

# Mechanistic Aspects of Photoconversion at Semiconductor-Liquid Junctions and in Facilitated Transport Membranes

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## A. Summary

A major portion of the research completed during this funding period involved the use of rotating ring-disk electrochemical techniques in conjunction with carefully chosen solution redox systems to investigate hot electron transfer reactions at the semiconductor electrolyte interface (SEI). Initially, an attempt was made to observe hot electron processes at GaAs/AlGaAs superlattice materials (provided by NREL) in acetonitrile solutions containing redox couples that had been developed in prior studies at p-InP electrodes (Section B). It was found that the superlattice electrodes only exhibited stable photocurrents in solutions containing very reducing cobaltocene-based redox couples. These reducing conditions were not compatible with the available compounds capable of detecting hot electrons, so a wide variety of alternative systems were synthesized and characterized. Although a suitable redox system composed of dicarbomethoxy-cobaltocene<sup>+0</sup> and dibromo-3,3-dimethylbutane was developed, illumination of GaAs/AlGaAs superlattice electrodes in these solutions showed no evidence for hot electron transfer into the solution.

Due to the stability problems observed with the superlattices, the photoelectrochemical properties of an alternative material, p-GaAs electrodes passivated by a thin (30-50 Å) GaInP<sub>2</sub> overlayer (also provided by NREL), were investigated (Section C). These studies, which involved photocurrent and capacitance measurements as a function of solution redox potential, indicated that the GaInP<sub>2</sub> surface layer did reduce the surface states in the middle and lower regions within the band gap, producing a nearly ideal interface with respect to interfacial energetics. Slight band edge movement under illumination indicated that there were high energy surface states, predominantly within 0.4-0.5 eV of the conduction band, that were accessible to photogenerated minority carriers (electrons). Unfortunately, the photocurrent onsets observed in these studies indicated that while the GaInP<sub>2</sub> overlayer successfully passivated p-GaAs, the reaction of photogenerated electrons with redox couples in solution was relatively slow. This result implies that observation of hot electron transfer at these materials would not be expected and, indeed, was not observed.

Prior studies of photoreduction processes at p-InP electrodes had indicated that evidence for hot electrons could be observed, but not reproducibly. Attempts at improving these experiments by varying the surface etching procedures were unsuccessful. This led to a careful re-examination of the original experiments from which there were two overall conclusions (Section D). First, photoreduction of the hot electron probe, dibromoethylbenzene (DBEB), was inevitably associated with some degree of band edge movement. Therefore, it was not possible to ascertain whether observed reduction of DBEB was due to hot electrons with redox energies higher than the conduction band edge or to thermalized electrons that had accumulated at the interface as a result of steady-state

illumination. Second, metallocene redox couples such as decamethylferrocene<sup>+/0</sup>, which are necessary in these experiments to fix the solution potential and stabilize the band edge positions during illumination, reacted with photogenerated minority carriers with rate constants that are orders of magnitude faster than the rate constant for reduction of DBEB. Therefore, significant photoreduction of DBEB in the presence of metallocenes requires concentrations of DBEB that cannot be achieved due to solubility limitations.

Even though evidence for hot electrons could not be obtained at the three SEI's discussed above, the studies provided detailed information about the interfacial energetics, the abundance and approximate energies of surface states, and the relative rates of electron transfer to reversible, outer-sphere, one electron couples (metallocenes) and to irreversible couples that produce detectable products (alkyl bromides). Several new redox systems capable of detecting hot electrons were developed; however, successful use of these systems will require discovering materials or surface treatments that provide more rapid transfer of photogenerated electrons to the alkyl bromide. Some possibilities for achieving this goal are suggested in the renewal proposal.

The RRDE studies involving photoelectrochemistry at III-V semiconductor electrodes led to a project involving detection of products at particulate TiO<sub>2</sub> electrodes (section E). Other studies had indicated that controlled periodic illumination (CPI) of TiO<sub>2</sub> slurries resulted in significantly greater photoefficiencies than constant illumination. The results, which involved the photo-oxidation of 2-methyl,1-4-hydroquinone (MHQ) at the TiO<sub>2</sub> disk and subsequent reduction of the benzoquinone product at the Pt ring, confirmed that the CPI effect was also operative at TiO<sub>2</sub> particulate films. These results demonstrated that photocatalytic rates observed at TiO<sub>2</sub> particulate films are highly dependent on illumination intensity, illumination time, and dark times between illumination periods. At high light intensities, high photooxidation rates can be maintained for a few tenths of a second after which they decay to < 50% of their initial values. Placing the TiO<sub>2</sub> in the dark for several seconds restores the high rate. These results have important implications for the design of efficient, semiconductor-based photocatalytic reactors.

The other project supported by this grant (Section F) was an investigation of photoresponsive facilitated transport membranes (PFTM). Previous studies involving PFTMs had demonstrated the photomodulation of transport rates or the photo-pumping of solutes against their concentration gradient. However, none represented a fundamental study of the transport mechanism. Preliminary studies were performed to investigate the transport of salts across hydrophobic liquid membranes using the photoactive dye 8-nitro BIPS as the carrier for the system. Convective liquid membrane cells that exhibited minimal mass transfer effects, photocontrol of mass transport rates with visible light, complete and uniform irradiation of the interfaces, and allowed concentration measurements of carrier and solutes in the membrane under different experimental

conditions were designed and characterized. The improvements of our system's performance over similar ones reported were evidenced by improved facilitation factors, better photoefficiency, and a greater quantity of solutes concentrated. In addition to these dynamic measurements, equilibrium measurements to determine parameters such as partition coefficients and spectroscopic studies to characterize the photochemical properties of the carrier were completed. The analysis of these results indicated that membranes containing 8-nitro BIPS are far from ideal PFTMs.

Rather than pursuing other systems blindly, it was decided that developing a mathematical model of the system would aid in the future selection of carriers, solutes, solvents, membrane thickness, and other important factors in an effective system. A general steady-state model describing photofacilitated transport in liquid membranes was developed. The model can be used to consider photoactive carriers with a wide range of thermodynamic and kinetic properties in order to calculate photoinduced transport of solutes down their concentration gradient (photomodulation) and against their concentration gradient (photopumping). The description of transport in these systems is generalized by combining the relevant physical constants (diffusion coefficients, rate constants, concentrations, molar absorptivities, light intensity, etc.) into dimensionless parameters.

### **B. Photoreduction Reactions at GaAs/AlGaAs Superlattice Electrodes**

Certain properties of GaAs/AlGaAs superlattice materials indicated that these materials may exhibit hot electron injection into solution. AlGaAs layers act as barriers to electrons while the GaAs layers form wells in which the energy levels are quantized. Illumination of the superlattice with different wavelengths of light causes transitions to different energy levels within the quantized GaAs wells. Theoretical analysis by Nozik and Ross have shown that compared to the maximum conversion efficiency in single threshold bulk materials of 30%, the conversion efficiencies of a solar energy converter utilizing such multiple threshold devices can reach 66%. Superlattice semiconductor materials were obtained from Nozik and coworkers at the National Renewable Energy Laboratory (NREL) and consisted of alternating thin layers of lattice matched gallium arsenide (150 Å) and aluminum gallium arsenide (17 Å). The superlattice materials were fabricated into rotating ring disk electrodes and electrochemical experiments were performed to study electron transfer at the superlattice/electrolyte interface. The effect of solution potential on the photoelectrochemical behavior of the superlattice electrodes were determined.

The results provided insight into the nature of the superlattice/acetonitrile interface and the solution conditions required for the detection of hot electron transfer. The superlattice electrodes did not exhibit stable photocurrent in decamethylferrocene

(DFER<sup>+,0</sup>) solutions due to surface electron traps. Stable photocurrent was observed in couples with more negative redox potentials such as dicarbomethoxycobaltacene (DCMC<sup>+,0</sup>) and cobaltocene (COB<sup>+,0</sup>), which indicates that the surface states have energies in the lower region of the GaAs band gap. These results indicated that surface states play an important role in the design of a suitable system for hot electron detection at superlattice electrodes by RRDE collection experiments. A redox couple is required that is reducing enough to fill surface states in the lower region of the band gap and that stabilizes the position of the band edges under illumination. This couple needs to have a reduction potential negative of DFER<sup>+,0</sup> ( $E^0 = -0.4$  V). However the redox couple must not be so reducing that it reacts with the possible hot electron acceptor species. For example, a COB<sup>+,0</sup> ( $E^0 = -1.2$  V) solution is too reducing to be used with dibromoethylbenzene (DBEB) as a hot electron acceptor.

The optimization of a solution system meeting all the criteria for hot electron detection at GaAs/AlGaAs superlattices was extensively explored. The most ideal solution system was found to be with DCMC<sup>+,0</sup> as a thermalized electron acceptor and dibromo-3,3-dimethylbutane (DBDMB) as a hot electron acceptor species. However, photoreduction of DBDMB in the presence of DCMC<sup>+</sup>, which would have indicated hot electron transfer from superlattice electrodes, was not observed. It is possible that the kinetics of electron transfer to DBDMB was slow compared to the competing reaction to DCMC<sup>+</sup>, making it impossible to detect hot electrons even if they reach the interface.

### C. Photoelectrochemistry at GaInP<sub>2</sub> Capped p-GaAs Electrodes

GaAs potentially offers several advantages over Si in solar conversion devices, such as a higher theoretical conversion efficiency, enhanced radiation resistance, and a higher temperature of operation. However the efficient performance of GaAs conversion devices requires some sort of surface treatment to (a) minimize surface recombination, (b) enhance minority carrier lifetimes, (c) increase the rate of electron transfer, and/or (d) minimize photocorrosion at the surface. In solid state conversion devices, AlGaAs has been shown to provide nearly perfectly passivated GaAs surfaces; however, this surface is highly prone to oxidation which adversely affects the long term performance of such devices.

GaAs/GaInP<sub>2</sub> interfaces have been shown to provide significantly more stable surfaces than comparable GaAs/AlGaAs junctions with similar characteristics. P-type GaAs electrodes passivated by a thin (30-50 Å) GaInP<sub>2</sub> layer were reported by Nozik et al. at NREL to exhibit near-perfect passivation of surface energy levels (surface states) leading to nearly ideal kinetic behavior. However, prior to this study, there was little in the literature on the photoelectrochemical behavior of GaInP<sub>2</sub> capped GaAs electrodes.

An understanding of the interfacial energetics at SEIs is crucial to the interpretation of results from photoelectrochemical studies of electron transfer kinetics. In this study, we

investigated the photoelectrochemical behavior of an 80 Å  $\text{Ga}_{0.52}\text{In}_{0.48}\text{P}$  capped p-GaAs, rotating disk electrode in acetonitrile solutions containing metallocene redox couples with reduction potentials ranging between -0.3 V and -1.2 V (versus a Ag/0.01 M  $\text{AgNO}_3$  reference electrode). Metallocenes are known to be non-adsorbing and to exhibit outer sphere electron transfer at metal and semiconductor electrodes. By varying the solution reduction potential and the concentration of reduced and oxidized redox species, and by studying the effect on the band edge positions in the dark and under illumination, insight was gained into the energetics of this SEI and the surface states that may exist in the semiconductor band gap.

The studies on the variation of solution potential within the GaAs band gap indicated that the  $\text{GaInP}_2$  surface layer does appear to significantly reduce the surface states in the middle and lower regions within the band gap of the semiconductor. However, band edge movement under illumination indicated that there are high energy surface states, predominantly within 0.4-0.5 eV of the conduction band, that are accessible to photogenerated minority carriers (electrons).

These results have important implications about the use of these electrodes in studying the kinetics of electron transfer to solution. At an ideal semiconductor electrolyte interface, electron transfer may occur at the conduction band edge. However, the presence of surface states allows for surface state mediated electron transfer, and their role must be taken into account in any kinetic study. From this study, it was not possible to determine whether the high energy surface states exist at the GaAs/ $\text{GaInP}_2$  junction or at the  $\text{GaInP}_2$ /electrolyte interface. Using time-resolved photoluminescence (TRPL), Nozik and co-workers have shown that the  $\text{GaInP}_2$  passivated surfaces exhibit very low surface recombination velocities ( $\text{SRV} < 200 \text{ cm/s}$ ). These results indicate that the GaAs/ $\text{GaInP}_2$  junction is almost completely free of defect sites that may contribute to surface recombination. Therefore we proposed that the high energy surface states in the band gap exist at the  $\text{GaInP}_2$ /electrolyte interface where recombination in the TRPL studies is less likely.

#### **D. Further Investigation of p-InP Photocathodes**

The efficiency of photoelectrochemical cells could be improved if charge carriers with significantly greater energy than the band edge (i.e. hot carriers) reacted efficiently with redox species in solution. While hot electrons are well documented in the solid state, the question as to whether they can be utilized in liquid junction cells is still under discussion. Our group initially reported that hot electrons could be detected in a photoelectrochemical cell consisting of a p-InP photocathode and an acetonitrile solution containing decamethylferrocene/decamethylferrocenium ( $\text{DFER}^{+/0}$ ) and dibromoethylbenzene (DBEB). In these rotating ring-disk electrode (RRDE) experiments,



the reversible  $\text{DFER}^{+}/0$  couple was used to accept photogenerated electrons and stabilize the band edges, while the DBEB could be reduced at a kinetically limited rate by hot electrons. The irreversible two electron reduction of DBEB produced styrene, an electroinactive species, and bromide ions, which could be oxidized to  $\text{Br}_3^- / \text{Br}_2$  at Pt. Thus,  $\text{Br}^-$  oxidation detected at the Pt ring was attributed to hot electron reduction of DBEB. Evidence for hot electrons was observed on several occasions, although it was reported that there were problems with reproducibility. These problems made it difficult to present a conclusive argument for the existence of hot electrons. Therefore, we performed more detailed experiments aimed at elucidating the effects of band edge movement and of relative concentrations of acceptors in solution on photoreduction products in these cells.

In order for hot electrons to be detected through the use of both a thermalized electron and a hot electron acceptor in solution, many conditions must be met. Among the kinetic requirements is that the thermalized acceptor must be capable of removing all photo-generated electrons from the semiconductor-solution interface fast enough in order to prevent charging of the surface, which causes band edge movement. Additionally, the hot electron acceptor must be able to compete for any electrons which reach the interface with energies greater than the conduction band edge. This requires that the kinetics for reduction of the hot electron acceptor be no more than an order of magnitude slower than that of the thermalized acceptor. A slow rate of reduction for the hot electron acceptor can be offset to some degree by increasing its concentration.

It had been shown that the reduction of metallocenes including decamethylferrocenium<sup>+</sup> ( $\text{DFER}^+$ ) and dicarbomethoxycobalticenium ( $\text{DCMC}^+$ ) at bromine etched p-InP in acetonitrile is rapid, as evidenced by the behavior of these electrodes at high reverse bias which suggests deep depletion instead of inversion. Therefore, these metallocenes were well suited for stabilizing the band edges under illumination. The irreversible two electron reduction of DBEB has been investigated at n-InP under accumulation conditions, where a rotated voltammogram reveals an  $E_{1/2}$  at -1.12 V. However, no study comparing the relative rate constants of  $\text{DFER}^+$  and DBEB reduction had been done. Low and high doped p-InP electrodes were investigated under various illumination conditions and acceptor concentrations. Collection experiments showed that the fraction of photocurrent which reduced DBEB decreased from one to zero as oxidized metallocene,  $\text{DFER}^+$  or  $\text{DCMC}^+$ , was added to a DBEB solution. Mott-Schottky data revealed a corresponding decrease in the negative shift of the band edges under illumination. This shift went to zero at the same metallocene concentrations at which DBEB reduction was no longer detected. Voltammograms revealed hysteretic double waves in cases where the metallocene was not present in large enough concentrations to accept all electrons. The data indicate that the rate constants for reduction of  $\text{DFER}^+$  or

DCMC<sup>+</sup> by conduction band electrons are at least two orders of magnitude larger than for reduction of DBEB.

There are two overall conclusions that can be drawn from the more detailed experiments on illuminated p-InP alkyl halide, metallocene, acetonitrile interfaces.

1) Over the limited range of light intensities and solution concentrations investigated, photoreduction of DBEB is inevitably associated with some degree of band edge movement. Therefore, it is not possible to ascertain whether observed reduction of DBEB is due to hot electrons with redox energies higher than the conduction band edge or to thermalized electrons that have accumulated at the interface as a result of steady-state illumination.

2) Metallocene redox couples such as DFER<sup>+,0</sup> and DCMC<sup>+,0</sup>, which are necessary in these experiments to fix the solution potential and stabilize the band edge positions during illumination, react with photogenerated minority carriers with rate constants that are orders of magnitude faster than the rate constant for reduction of DBEB. Therefore, having an appreciable fraction of the photocurrent result in reduction of DBEB, which would, in principle, allow for hot electron processes to be examined, requires concentrations of DBEB that cannot be achieved.

Despite the conclusions drawn above for this particular redox system, it should still be possible to use competitive photoreduction of solution acceptors to investigate hot electron transfer at semiconductor electrodes. The problem with the metallocene/alkyl bromide system that has been identified in this paper is the huge difference in rate constants for reduction of the two species by thermalized electrons. It may be possible to address this difficulty by using reversible couples other than metallocenes with significantly larger reorganization energies or by using irreversible couples other than alkyl bromides which display more facile reduction kinetics. Another approach is to explore other surface treatment procedures, such as plasma etching, to produce an interface where the reduction of metallocenes and alkyl bromides occur at more similar rates.

#### E. Rotating Ring Disk Photoelectrochemistry at TiO<sub>2</sub> Films

Heterogeneous photocatalysis using particulate TiO<sub>2</sub> to treat aqueous waste streams contaminated with organics and/or metals has the potential to compete with standard treatment technologies. Unfortunately, TiO<sub>2</sub> photocatalysis currently has limitations including very low photoefficiencies, poor overlap with the solar spectrum, and an incomplete understanding of the mechanisms involved. Photoefficiencies for TiO<sub>2</sub> decomposition of organics in aqueous solution are typically between 1-10%. Recently, it has been shown that the photoefficiency of formate oxidation at TiO<sub>2</sub> can be increased by a factor of 2-3 through controlled periodic illumination (CPI). These studies involved the periodic illumination of suspensions of TiO<sub>2</sub> particles. The durations of both the

illumination periods and dark periods were found to affect the efficiency of the photooxidation reaction.

In addition to low reaction rates, reactors using  $\text{TiO}_2$  suspensions require filtration of the  $\text{TiO}_2$  from the discharging water stream. One way that these difficulties related to the use of suspensions can be avoided is to attach a layer of  $\text{TiO}_2$  on a solid support so that it is in the waste stream flow path and can also be irradiated. Unfortunately, researchers have often found that supported photocatalysts are less efficient than suspensions. Therefore, we utilized the use of rotating ring-disk electrochemistry (RRDE) to study controlled periodic illumination effects at thin films of  $\text{TiO}_2$  particles. We developed a method for producing a stable thin film of  $\text{TiO}_2$  particles on a glass disk that could be mounted in the RRDE. Experiments were performed using the photooxidation of 2-methyl,1-4-hydroquinone (MHQ) at the  $\text{TiO}_2$  disk and subsequent reduction of the benzoquinone product at the Pt ring.

Assuming that the ring currents are a direct measure of MHQ oxidation at the  $\text{TiO}_2$  coated disk, these preliminary results clearly demonstrate that photocatalytic rates observed at  $\text{TiO}_2$  particulate films are highly dependent on illumination intensity, illumination time and dark times between illumination periods. At high light intensities, high photooxidation rates can only be maintained for a few tenths of a second after which they decay to < 50% of their initial values. Placing the  $\text{TiO}_2$  in the dark for several seconds restores the high rate.

If the CPI effect discussed here applies to photooxidation processes in general, it represents an important consideration for design of reactors that utilize semiconductor films as the photocatalyst. Simple reactors will only exhibit high photoefficiencies at low light intensities. High photoefficiencies at high light intensities will only be obtained if the photocatalyst is periodically illuminated.

#### F. Photomodulation of Interfacial Mass Transport Rates

There have been numerous studies involving the use of light to generate electricity directly or to store solar energy in fuel cells. However, few studies have explored the use of solar energy to facilitate separation of chemical species or to pump molecules against a concentration gradient. Photopumping of chemical species has been successfully utilized by a photosynthetic bacterium. This bacterium uses a transmembrane protein called bacteriorhodopsin which acts as a light-driven proton pump. The existence of such a photofacilitated membrane in nature suggests that incorporation of photoactive compounds into a membrane could provide a means to use light to separate or pump chemical species. In addition, a photoresponsive membrane could provide a new type of sensor which would respond to both chemical (ions) and physical (light) signals.

Previous studies involving photoresponsive facilitated transport membranes (FTM) merely demonstrated the photomodulation of transport rates or the photo-pumping of solutes against their concentration gradient. None represented a thorough, fundamental study of the transport mechanism and or demonstrated the control of interfacial processes. Such studies would require better measurements and more adequate characterization of the transport system than those reported. Our photoresponsive FTM studies were designed with this goal in mind.

Preliminary studies on the transport of salts across hydrophobic liquid membranes performed by T. To were quite encouraging. She chose the photoactive dye 8-nitro BIPS as the carrier since it had shown promise in previous studies. She designed and characterized a convective liquid membrane cell that exhibited minimal mass transfer effects, photocontrol of mass transport rates with visible light, complete and uniform irradiation of the interfaces, and allowed concentration measurements of carrier and solutes in the membrane under different experimental conditions. The improvements of her system's performance over similar ones reported were evidenced by higher facilitation factors, better photoefficiency, and greater quantity of solutes concentrated. She also measured the effects of carrier concentration and light intensity on the mass transport rates and showed the reversibility of dark and light rates. In addition to these dynamic measurements, she also carried out equilibrium measurements to determine quantities such as partition coefficients, and characterized the photochemical properties of the carrier.

In systems with 15 mM of the photoactive carrier, a facilitation factor of 14 was observed. The system also exhibited photomodulation of transport rates that depended on the direction of irradiation. The facilitation factor increased to 60 when the release side of the membrane was irradiated and decreased to 4 with the irradiation of the uptake side. As much as 20% of the solute was concentrated from one dilute solution on the dark side of the membrane to another on the irradiated side. A mechanism was proposed to explain the observed photofacilitation and photopumping based on the results of measurements and calculations.

In 1995, Ms. To completed her M.S. degree and left the research group. Dr. Longin was hired to continue her investigations. Dr. Longin's research revealed several problems with To's experiments and their interpretations. Consequently, this system does not warrant further study at this time.

A general steady-state model describing photofacilitated transport in liquid membranes was developed. The model can be used to consider photoactive carriers with a wide range of thermodynamic and kinetic properties in order to calculate photoinduced transport of solutes down their concentration gradient (photomodulation) and against their concentration gradient (photopumping). The description of transport in these systems is generalized by combining the relevant physical constants (diffusion coefficients,

rate constants, concentrations, molar absorptivities, light intensity, etc.) into dimensionless parameters. Detailed descriptions of photomodulation and photopumping were presented for the case where the carrier has properties that are optimal for downhill transport in the dark (thermal transport). Absorption of light by the carrier and carrier-solute complex can cause downhill transport to increase by 50% or to decrease by a factor of four depending on the light intensity. Photopumping can be maintained against a tenfold concentration gradient. The transport efficiencies for photomodulation and photopumping were also discussed.

This model is quite general, applying to systems in which the weak forms of the carrier and complex are short-lived photoexcited states, as well as systems where both the strong and weak forms of carrier and complex are thermally stable. This study suggests that both photofacilitation and photopumping are possible with systems that are optimal for thermal facilitated transport. High molar absorptivities are required to obtain either phenomenon. There is a balance between light intensity and thermal rates of interconversion between forms. At the light intensity for greatest photofacilitation, there is a significant concentration of strong form of the carrier and complex at the feed interface, while the concentration falls off significantly within about 25%-50% of the feed interface. This corresponds to a light profile in which the light penetrates most of the way across the membrane but drops to nearly zero at the feed interface.

An analysis of photoefficiencies indicates that the highest facilitation is not necessarily the most efficient. In general, the most photoefficient light intensities were well below those resulting in the greatest degree of photofacilitation. Thus, in choosing a system, there will be a trade-off between high flux and maximum efficiency.

Our model describing photofacilitated transport in liquid membranes was used to consider photoactive carriers with a wide range of thermodynamic and kinetic properties in order to calculate photoinduced modulation in the transport rates of solutes (photomodulation). The description of transport in these systems is generalized by combining the relevant physical constants (diffusion coefficients, rate constants, light intensity, etc.) into dimensionless parameters. Most experimental and theoretical studies have focused on systems in which strongly binding forms of the carrier and carrier-solute complex absorb light to convert to weakly binding forms. For such systems, absorption of light can cause photomodulation increases up to a factor of three. However, the maximum photoefficiencies are only a few percent. Conversely, if the weakly binding forms of the carrier and complex are photoactive, photomodulation increases of a factor of twenty can be achieved, along with photoefficiencies well over 10%. This study provides guidelines for the selection of carriers for future experimental investigations of photofacilitated liquid membranes.

Our steady-state model describing photofacilitated transport in liquid membranes was also used to consider photoactive carriers with a wide range of thermodynamic and kinetic properties in order to investigate active transport against a concentration gradient (photopumping). Most experimental and theoretical studies have focused on systems in which strongly binding forms of the carrier and carrier-solute complex absorb light to convert to weakly binding forms. For such systems, absorption of light can result in transport against a concentration gradient greater than a factor of five. However, the maximum photoefficiencies are less than 0.01%. Membranes containing carriers in which the weak forms of the carrier and complex are photoactive exhibit similar photopumping performance with an order of magnitude higher photoefficiencies. This study provides guidelines for the selection of carriers for future experimental investigations of photofacilitated liquid membranes.

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