bartlett's group had a congenial, collegial spirit. That's one of the most important things I remember about the Bartlett experience.

As a result, creative, energetic, hard-working people developed collaborations that went far beyond their current research projects. Consequently, research from the Bartlett group went well beyond the contributions of a single Harvard professor and still another graduate student or postdoctoral. Paul Bartlett was years ahead of time in understanding how to get the most of bright people; therein lies still another secret of his success.

Happy Birthday, Paul! Your former colleagues, nationwide and worldwide, wish you the very best as your years become four score and ten. Please send P.D. a birthday card at Brookhaven at Lexington, 1010 Waltham St., Lexington, Massachusetts 02173. You can also find out more information about the card project at: <http://koerner.chem.yale.edu/bartlett.html>.

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the ultimate photocatalytic reactor design. Finally, the role of oxygen or OH as the primary initiating species remains somewhat unclear, and may also depend on reaction conditions or the nature of the organic reactant. There is a need to understand structural and dynamical issues at a more fundamental level such that photocatalytic methods may be further developed.

Solid-state NMR methods can contribute significantly in answering many of the persistent questions regarding photocatalytic oxidation, since NMR provides a wealth of structural and dynamical information and therefore acts as a powerful method for probing catalytic surface chemistry.¹³⁻¹⁵ NMR can sensitively probe surface structure, and has successfully addressed a variety of important issues in catalysis. In addition, NMR provides unique dynamical information relevant to catalysis, including the characterization of molecular motions and diffusion. NMR thus provides complementary information to that obtained with other methods. The application of solid-state NMR to study environmental catalysis is a developing area of research.

Solid-State NMR Studies

The application of *in situ* detection methods to reactions provides a means to obtain fundamental understanding of the underlying processes. We have developed an *in situ* magic angle spinning (MAS) NMR probe (see Figure 2) and sample preparation method to allow us to initiate photocatalytic reactions and to observe the reaction kinetics as they transpire inside our NMR magnet.¹⁶ MAS experiments are conducted by rapidly spinning the sample about an axis inclined at an angle $\theta = 54.7^\circ$ with respect to the applied field. The broadening due to anisotropic chemical shift interactions is averaged to zero as a result, leaving a sharp spectrum consisting of the isotropic chemical shift (as is observed in the NMR spectra of liquids) plus modulation side bands at the sample rotation speed that contain information on the anisotropic chemical shift interaction. Consequently, MAS provides the line narrowing capability necessary to study amorphous solids and adsorbates with high resolution, and gives information on the full three-dimensional chemical shift tensor for use in molecular structure determination.

Our home built optical/MAS NMR probe is doubly tuned for proton and carbon observation and allows us to reliably spin sealed samples up to 3 kHz. The probe incorporates a light pipe to bring the UV light to the sample through a gap in the radio frequency coil. The UV light diverges from the light pipe to cover the entire sample region. Samples sealed in 5 mm glass NMR tubes allow us to control carefully the reaction conditions and coreactant concentrations and at the same time transmit over 80% of the UV light (out to 300 nm) to the sample. Using this method to study photocatalytic reactions, we have identified new species that further our understanding of the mechanisms involved in the surface chemistry.

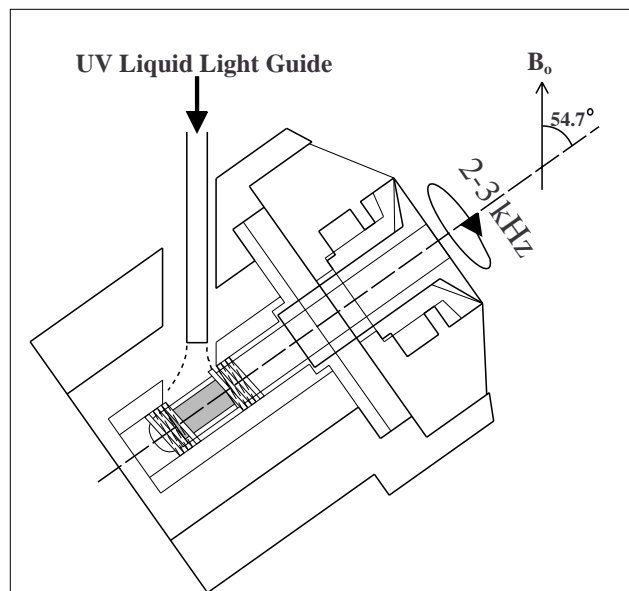


Figure 2. *In situ* magic angle spinning NMR probehead used for the study of photocatalytic surface chemistry.

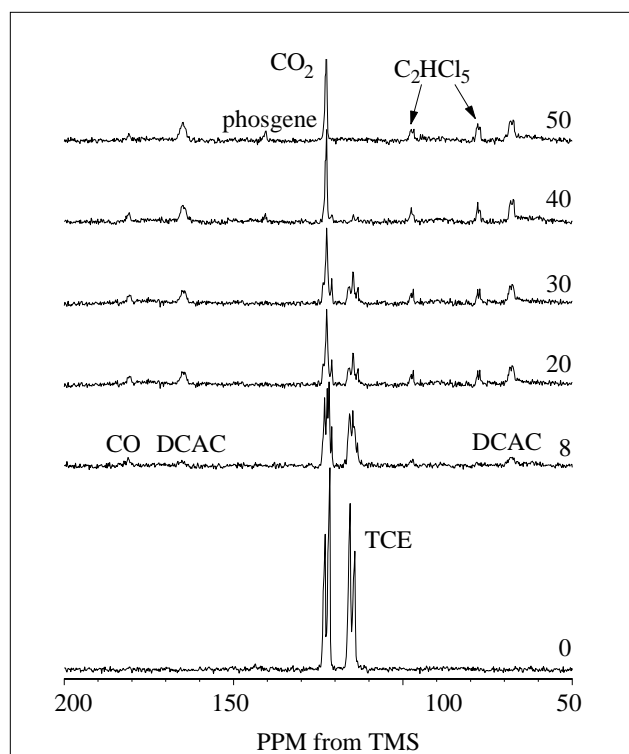


Figure 3. ¹³C NMR spectra acquired during the *in situ* irradiation of TCE in the presence of O₂ and Degussa TiO₂ powder. The irradiation time is indicated to the right of each spectrum.

Two types of catalysts, commercially available Degussa P-25 powder, and monolayer TiO_2 catalysts supported on Vycor porous glass were used to study the photodegradation of TCE in the presence of varying amounts of water and O_2 .¹⁶ Spectra taken every few minutes under continuous irradiation allow the reactions to be followed. Figure 3 shows proton-decoupled ^{13}C MAS NMR spectra obtained from the photooxidation of TCE in the presence of O_2 and Degussa TiO_2 powder. The NMR spectra show the degradation of TCE and formation of DCAC, CO, phosgene, and pentachloroethane (C_2HCl_5), and their conversion to the final product CO_2 . The narrow line widths of the peaks indicate that these species are very mobile, and most likely exchange rapidly between the surface and the gas phase. Assignments of these intermediates are confirmed by comparing ^{13}C NMR shifts for liquid samples reported in the literature¹⁷ or prepared in our lab, and from proton coupled spectra during the photoreactions.

Most of the intermediates identified above are in good agreement with previous reports.^{12,18,19} There was no indication of the formation of mono- or dichloroacetaldehyde observed in previous studies.²⁰

A carbon balance obtained from the peak areas of the aforementioned five species, however, indicated a significant loss (up to 50%) of signal from the original TCE concentration. A separate spectrum obtained with ^1H to ^{13}C cross polarization (Figure 4) exhibits additional broad peaks which account for the apparent loss in signal. The new signals arise from a strongly adsorbed species, which we identify as dichloroacetate (DCAC). DCAC presumably forms from the reaction of DCAC with surface hydroxyl groups. The observed line widths result from adsorption site heterogeneity. Continued UV irradiation did not break up DCAC, while other, more mobile species were converted into CO_2 . These results indicate that some reaction intermediates such as DCAC migrate to the nonirradiated, central portion of the catalyst and react to form stable, strongly surface bound species. Such species may play a role in the observed deactivation of titania catalysts.^{21,22}

A second TiO_2 photocatalyst consisting of highly dispersed TiO_2 (roughly 25% of a monolayer) on the surface of transparent porous Vycor²³ glass (PVG) was synthesized following methods developed by Anpo and co-workers²⁴ and employed in order to minimize the UV light scattering problem of the powdered catalyst. A ^{13}C MAS NMR spectrum (see Figure 5) taken after UV irradiation shows that TCE breaks down to form a number of reaction intermediates. Among these species, DCAC, phosgene and CO_2 were observed, as in reactions using the powdered catalyst, and in agreement with recent reports.^{10,12} New intermediates: trichloroacetyl chloride (Cl_3CCOCl , TCAC) and trichloroacetic acid ($\text{Cl}_3\text{CCO}_2\text{H}$, TCACOH), which forms after reaction with residual surface water, were also identified.

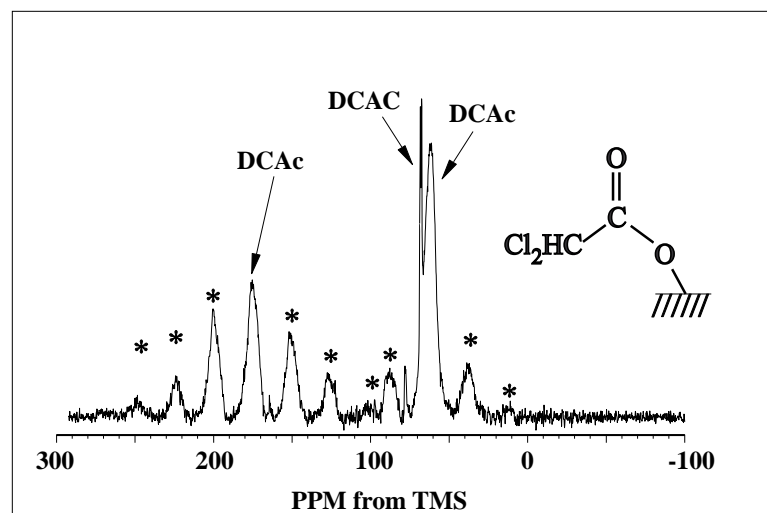


Figure 4. A spectrum acquired using cross polarization shows the signal arising from surface adsorbed DCAC, whose structure is represented above the spectrum. Asterisks denote spinning side bands of DCAC.

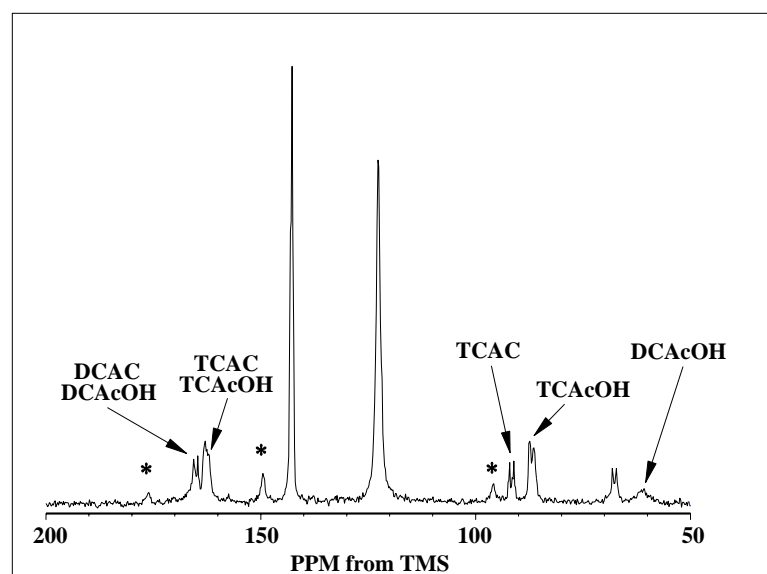


Figure 5. ^{13}C NMR spectrum after UV irradiation of TCE in the presence of O_2 and TiO_2 /Vycor catalyst.

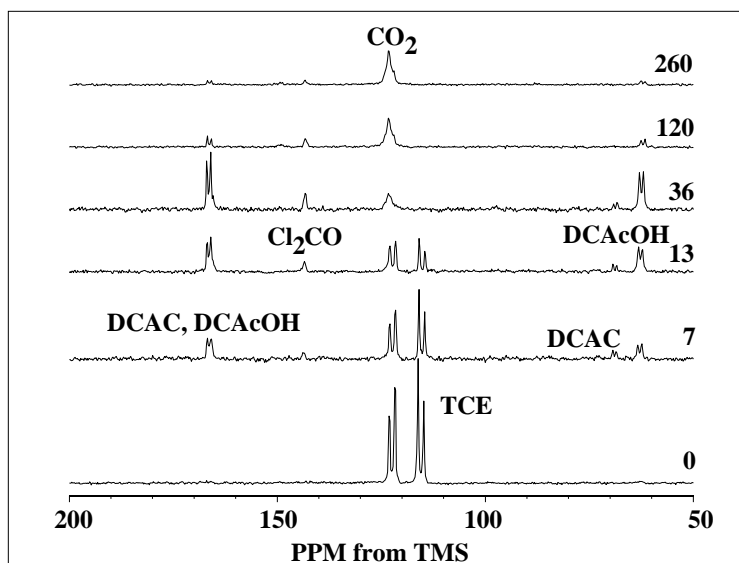


Figure 6. NMR spectra acquired during the *in situ* photocatalysis of TCE in the presence of O_2 , H_2O and TiO_2 /Vycor catalyst.

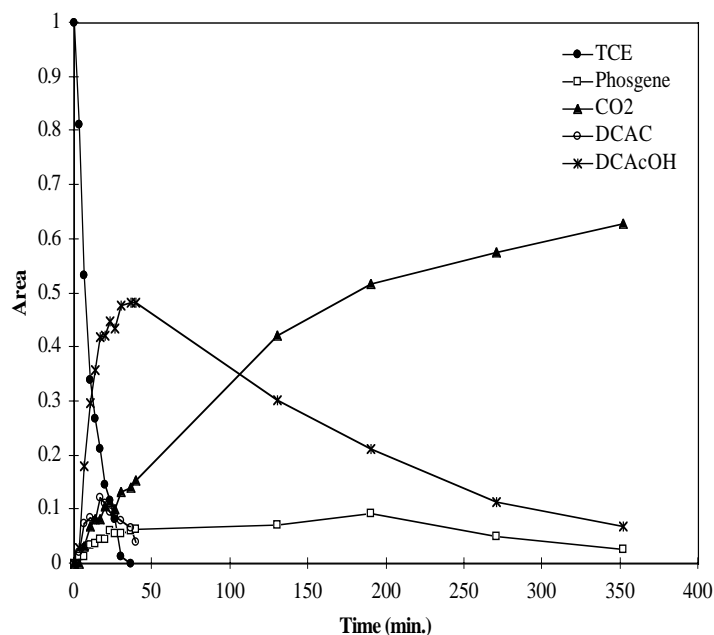


Figure 7. Kinetics of the degradation obtained from the integration of the peak areas in the spectra shown in Figure 6.

Photocatalytic reactions in the presence of roughly a monolayer of surface H_2O as a coreactant (Figure 6) resulted in the observation of similar intermediates, and phosgene was rapidly and almost completely converted to CO_2 . DCAC was found to react with H_2O to form dichloroacetic acid (Cl_2HCCO_2H , DCACOH). No surface-bound species were observed from the photocatalytic degradation of TCE on the TiO_2 -anchored PVG catalyst in contrast to the powdered catalyst. In separate experiments under dry conditions additional species trichloroacetaldehyde (Cl_3CCHO , TCAA) and oxalyl chloride ($ClCOCOCl$) were observed.¹⁶

Quantitative information on the fate of each species can be acquired from the direct integration of peak areas in the spectra. Figure 7 shows such a kinetic plot from the experimental results of Figure 6. Kinetic studies showed that the fastest rates of catalysis were observed under conditions of excess oxygen and low concentrations of water. However, the addition of water was useful in decreasing the lifetime of potentially harmful intermediates such as phosgene. The initial rate for TCE degradation without added oxygen was very slow. A detailed kinetic analysis of the photooxidation is currently under investigation.

Summary

In situ solid-state NMR methods are useful in the study of fundamental issues related to photocatalytic surface chemistry at the gas-surface interface. Observations of surface-bound species identified using cross polarization MAS NMR techniques indicate the need to remove or minimize the light scattering problem of powdered photocatalysts under packed conditions. Two possible solutions to this problem are thin film and supported catalysts which reduce or eliminate the buildup of long-lived intermediates in dark regions of the catalyst. Besides the identification of intermediates and determination of reaction kinetics, studies of the structure and dynamics of surface species using solid-state NMR methods are currently underway in our laboratory and are aimed at advancing the understanding of the mechanisms, efficiencies and pathways of photocatalysis. We hope that ultimately this work will result in improving the feasibility and applicability of photocatalytic processes.

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Spatially-Localized Band-Filling Effects and Band-Gap Renormalization in Growth-Interrupted Quantum Wells

Yujie J. Ding, Department of Physics and Astronomy, Centers for Materials and Photochemical Sciences, Bowling Green State University; Jacob B. Khurgin, Department of Electrical and Computer Engineering, The Johns Hopkins University

Growth interruption has become essential to improvement of interface roughness of epitaxial layers. It implies that during the growth of epitaxial layers at an interface formed by two epitaxial layers the growth of additional atomic layers is stopped for a short period of time. Since most growth is done at a high substrate temperature, during growth interruption some surface atoms move to the sites such that the total energy of the atoms as a result of atomic bonding is lower. As a result, many islands with small lateral sizes can join together to form one island with a large lateral size. Photoluminescence (PL) spectroscopy has been an effective technique to characterize interface properties of epitaxial layers.

After growth interruption at interfaces, one broad PL peak breaks into multiple ones.^{1,2} This is due to recombination of free excitons and localized ones in interface islands with their sizes larger than the exciton radius. The well widths at the islands differ by multiple monolayers (ML's) with respect to the designed width.³ At 4 K, all the carriers generated by the pump laser will be eventually relaxed down to the lowest energy level and spatially localized in the islands, resulting in huge carrier densities. If the total area of the islands is small, it would be possible to completely fill exciton states in these islands at relatively low laser intensities that may manifest itself as the saturation of the PL peaks. Although band-filling effects in a growth-interrupted single quantum well (QW) structure were first mentioned in Reference 4, any of the split bands was far from complete filling. In growth-interrupted samples, band-filling effects and band-gap renormalization are spatially-localized effects, since all the islands are spatially isolated.

In this short note, we review our results on six samples which have different structures and/or doping profiles. The three-well sample (sample #1)⁵ grown by MBE consists of 10 periods, each of which is composed of three narrow asymmetric coupled GaAs QW's with the widths of 17, 10, 15 ML's, coupled by 14-ML Al_{0.3}Ga_{0.7}As barriers. The adjacent periods are also coupled by 14-ML Al_{0.3}Ga_{0.7}As barriers. We interrupted the growth at every interface for 60 s. At 4 K, the PL peak corresponds to recombination of localized excitons at interface islands. Its linewidth is as narrow as 1 meV. We have observed pronounced broadening of the linewidth when the laser intensity increases. However, for the range of the laser intensities: 0.54 W/cm² - 1.9 kW/cm², the transition energy at the PL peak position stays the same. The PL linewidth broadening, which has not been observed before, is caused by spatially-localized band-gap renormalization. The modulation-doped three-well sample (sample #2)⁵ has the same structure as sample #1 except that the barriers between the 17-ML and the 10-ML wells were doped with Si of density 10¹⁷ cm⁻³. The PL spectrum is dominated by impurity emission at low laser intensity. However, as the laser intensity increases, the emission peak due to the recombination of the spatially-localized excitons dominates. As the laser intensity increases further, the free-exciton recombination dominates. We have almost completely filled the impurity sites and localized exciton states sequentially (band-filling effect). We have determined the PL decay time constant to be 438 ps. The saturation intensity required to completely fill the spatially-localized e₁hh₁ exciton states is about 1.2 kW/cm². The corresponding exciton area density is 1x10¹⁰ cm⁻², which is an order of magnitude smaller than that outside the islands.

The third sample⁶ grown by MBE consists of 20 isolated periods, each of which is composed of two narrow asymmetric coupled GaAs QW's with the designed thicknesses of 50 Å and 65 Å, coupled by 35Å-Al_{0.35}Ga_{0.65}As barriers. The growth is interrupted for 60 seconds at every interface. At the laser intensity of 9.7 mW/cm² there are two emission peaks in the PL spectra: the one at ~7780 Å corresponds to the emission of excitons at the interface islands while the other one at ~7773 Å corresponds to the free excitons. When we change the laser intensity from 9.7 mW/cm² to 1.4 W/cm² at 4 K, the emission peak for the localized excitons loses its relative strength. This is due to the band filling effect at the spatially-localized islands. The PL signal at the e₁hh₁ emission peak has a decay time of about 270 ps. The laser intensity required to completely fill the e₁hh₁ exciton states is about 1.4W/cm². The corresponding exciton density is then estimated to be 9.8x10¹² cm⁻³, which is more than two orders of magnitude lower than that for the three-well sample. The fourth sample⁶ is designed to have the structure identical to the third sample. At the laser intensity

of 25 W/cm², the PL spectrum consists of three peaks. The peak located at 7777 Å corresponds to the free excitonic e₁hh₁ emission. The other two peaks at 7788 Å and 7808 Å correspond to the recombination of the excitons at the interface islands. As the laser intensity increases, the relative strengths of the two peaks on the low-energy side decrease. At the laser intensity of 153 W/cm², these two peaks are almost completely saturated. The linear exciton recombination time is determined to be 280 ps. The exciton density for saturating the PL peaks at the islands is 1.1x10¹⁵ cm⁻³. This is about two orders of magnitude higher than that for sample #3, mainly due to the difference in interface roughness.

The fifth sample is designed to have the identical structure as that for samples #3 and #4 except that the 65 Å well in each unit is compensate-doped with Be and Si of densities 3x10¹⁷ cm⁻³. At the laser intensity of 0.5 W/cm², the broad peak located at 7950 Å in the PL spectra corresponds to donor-to-acceptor transition. The second peak located at 7800 Å corresponds to free excitonic transition. As the laser intensity increases, the relative strength of the free excitonic peak increases. At the laser intensity of 423 W/cm², it dominates the PL spectrum. Meanwhile, there is a blue shift of the broad peak. The maximum amount of the shift is about 11 meV as the laser intensity increases from 0.5 W/cm² to 423 W/cm². The amount of the shift is several times larger than that in bulk sample. Time-resolved PL measurements are on the way for identifying the exact origin of the blue shift.

The sixth sample⁷ had 20 isolated periods, each of which consists of 23 and 18 ML QW's, coupled by a 12 ML Al_{0.2}Ga_{0.8}As barrier. The growth was interrupted for 10 s at each interface. We observed relative saturation among excitonic emission peaks at different sets of interface islands due to sequential filling of excitonic states at different sets of interface islands. As a result of the relative saturation, an effective blue-shift of the apparent excitonic emission peak at the islands, with a magnitude as large as ~6.1 meV, is observed when the laser intensity increases from ~1.6W/cm² to ~215W/cm². The highest intensity required to observe the effective blue-shift is about two orders of magnitude lower than that needed to observe a similar effect for a free excitonic emission peak.

In conclusion, we have studied six samples of multiple quantum wells based on photoluminescence spectroscopy. We have varied amount of growth-interruption time at every interface and doping density. Consequently, we have observed their dramatic effects on the photoluminescence spectra. Even for the samples grown under the same growth condition and same growth-interruption time, photoluminescence spectra and saturation behaviors can be completely different. While it is obvious that additional study is necessary, photoluminescence spectroscopy remains to be an effective technique to characterize interface islands.

Acknowledgment

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Mentors and Mentees

**George S. Hammond, McMaster Distinguished Visiting Professor, Center for Photochemical Sciences,
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According to Ancient Greek history, Mentor was a friend of Odysseus entrusted with the education of the latter's son, Telemachus. The term has come to mean any trusted guide or coach. Although common usage has come to broaden the meaning somewhat the word still refers most commonly to a one-on-one instruction and guidance relationship. Mentor-mentee pairs may be found in all walks of life--prisons, churches, on-the-job work situations and so on. However, the most familiar to many of us is the relationship between graduate (post graduate) students including many postdoctoral fellows, and the research directors with whom they are associated. In the sciences and engineering this informal, but widely practiced, system is the core of advanced education in the technical arena.

The style of graduate education is usually set largely by individual research directors although there is guidance from above--departments and the institution. It is the first level at which real mentoring occurs, guidance from on high is largely in the form of rules, some useful and some of questionable value. A research director may appear in various forms to his mentees--an all wise pundit, a tyrant, a humane counselor, a source of financial support, an absentee landlord, a hopelessly conceited jerk, a friend or a foe. To the director students may be incredibly bright, incredibly stupid, surprisingly familiar with modern instruments, incurable klutzes in hands-on operations, industrious, lazy, deaf to any instructions, wonderfully perceptive about laboratory operations, a friend or the enemy. Some students come to idolize their mentors excessively. I recall one who came to consult me late at night asking help in his decision as to whether he should shoot his mentor, himself or both of them. I was also once warned by some of my own students that X kept a gun in which he was seriously considering turning on me.

The spectrum of mentor-mentee relationships is so wide that it teaches us immediately that there can be no set formula for success. The relationship is highly personal and requires tailoring to suit the personae of those involved. In some cases such adjustment is impossible or at least too difficult to warrant the time and effort to make it work. The people should then recall that it is no disgrace to either if the student then moves on to another mentor.

In the sciences, at least, a principal purpose of a program of graduate study is to facilitate the transition of the mentee from the role of student to the role of scientist. The graduate research director is the principal facilitator of this process. In order for the process to work well both parties must have that goal in mind and accept the consequent responsibilities. The process must be a partnership. I have always decried use of the expression, "X works for Prof. Y". If X isn't working **with** Y someone is missing the boat. The notion that a graduate student puts in three to five years of indentured servitude to earn a license to practice as a professional is far off base. In some ways the practice in some of the humanities in which the doctoral thesis is a work of scholarship produced by the student working essentially alone may be appropriate but it is also obviously lacking if the mentor contributes little or nothing to the work.

If the mentor-mentee relationship is to have the desired outcome, the maturation of the student to become a scientist, both parties have responsibilities. The ways in which these responsibilities are met will vary greatly, depending on the personalities of the people involved and the surrounding circumstances. There are not set formulas for the way in which a research director should direct, nor for the way in which a student should respond to the director. Some academic moguls run their research groups as mini-factories in which their junior coworkers are hired hands assigned to carry out some specific job on the assembly line. This can be a reasonable *modus operandi* if the workers have a fairly clear notion of the grand plan, how their work fits into it, and what their peers are contributing. The common overall goal may provide a basis for instructive dialogue among them. In any academic research group at least two thirds of scientific growth comes from interaction among the workers rather than with the person at the top.

My own style as a research director has been quite different from the factory operation. I have usually had a number of loosely related themes in progress and have suggested two or more problems which new students or postdocs might undertake. When one was chosen I have tended to retire, at least partly, to the role of a consultant who is a source of some information and ideas. I always required brief monthly reports from my coworkers, even when the report simply stated, "I did nothing". We held regular group meetings which were devoted partly to discussion of our

research and partly to general subjects, usually stimulated by current literature. In short, I ran a very loose ship. It suited some of my people, but not all. On occasion students would complain that they needed more specific direction and discipline. I could understand the complaint but insisted that I did best when I worked in a way which suited my temperament. I did, however, point out that there were always other professors around who ran much tighter ships, and that I would facilitate transfer to one of those groups if it seemed desirable. Some students took up the offer; others did not.

There is one policy that I have found to always be desirable in research direction. One **must have and show respect** for one's coworkers. I believe that many professors fail in this respect. They cannot escape from the feeling that, because they are the boss, their coworkers must be a lesser lot. The respect must not only be shown, it must also be felt. That requires that I, as a professor, look at my students and see first what there is in them to respect. There is always a lot there. Those who look at their students only to see what is wrong and in need of repair are missing the boat!

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Electron-Transfer Within A Model Metalloprotein

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Due to their fundamental importance to biological energy-conversion, the study of electron-transfer (ET) reactions has been the focus of considerable interest. Early work in this field used covalently-bound donor/acceptor compounds to determine how such factors as donor-acceptor distance, orientation, and driving force can affect the magnitude of intramolecular ET rates.^{1,2} However, in contrast to these chemically discrete model compounds, the cofactors involved in biological ET reactions are often embedded within a complicated protein matrix which may, or may not, play a role in mediating long-range electronic coupling. Thus, it has been a goal of biological chemists to investigate the putative role of specific protein structure motifs in propagating long-range electron-transfer reactions. Much work has been done within the last 15 years to investigate the ET properties of a variety of biological model compounds. Results from these studies have produced an interesting controversy concerning the role of the protein matrix in mediating long-range electron-transfers. Dutton and co-workers³ have compared many of the available ET data and concluded that the natural protein matrix appears to behave much like an isotropic solvent which presents a *homogeneous barrier* to electron tunneling. However, numerous studies of semi-synthetic systems have shown that different regions of a given protein can indeed display different barriers to electron tunneling.⁴

The resolution of this debate requires that further studies be undertaken to systematically investigate the role, if any, of specific protein structures in mediating long-range electron-transfer reactions. To this end, several workers have investigated the properties of polypeptide-based electron-transfer compounds which are known to adopt specific conformational forms. These include the study of derivatized α -helices,⁵ proline helices,⁶ artificial β -strands,⁷ and β -sheets.⁸ Such work offers an interesting conceptual link between studies of covalently bound donor/acceptor compounds and those of native biological systems. However, whereas many *in vivo* ET reactions occur across a *non-covalent* protein-protein interface, the primary role of the peptide-spacers found in all current model systems is to provide a *covalent* link between the donor and acceptor sites. As such, these systems are poorly suited to probe the mechanisms of ET reactions occurring across a peptide-peptide interface.

We have recently reported the first study of an electron-transfer reaction occurring across a non-covalent peptide-peptide interface within a *de novo*-designed metalloprotein.⁹ A 31 residue polypeptide was prepared by solid-phase methods whose sequence was similar to the two-stranded coiled-coils recently studied by Hodges, Kay and co-workers.¹⁰ However, the sequence was modified to incorporate a single histidine residue at position 21 which is the most highly solvent-exposed position of the third heptad repeat. This modification, called H21(31-mer), provides a convenient binding site for a metal-based redox center. The H21(31-mer) apo-peptide was purified by reverse-phase HPLC and characterized by MALDI-MS (Calculated: 3404; Found: 3405).



Figure 1 shows the circular dichroism (CD) spectrum of H21(31-mer) taken in aqueous solution (pH 7, 25° C) which consists of a positive signal at 195 nm ($\theta > +39,000 \text{ deg cm}^2 \text{ dmol}^{-1}$), and a pair of negative signals at 208 nm ($\theta = -21,800 \text{ deg cm}^2 \text{ dmol}^{-1}$), and 222 nm ($\theta = -22,000 \text{ deg cm}^2 \text{ dmol}^{-1}$). These results indicate that the peptide is $> 69\%$ α -helical.¹⁰ We note that the value of $[\theta_{222}] / [\theta_{208}] = 1.01$ observed for H21(31-mer) is characteristic of an α -helical coiled-coil. In contrast, single α -helices have values of $[\theta_{222}] / [\theta_{208}] = 0.86$.¹⁰ Thermal denaturation studies show that the non-covalent dimer is extremely stable, displaying a non-cooperative melting curve with $T_m = 65^\circ \text{ C}$ (inset, Figure 2). Interestingly, when the 31-mer is dissolved in methanol, the dimer dissociates into two separate α -helices, showing a CD spectrum in which $\theta_{222} = -27,000 \text{ deg cm}^2 \text{ dmol}^{-1}$, and $[\theta_{222}] / [\theta_{208}] = 0.85$.

To further characterize the oligomerization state of the peptide in aqueous solution, discontinuous SDS polyacrylamide gel electrophoresis was performed on samples of the ET metallopeptide discussed below. These samples were prepared in HEPES buffer (pH 7) either at room temperature, or after heating to 80° C for 15 minutes prior to loading.

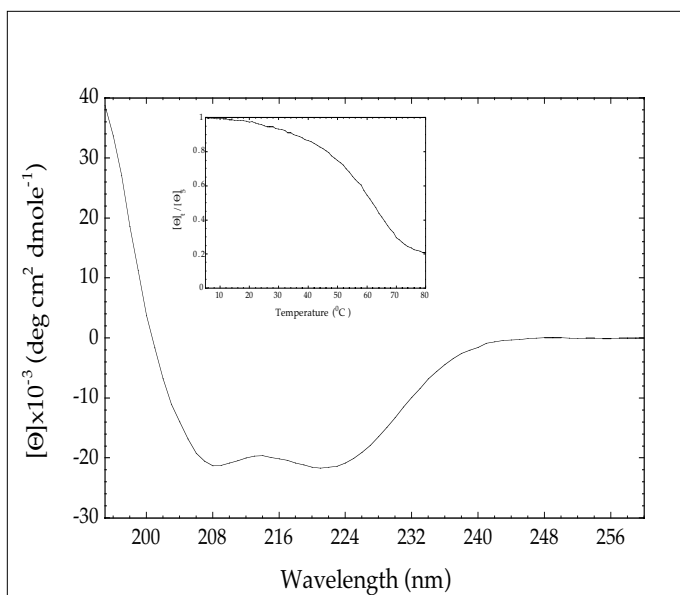


Figure 1. Circular dichroism spectrum of the H21(31-mer) apo-peptide. Inset: Molar ellipticity at 222 nm measured as a function of temperature. The values are normalized to that obtained at 5°C.

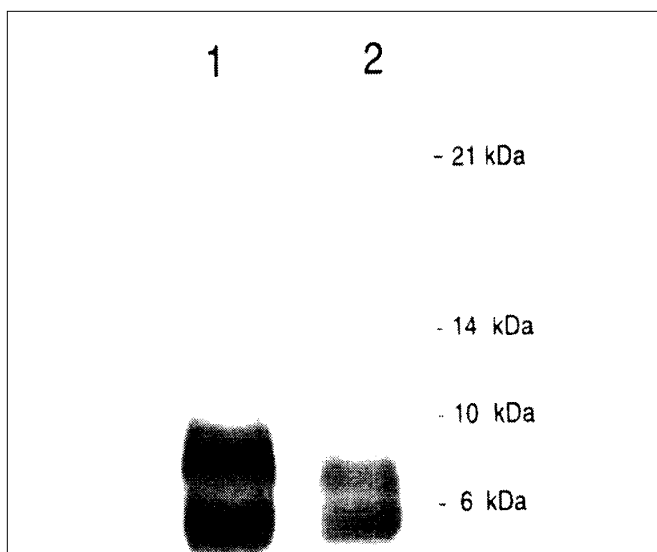


Figure 2. Discontinuous gel electrophoresis performed in the presence of sodium dodecyl sulfate (200 V for 45 minutes). The metallopeptides were solubilized (HEPES buffer, pH 7) at room temperature (lane 1), and after heating to 80°C for 15 minutes (lane 2).

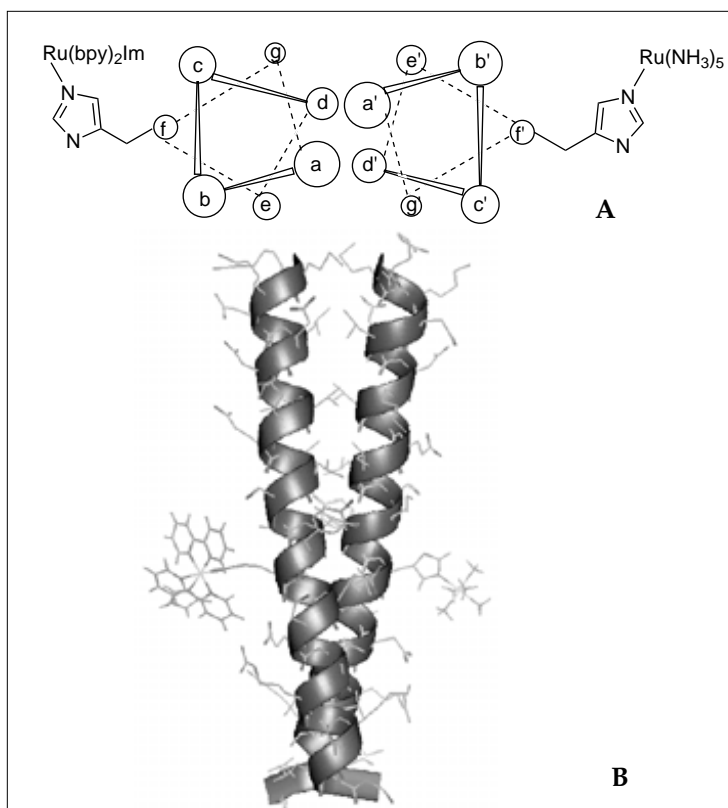


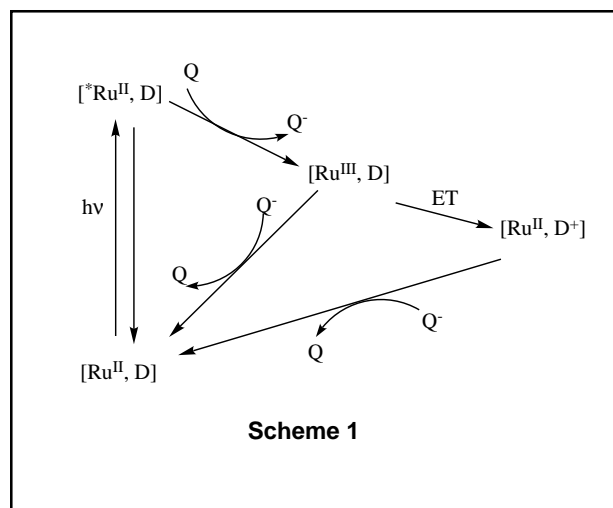
Figure 3. Schematic views of (A) the third heptad repeat of the ET heterodimer and (B) the three-dimensional structure of $[\text{Ru}(\text{bpy})_2\text{ImH21}(31\text{-mer})/\text{Ru}(\text{NH}_3)_5\text{H21}(31\text{-mer})]$ produced by docking Ru sites to the structure of GCN4.

The molecular mass standards, aprotinin (6 kDa), plastocyanin (10 kDa), lysozyme (14 kDa), and cytochrome *c* (21 kDa) were run in parallel for comparison. The results showed the existence of two species having molecular weights of ca. 3.5 and 7 kDa, respectively to indicate that a population of peptide monomers and dimers exists in solution (Figure 2). Significantly, no evidence for higher oligomeric forms was observed. The similarity of the results obtained before and after heating to 80°C indicates that the peptide dimer reforms quickly upon cooling back to room temperature. This property will be used below in the preparation of the desired electron-transfer systems.

The metallo-homodimers, $[\text{Ru}(\text{bpy})_2\text{ImH21}(31\text{-mer})]_2$ and $[\text{Ru}(\text{NH}_3)_5\text{H21}(31\text{-mer})]_2$ (bpy = 2,2'-bipyridine, Im = imidazole) were prepared by appropriate modification of methods described previously for the ruthenium modification of cytochrome *c*.^{11,12} The absorption spectrum of $[\text{Ru}(\text{bpy})_2\text{ImH21}(31\text{-mer})]_2$ shows maxima at $\lambda_{\text{abs}} = 203, 245, 290, 340,$ and 485 nm, which is similar to that of $[\text{Ru}(\text{bpy})_2\text{Im}_2]^{2+}$. The emission properties of the metallo-homodimer ($\lambda_{\text{em}} = 688$ nm, $\tau = 79$ ns in H_2O) are also nearly identical to those of $\text{Ru}(\text{bpy})_2\text{Im-cyt } c$. The cyclic voltammogram of $[\text{Ru}(\text{NH}_3)_5\text{H21}(31\text{-mer})]_2^{3+}$ shows a single reduction at $E^0 = +0.078$ V vs. NHE, which is identical that reported for $\text{Ru}(\text{NH}_3)_5$ -modified cyt *c*.¹¹

Significantly, metallation of the H21(31-mer) does not alter its conformational properties as its CD spectrum remains essentially unchanged from that of the apodimer. However, the metallo-homodimers exhibit a slightly higher CD melting temperature ($T_m = 70^\circ \text{C}$) which suggests that the placement of charged metal complexes at the solvent-exposed sites of the helices reinforces the amphipathic nature of the peptide.

The desired ET heterodimer (Figure 3), $[\text{Ru}(\text{bpy})_2\text{ImH21}(31\text{-mer})]/\text{Ru}(\text{NH}_3)_5\text{H21}(31\text{-mer})$, was prepared by heating an approximately equimolar solution of the two homodimers to 80°C for 30 minutes, and allowing the sample to cool back to room temperature. It is noted that this procedure should produce a statistical mixture of the homo- and heterodimers. However, only the latter species can display intracomplex electron-transfer. Computer modeling studies using the Spartan software package (Wavefunction, Inc., Irvine, CA) suggest that the metal-to-metal distance in the heterodimer is roughly estimated to be $23 \pm 2 \text{ \AA}$, assuming that the peptide remains isostructural to GCN4.¹³ The uncertainty in this estimate arises from consideration of the various rotameric forms of the metal-peptide conjugate. The short emission lifetime of the $[\text{Ru}(\text{bpy})_2\text{ImH21}(31\text{-mer})]_2$ homodimer precludes the use of direct laser flash photolysis to measure ET rates over long distances. Instead, the oxidative laser flash-quench technique¹² was employed (Scheme 1) in which $\text{Q} = \text{Ru}^{\text{III}}(\text{NH}_3)_6$. In this experiment, the ruthenium polypyridyl complex is photoexcited by a ca. 7 ns laser flash (532 nm, Nd:YAG) in the presence of a large excess of



$\text{Ru}^{\text{III}}(\text{NH}_3)_5$. The resulting quenching reaction rapidly produces a small amount ($< 10^{-6} \text{ M}$) of $\text{Ru}^{\text{III}}(\text{bpy})_2$ -peptide which decays slowly by a second-order recombination with the reduced quencher. The newly formed Ru^{III} polypyridyl site ($E^0 = +1.07 \text{ V}$) can also oxidize the proximal $\text{Ru}^{\text{II}}(\text{NH}_3)_5$ center by intra-complex electron-transfer which can be monitored by transient absorption spectroscopy. The driving force of the ET reaction is calculated to be $\Delta G^0 = 0.99 \text{ V}$, using $E^0 = +1.07 \text{ V}$ vs. NHE for $[\text{Ru}(\text{bpy})_2\text{H21}(31\text{-mer})]^{3+/2+}$.¹⁴

In a preliminary control experiment, photoexcitation of a solution containing the $[\text{Ru}^{\text{II}}(\text{bpy})_2\text{ImH21}(31\text{-mer})]_2$ homodimer ($21 \mu\text{M}$) and $\text{Ru}^{\text{III}}(\text{NH}_3)_6$ (9 mM) produced a prompt increase in absorption at 306 nm , and a bleach at 480 nm (Figure 4) indicating rapid formation of the oxidized ruthenium polypyridyl complex. No evidence for the bimolecular recombination reaction was observed under these conditions (inset, Figure 5) due to the small yield of $^*[\text{Ru}(\text{bpy})_2\text{Im-peptide}]$ produced by the laser flash ($5 \times 10^{-7} \text{ M}$). However, higher initial peptide concentrations produced a larger concentration of flash-quench products which recombined with a measurable second order rate constant of $k_{\text{rec}} = 2.0 \pm 0.3 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$.

When the flash quench experiment was performed on a dilute ($64 \mu\text{M}$) sample of the statistical mixture of homo- and heterodimers, an identical transient difference spectrum was observed. However, the spectral changes followed very different kinetics. Figure 5 shows that the bleach at 480 nm decayed with a *first-order* rate constant of $k_{\text{et}} = 3.5 \pm 0.2 \times 10^3 \text{ s}^{-1}$ to a persistent negative baseline. Similar kinetics were observed at 306 nm , except that a persistent increase in absorption was seen at longer times (not shown). The long-lifetime component observed in both curves is consistent with the presence of a population of $[\text{Ru}^{\text{III}}(\text{bpy})_2\text{ImH21}(31\text{-mer})]_2$ homodimer which undergo slow recombination. However, the *first-order* rate constant is independent of peptide concentration ($21 - 140 \mu\text{M}$)

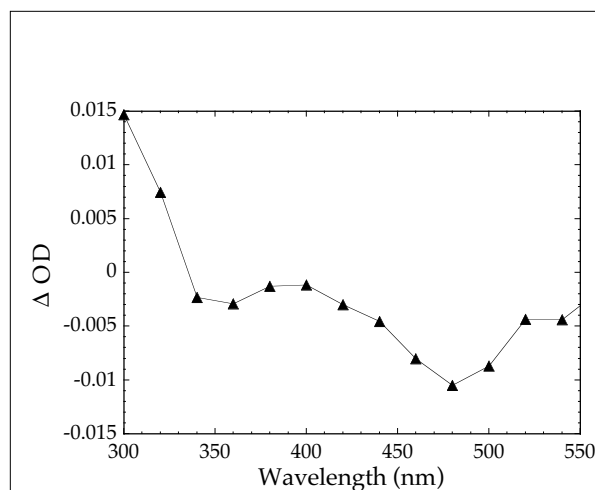


Figure 4. Transient absorption spectrum obtained 26 ms after photolysis of a solution of the $[\text{Ru}(\text{bpy})_2\text{ImH21}(31\text{-mer})]_2$ homodimer (21 mM) and $\text{Ru}^{\text{III}}(\text{NH}_3)_6$ ($9 \times 10^3 \text{ mM}$).

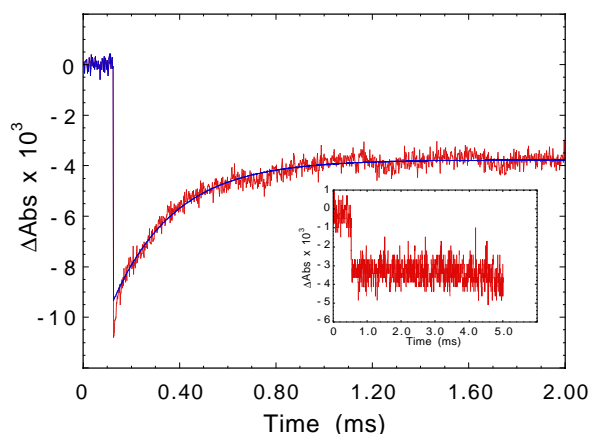


Figure 5. Transient absorption kinetics obtained after photolysis of a solution of the $[\text{Ru}(\text{bpy})_2\text{ImH21}(31\text{-mer})_2]$ homodimer, $[\text{Ru}(\text{NH}_3)_5\text{ImH21}(31\text{-mer})_2]$ homodimer, and $[\text{Ru}(\text{bpy})_2\text{ImH21}(31\text{-mer})\text{-Ru}(\text{NH}_3)_5\text{H21}(31\text{-mer})]$ heterodimer (total peptide concentration = 64 mM) and excess of $\text{Ru}^{\text{III}}(\text{NH}_3)_6$ at 480 nm. The solid lines are fits to a single exponential decay expression in which $k_{\text{et}} = 3.5 \pm 0.2 \times 10^3 \text{ s}^{-1}$. Inset: flash-quench kinetics obtained from a sample of $[\text{Ru}(\text{bpy})_2\text{ImH21}(31\text{-mer})_2]$ homodimer (21 mM).

and can be observed only in the presence of the heterodimer. This process is therefore assigned to the electron-transfer reaction occurring across the peptide-peptide interface over a distance of ca. 23 Å (Figure 3b).

The work described above provides an early example of a model protein that has been specifically designed to perform a simple photoinitiated chemical reaction, and may contribute towards the design of artificial photoenzymes and peptide therapeutics. Future work in our lab will attempt to exploit some of the unique features of this system to further our understanding of the mechanisms of biological electron-transfer reactions.

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