UTILIZING NAD+/NADH ANALOGS FOR THE SOLAR FUEL FORMING REDUCTIONS

Stefan Ilic

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Committee:

Ksenija D. Glusac, Advisor

R. Marshall Wilson
ABSTRACT

Ksenija D. Glusac, Advisor

Recent scientific efforts aim to blend light harvesting with the fuel forming catalysis, as a novel method to store the energy captured from the Sun. Our approach is to construct an efficient photoelectrochemical cell using earth-abundant materials. The proposed system contains bioinspired metal-free hydride donors suitable for fuel forming reductions and a p-type semiconductor that serve as a light harvester and source of electrons. In this thesis, we investigate fundamental steps that determine the efficiency of the photoelectrochemical cell: photoreduction of NAD\(^+\) dyes by p-GaP semiconductor and the hydricity of NADH analogs. First, thermodynamics for photo-induced electron transfer from p-GaP to NAD\(^+\) dyes are evaluated using steady-state UV/Vis absorption and cyclic voltammetry experiments. Photoelectrochemical measurement conducted on p-GaP electrodes immersed in aqueous electrolytes and dye show sensitization for only two dyes. Pump-probe measurements reveal that the “inefficient” dyes have short-lived excited states, inhibiting the successful charge transfer into p-GaP surface. This work provides an insight on timescales of hole-injection rates during dye-sensitization processes. Furthermore, we evaluate the hydricity for model NADH analogs using experimental methods and calculations. The obtained hydricity values display a strong dependence on structural and electronic properties of the model compounds. When compared with metal-based analogs, NADH analogs show similar hydride donor ability. However, the high reduction potentials for metal-free hydride donors hinder their applicability in the catalysis. This work offers a reasonable explanation on why NADH analogs have not been utilized in fuel forming catalysis and provides the answers how to overcome these limitations.
To my parents and friends.
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CHAPTER 1. INTRODUCTION

1.1 BACKGROUND

Throughout the past few decades, water-splitting dye-sensitized photoelectrochemical cells (WS-DSPECs) have attracted a lot of attention in solar cell research mainly because of their simple assembly, inexpensiveness and environment friendliness. \(^1-^6\) In addition to conventional dye-sensitized solar cells, WS-DSPECs use molecular sensitizers and catalysts that are adsorbed or covalently attached onto the surface of semiconductor. This attractive approach uses light energy to stimulate the thermodynamically uphill conversion of water into molecular oxygen and hydrogen.

DSPECs that employ dye-sensitized cathodes have been investigated to a limited degree. \(^7\) Excitation of the dye triggers a fast electron transfer from the valence band of p-type semiconductor (hole injection). (Figure 1) Photo-reduced dye molecule transfers the electron to hydrogen-evolving catalyst (HEC), regenerating the sensitizer. The first example of hydrogen production dye-sensitized photocathode was shown by Sun and co-workers in 2012. \(^8\) Nano-structured nickel oxide, sensitized by a triphenylamine dye, was coupled with a cobaloxime complex as a HEC. In their work, they pointed that the main reason of photo-current decay is decomposition or leaching of the catalyst and the dye from the electrode surface, suggesting that this could be overcome by immobilizing/linking catalyst and dye to the surface of semiconductor. Mozer and co-workers \(^9\) constructed another system in 2012 using BiVO\(_4\) coated nickel oxide as a semiconductor, and a donor-acceptor dye serves both as a sensitizer and a catalyst, with the quantum yield up to 0.6 %. Wu and co-workers presented an assembly of sensitizer-catalyst dyad
in 2013,$^{10}$ where a ruthenium complex sensitizer was being a link between alumina coated nickel oxide and cobaloxime HEC.

Figure 1. Operation principles of p-type DS-PEC. Adapted from Ref. 7 with permission of The Royal Society of Chemistry

While all of these studies proved the concept, the efficiencies for hydrogen generation p-type DSPECs that match water oxidation n-type DSPECs efficiencies are yet to be achieved.$^{3-4,7,11-17}$ Scheme 1 shows our approach to construct an efficient p-type photoelectrochemical solar cell using earth-abundant materials. The cell contains a dual light-harvesting system composed of a blue-absorber semiconductor (p-type GaP, $\lambda_{\text{ABS}}<550$ nm) and a red-absorber dye (NAD$^+$-analogs, $\lambda_{\text{ABS}}>550$ nm), which increases the possible theoretical efficiency of the cell. The organic component serves both as a light absorber (NAD$^+$ analog) and as the HEC (NADH analog, Scheme 1). The absorbed light is used to photochemically drive the reduction of NAD$^+$ dyes by p-GaP semiconductor to produce NADH analogs, which can perform ground-state proton reduction to generate solar fuel.
Scheme 1. Evolution of hydrogen in the proposed DS-PEC: upon dye sensitization, NAD$^+$ analog is converted into NADH analog by photoreduction with p-GaP, which then serves to reduce protons to molecular hydrogen.

Interestingly, while NADH-analogs successfully transfer the hydride ion to a number of substrates, they have not been utilized for proton reduction, a key process in the hydrogen-evolving reaction catalysis. Even among all metal-free hydride donors, only a handful of examples of stoichiometric hydrogen evolution have been reported: (i) aldehydes in highly basic aqueous solutions, where the hydride transfer occurs from deprotonated geminal diols (Scheme 2A);$^{18-19}$ (ii) bridged alkanes in strongly acidic solutions, where the proton reduction is accompanied with the formation of hydrido-bridged cations (Scheme 2B);$^{20-21}$ (iii) nitrogen-containing hydrocarbons, such as orthoformamides$^{22}$ and dihydro-benzimidazolines,$^{23}$ in which the nitrogen centers play an important role in increasing the molecular hydricities by donating their lone pairs to the antibonding orbital of the C-H bond (Scheme 2C). Similar nitrogen-assisted hydride donors can also be found as cofactors in [Fe]-hydrogenases, where the hydride transfer from dihydroimidazoline to protons is catalyzed by an Fe-complex.$^{24-26}$
Scheme 2. Structural motifs of reported metal-free hydride donors capable of stoichiometric proton reduction: (A) deprotonated geminal diols,\textsuperscript{18-19} formed from aldehydes in highly basic conditions. Release of hydride ion is facilitated by π–delocalization of formed carboxylic product. (B) Bridge alkanes\textsuperscript{20-21} in the presence of superacids. Hydride release is accompanied by the formation of bridged cation stabilized by hyperconjugation. (C) Orthoformamides\textsuperscript{22} and dihydro-benzimidazolines,\textsuperscript{23} where the hydride release is assisted by stabilization of formed cation with neighboring nitrogen lone pairs.

1.2 THESIS SUMMARY

In this thesis, the development of the photoelectrochemical cell using earth-abundant materials is proposed. The proposed system contained bio-inspired NAD$^+/\text{NADH}$ analogs, which
served both as light absorbers and hydrogen evolution catalyst, and mid-sized band p-GaP semiconductor (2.26 eV) as a light absorber and a source of electrons for NADH recovery. Fundamental studies on the individual steps, essential for the performance of a hydrogen evolving DS-PEC, were examined.

In Chapter 2, the photochemical reductions with p-GaP semiconductor were tested for the several triarylmethane (6O⁺), acridine (4O⁺, 2O⁺, Me2N-Acr⁺, T-Acr⁺) and flavin dyes (Et-Fl⁺). Thermodynamic profiles of the dyes, obtained using steady-state UV/Vis absorption and cyclic voltammetry experiments, revealed favorable properties for the successful electron transfer from p-GaP surface. However, the photocurrent measurements conducted on p-GaP electrodes immersed in aqueous dye solutions indicated dye-sensitization for only two dyes (2O⁺ and Et-Fl⁺). Transient absorption spectroscopy provided an explanation for such behaviors pointing out that “efficient” dyes exhibited the slow excited-state deactivation (>600 ps), enabling the successful charge injections. This work provides an insight on the electron transfer kinetics between p-GaP surface and the dyes in solution.

In Chapter 3, the ground-state ability of biomimetic metal-free hydride donors for proton reduction has been evaluated by obtaining hydricities for those molecules, both computationally and experimentally. The calculated hydricity values were acquired for two solvent systems (dimethyl sulfoxide and acetonitrile) using density functional theory (DFT) calculations, and they were confirmed using experimental methods: “potential-pKa” method and “hydride-transfer” method. The obtained hydricities for model metal-free hydride donors revealed the similar proton-reduction ability as majority of metal-based hydride donors. However, the standard reduction potentials of the conjugated hydride acceptors of metal-free hydride donors were shifted towards more negative potentials, when compared to metal-based analogs. This
work provides a reasonable explanation why the metal-free hydride donors haven’t been exploited in proton reduction catalysis.

In Chapter 4, a summary is presented with the key findings from the study on the interfacial electron transfer from the p-GaP surface and the model NAD$^+$ compounds, along with the hydricity values for model NADH compounds. Also, the future outlook on the follow up projects will be briefly discussed.
CHAPTER 2. SENSITIZATION OF P-GAP WITH MONOCATIONIC DYES: THE EFFECT OF DYE EXCITED-STATE LIFETIME ON HOLE INJECTION EFFICIENCIES


2.1 INTRODUCTION

Gallium phosphide (GaP) is a potential photocathode material actively being explored for solar fuel-forming photoelectrochemical cells.\textsuperscript{27-29} The indirect band gap is 2.26 eV, which allows for efficient harvesting of the blue portion of the solar spectrum (\(\lambda < 550 \text{ nm}\)). Furthermore, the conduction band potential of GaP (-1.05 V vs. NHE\textsuperscript{30-31}) is sufficiently negative to drive the reduction of protons and carbon dioxide, which was utilized almost forty years ago to perform photoelectrochemical hydrogen\textsuperscript{32} and methanol\textsuperscript{33} formation using p-doped GaP photocathodes. More recently, the incorporation of appropriate electrocatalysts to the p-GaP surface has lead to an improvement of photoelectrochemical conversion efficiencies for these fuel-forming reactions.\textsuperscript{34-39} The exploitation of p-GaP as the photocathode material requires the improvements in the stability of GaP surface\textsuperscript{19,31,40-45} and matching of the charge carrier diffusion lengths relative to the absorption depths of the semiconductor.\textsuperscript{46-50} Recent developments in these research areas suggest that the design of photoelectrodes using GaP
nanostructures with high aspect ratios can be used to increase the charge collection efficiencies. Furthermore, the stability of GaP surface can be improved by chemical modifications using covalent attachment of organic molecules or by the deposition of a thin layer of metal oxides.

To expand light-harvesting efficiencies, the hole injection into p-GaP can be sensitized using organic dyes or quantum dots that absorb the light with wavelengths above 550 nm. Organic dyes, such as triarylmethane, acridine or xanthene compounds, are particularly promising sensitizers for p-GaP, since they can be readily tailored to exhibit strong absorption in the red portion of the visible spectrum. In addition, the excited state reduction potentials of most dyes are sufficiently positive to allow the hole injection into p-GaP and other semiconductors. Finally, the LUMOs of many organic dyes are sufficiently negative to enable the electron transfer to Pt, Fe, Ni or Co-based H2-evolving catalysts. Even in the absence of the metal catalyst, the reduced dye can exhibit some H2-evolving catalytic activity.

In this context, one could envision a bio-inspired NAD+/NADH approach towards dye-sensitized photocatalytic water reduction, where NAD+ analogs serve as dyes for the p-GaP sensitization, while the two-electron reduced forms of the dye (NADH analogs) are capable of reducing water. Previous reports have shown that proton reduction by metal-free hydrides is possible if compounds with sufficient hydricities are used. Driven by this possibility, we investigated here the efficiencies of p-GaP sensitization by a series of cationic dyes made of flavin (Et-Fl+), acridine (T-Acr+, Me2N-Acr+, 4O+ and 2O+), and triarylmethane-based (6O+) frameworks (Scheme 3). Based on the UV/Vis absorption spectra and cyclic voltammetry of the model compounds, we found that all six dyes exhibited favorable thermodynamics for the
photoinduced hole injection into p-GaP. However, the sensitization experiments revealed that only two of the six dyes sensitized p-GaP at wavelengths above 550 nm. The explanation for such behavior was obtained from ultrafast pump-probe experiments, which showed that the four “inefficient” dyes exhibited very fast excited-state deactivation to the ground state (few picoseconds). These results provided valuable insights into the design of future, more efficient photosensitizers for p-GaP. The following text affords a more detailed description of our findings.

Scheme 3. Structures of cationic dyes used in this study.

2.2 EXPERIMENTAL AND COMPUTATIONAL METHODS

All chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. $^1$H NMR spectra were recorded on a Bruker Avance 300 MHz system. UV/Vis absorption spectra were recorded on Varian Cary 50 Bio spectrometer in a 1 cm quartz cell.

SYNTHESIS. Et-FI$^+$ was synthesized according to the previously published procedure.$^{76}$
9-((4-(dimethylamino)phenyl)ethynyl)-10-methylacridinium perchlorate (T-Acr⁺): Under argon, 4-ethynyl-N,N-dimethylaniline (400 mg, 2.75 mmol) was dissolved in 10 mL of tetrahydrofuran and a 2.5 M solution of n-butyllithium in hexane (1.3 mL, 3.3 mmol, 1.2 eq) was added dropwise at -78°C. After 20 min, a suspension of 10-methyl-9(10H)-acridone (690 mg, 3.3 mmol, 1.2 eq) in 15 mL of THF was added, temperature was raised to room temperature and the mixture was stirred for 6 hours. The orange reaction mixture was quenched by addition of saturated aqueous solution of ammonium chloride and extracted with dichloromethane. Organic
layers were combined, dried and solvent evaporated to yield yellow oil. Oily residue was dissolved in minimal volume of acetonitrile and solution changed color to blue upon addition of small amount of water. Product was precipitated by addition of ether, filtered and washed with copious amount of ether to yield 275 mg of dark blue product (25%). $^1$H- NMR (CD$_3$CN, 300 MHz): 8.95 (d, 2H), 8.67 (d, 2H), 8.38 (t, 2H), 8.04-7.96 (m, 4H), 6.92 (d, 2H), 4.70 (s, 3H), 3.15 (s, 6H).

Tris(2,6-dimethoxyphenyl)methylium perchlorate (6O$^+$): 6O$^+$ was synthesized according to the literature under modified conditions. Under argon, dimethoxybenzene (6.5 mL, 50 mmol, 3.5 eq) was dissolved in 35 mL of THF and a 2.5 M solution of n-butyllithium in hexane (20 mL, 50 mmol, 3.5 eq) was added dropwise at -78°C. After 30 min, the reaction mixture was let to heat up to room temperature and stirred for 1 h. A solution of diethyl carbonate (1.7 mL, 14 mmol) in 80 mL benzene was added and resulting mixture was refluxed for 2 days. The reaction mixture was poured in cold water, extracted with dichloromethane, organic layers were combined, dried and solvent evaporated to yield brownish residue. The residue was dissolved in minimal amount of acetonitrile, perchloric acid was added until the solution turned purple and precipitated by addition of ether. Formed precipitate was filtered, washed with copious amount of ether and dried under vacuum to yield 4.5 g of deep purple product (62%). $^1$H- NMR (CD$_3$CN, 300 MHz): 7.60 (t, 3H), 6.55 (d, 6H), 3.65 (s, 18H).

9-(2,6-dimethoxyphenyl)-1,8-dimethoxy-10-methyl-9,10-dihydroacridin-9-ylium perchlorate (4O$^+$): 4O$^+$ was synthesized according to the previously published procedure. To a mixture of 6O$^+$ (1 g, 2 mmol) in 15 mL of N-methylpyrrolidine was added 1.2 mL of methylamine solution (33% solution in ethanol, 9.6 mmol, 4.8 eq). The resulting mixture was stirred at room temperature for 12 h, then poured into diethyl ether while stirring. A red
precipitate formed, which was filtered and washed with copious amount of ether. The crude precipitate was dissolved in dichloromethane and selectively precipitated by addition of ether until the filtrate was not longer purple, yielding 514 mg of red product (50%). $^1$H- NMR (CD$_3$CN, 300 MHz): 8.19 (dd, 2H), 7.89 (dd, 2H), 7.42 (t, 1H), 7.01 (d, 2H), 6.71 (d, 2H), 4.69 (s, 3H), 3.57 (s, 6H), 3.56 (s, 6H).

1,13-dimethoxy-5,9-dimethyl-5,9-dihydro-13bH-quinolino[2,3,4-kl]acridin-13b-ylium perchlorate ($2O^+$): $2O^+$ was synthesized according to the previously published procedure. To a solution of $4O^+$ (500 mg, 1.28 mmol) in 10 mL of N-methylpyrrolidine was added 6.5 mL of methylamine solution in ethanol (33%, 33.3 mmol, 26 eq) and the mixture was stirred at 90$^\circ$C for 8 h in ambient condition. The resulting dark green reaction mixture was allowed to cool to room temperature and poured in acidified (50% aq. HClO$_4$) ice cooled water. The precipitate was filtered and washed with copious amount of ether. The crude precipitate was dissolved in dichloromethane and selectively precipitated by addition of ether until the filtrate was not longer red, to yield 290 mg of green product (65%). $^1$H- NMR (CD$_3$CN, 300 MHz): 8.20 (t, 1H), 7.93(t, 2H), 7.57 (d, 2H), 7.52 (d, 2H), 6.95 (d, 2H), 4.15 (s, 6H), 3.78 (s, 6H).

Cyclic Voltammetry. Cyclic voltammetry was performed using a BASi epsilon potentiostat in a VC-2 voltammetry cell (Bioanalytical Systems) using platinum working electrode (1.6 mm diameter, MF-2013, Bioanalytical Systems), a nonaqueous Ag/Ag$^+$ reference electrode (MF- 2062, Bioanalytical Systems) and a platinum wire auxiliary electrode (MW-4130, Bioanalytical Systems) as a counter electrode. Acetonitrile was purchased from Sigma-Aldrich (anhydrous, 99.8%) and purified by reflux over CaH$_2$ for 8 h, followed by distillation. Tetrabutylammonium perchlorate (TBAP) was purchased from Sigma-Aldrich, recrystallized from methanol, and dried under vacuum. Electrochemical potentials were referenced to NHE by
adding 0.548 V to the experimental potentials.  

Electrode Fabrication. Polished p-type GaP(111)A wafers doped with zinc at $2.7 \times 10^{18}$ cm$^{-3}$ with a thickness of $350 \pm 25 \mu$m were purchased from ITME and p-type GaP(111)B wafers doped with zinc at $2.1 \times 10^{18}$ cm$^{-3}$ with a thickness $450 \mu$m ± $25 \mu$m, were purchased from MTI Corp. p-GaP(111)A and p-GaP(111)B wafers were diced into approximately 0.5 cm by 0.5 cm pieces. Ohmic contacts were prepared by soldering In:Zn onto the scratched back of wafers and subsequently annealed for 10 min at 400°C in forming gas. To fabricate the electrodes, the ohmic contact on the GaP pieces were connected with silver print (GC Electronics) to a tinned copper wire coil threaded through a glass tube. The tube was sealed on both ends with inert epoxy (Hysol C). Geometric areas of the electrodes were determined through analysis of digital optical photographs. Electrode areas were nominally between 0.1 and 0.2 cm$^2$ for all investigated samples. Immediately before use, p-type GaP(111)A and GaP(111)B electrodes were etched in doubly distilled H$_2$SO$_4$ for 30 seconds, rinsed with water, and dried using a stream of nitrogen.  

Chlorination and Grignard Reaction Sequence of Electrodes. Before surface modification, the epoxy was covered with Teflon tape to prevent chemical degradation. In a nitrogen-purged glovebox, etched GaP(111)A electrodes were reacted in a saturated solution of PCl$_5$ in chlorobenzene at 90-95°C for 50 minutes as previously described. After rinsing thoroughly with chlorobenzene and drying in the glovebox, the electrodes were alkylated with CH$_3$MgCl in a closed reaction vessel over 12 h at 100-110°C. After reaction, Teflon tape was removed and the electrodes were thoroughly rinsed with THF and subsequently anhydrous methanol. All samples were stored in the glovebox until use. CH$_3$-terminated GaP(111)A electrodes were not exposed to H$_2$SO$_4$ before measurement, but were rinsed with methanol and dried using a stream of nitrogen.
Photoelectrochemical Measurements. Photoelectrochemical measurements were performed in an airtight Pyrex cell with an optically flat bottom. A standard three-electrode setup was used, with a Pt mesh counter electrode with a larger area than the photoelectrode and a Ag/AgCl reference electrode. For all optical measurements, the distance between the optical window and the GaP face was nominally 1 mm. Wavelength-dependent external quantum yield measurements were obtained with an Oriel 150 W Xe arc lamp (Newport) and a quarter-turn single-grating monochromator (Model 74125, Newport). Sample measurements were recorded with chopped illumination (20 Hz). A quartz beam-splitter was used to simultaneously record the light output intensity with a separate Si photodiode (Model 70316NS, Newport) to adjust for fluctuations in lamp intensity. Absolute photocurrents were measured by a digital PAR 273 potentiostat at -0.4 V vs. NHE. The output current signal was connected to a Stanford Instruments SR830 lock-in amplifier. The output signals from the lock-in amplifier and the reference Si photodiode were relayed to a computer controlled by custom-written LabVIEW software. Measurements were carried out shortly after electrodes were submerged in a nitrogen-purged 1 M KCl solution, both with and without dissolved dyes. Dye concentration ranged from approximately 10 to 50 micromolar in 40:1 1M KCl:ACN for maximum dye solubility. For Et-Fl+, measurements were conducted in aqueous 1 M H2SO4 for dye stability. Measurements of T-Acr+ were performed in acetonitrile with 0.1 M tetrabutylammonium chloride supporting electrolyte with a Ag/AgNO3 reference electrode and a Pt mesh counter electrode.

Femtosecond Transient Absorption Experiments. The 800 nm laser pulses were produced at a 1 kHz repetition rate by a mode-locked Ti:sapphire laser and regenerative amplifier (Hurricane, Spectra-Physics). The output from the Hurricane was split into pump (85 %) and probe (10 %) beams. The frequency of the pump beam was sent into an optical paramagnetic
amplifier (OPA- 400, Spectra Physics) to obtain the desired excitation wavelength. The energy of the pump beam was <300 nJ/pulse. The probe beam was focused into a two-dimensionally translated 4 mm CaF2 crystal for white light continuum between 350 and 800 nm. The flow cell (Starna Cell Inc. 45-Q-2, 0.9 mL volume with 2 mm path length), pumped by a Variable Flow Mini-Pump (Control Company), was used to prevent photo-degradation of the sample. After passing through the cell at the magic-angle geometry, the continuum was coupled into an optical fiber and input into a CCD spectrograph (Ocean Optics, S2000). The data acquisition was achieved using in-house LabVIEW (National Instruments) software routines. The group velocity dispersion of the probing pulse was determined using nonresonant optical Kerr effect (OKE) measurements. Sample solutions were prepared at a concentration needed to have absorbance of 1.0 at the excitation wavelength.

Computational Methods. All calculations were performed at the Ohio Supercomputer Center. Ground-state geometry optimizations and frequency calculations were performed at wB98X- D/6-311G* level of theory using Gaussian 09. Excited-state calculations were performed using time dependent DFT at the wB98X-D/6-311G* level of theory. All calculations considered implicit solvation of acetonitrile using the CPCM model.

2.3 RESULTS AND DISCUSSION

MODEL COMPOUNDS. The stabilized carbenium ions for this study were selected based on their expected capacity to harvest light at wavelengths above 550 nm and inject holes into p-GaP. For example, the flavin-based dye Et-Fl+ has been previously studied by our group and was found to exhibit significantly red-shifted absorption spectrum relative to the
biologically-relevant flavin chromophores, and this red-shift was explained by the selective stabilization of the lowest unoccupied molecular orbital (LUMO) in Et-Fl$^+$ relative to the parent flavin. The triarylcarbenium cation $60^+$ is an important dye and a precursor to more planarized chromophores, such as $40^+$, $20^+$ and triangulenium cations. It exhibited a broad absorption in the 450-750 nm range that arose due to three quasi-degenerate transitions from HOMOs localized on one of the aryl rings to the LUMO that was delocalized over the entire molecule. Similarly, $40^+$ and $20^+$ exhibited absorption in the visible range that extended to 700 nm. The optical properties of acridinium ions Me$_2$N-Acr$^+$ and T-Acr$^+$ have not been reported previously, but our preliminary DFT calculations indicated a strong absorption in the visible range. These compounds were synthesized from N-methyl acridone as described in Scheme 4.

![Scheme 4. Synthetic pathways for preparation of Me$_2$N-Acr$^+$ and T-Acr$^+$.](image)

THERMODYNAMICS. To evaluate the thermodynamics for photosensitized hole injection to p-GaP, the UV/Vis absorption spectra and cyclic voltammograms for the model compounds were obtained. As expected, all dyes absorbed in the long-wavelength range of the visible region, with the absorption maxima ranging 500-620 nm (Figure 2). With the band gap of 2.26 eV, GaP absorbs light below 550 nm (shown as a vertical dashed line in Figure 2), thus the dye absorption bands relevant to GaP sensitization appear in the 550-700 nm range. All absorption bands arose due to $\pi\rightarrow\pi^*$ electronic transitions with a varying degree of the charge...
transfer character. The absorption spectrum of Et-Fl\textsuperscript{+} consisted of two bands centered at 557 and 414 nm, and these bands were previously assigned to S\textsubscript{1} and S\textsubscript{3} π→π* transitions (in-between is an S\textsubscript{2} state with the n→π* character and low oscillator strength).\textsuperscript{88}

In the case of 6O\textsuperscript{+}, the absorption band was broad with a maximum at 522 nm and a shoulder/tail that extended into the red. Previous studies of similar symmetric triarylmethane dyes (such as crystal violet) have also shown the presence of a broad absorption band with a shoulder whose wavelength was temperature and solvent dependent.\textsuperscript{97-99} The spectral hole burning experiments indicated that the two bands arose due to the presence of ground-state inhomogeneity with two proposed conformers: one was the propeller-type structure with the central C-atom in a trigonal planar geometry and the second conformer was assigned to the conformer with the central C- atom in a pyramidal geometry due to the interaction with solvent molecules.\textsuperscript{99} The broad absorption feature observed here for 6O\textsuperscript{+} likely arose due to similar conformational heterogeneity.
Figure 2. Absorption spectra for model compound dyes. Black horizontal dashed line represents GaP cut off (550 nm). Solid lines represent absorption for different dyes: purple (6O⁺), black (4O⁺), orange (2O⁺), dark blue (Me₂N-Acr⁺), light blue (T-Acr⁺) and maroon (Et-FI⁺).

When going from 6O⁺ (λ_max = 522 nm) to more planar 4O⁺ and 2O⁺ derivatives, one would expect that the absorption spectra red shift and increase in intensity. While this behavior was indeed observed for 2O⁺ (λ_max = 616 nm), 4O⁺ absorbed at a surprisingly high energy (λ_max = 508 nm). We attributed this behavior to the fact that 4O⁺ adopted a structure with an out-of-plane deformation of the central pyridinium ring. This assignment was supported by the previous NMR and X-ray studies, which showed that the groups attached to the N-center (methyl group in the case of 4O⁺) caused a varying degree of deformation of the pyridinium ring due to the strain induced by the atoms of the N-substituent. Additional support for this assignment comes from the fact that the sulfur-containing 4O⁺ analog absorbed at a considerably longer wavelength (λ_max = 640 nm).

The acridinium-based dyes Me₂N-Acr⁺ and T-Acr⁺ exhibited absorption bands in the red portion of the visible spectrum at λ_max = 558 and 615 nm, respectively. These transitions were evaluated computationally, and the calculated energies (λ_max = 450 and 525 nm, respectively) were within the 0.3-0.5 eV error expected for the DFT method. In both compounds, the absorption arose predominantly from the HOMO -> LUMO transitions. Based on the contour plots shown in Figure 3, the first excited state in both compounds exhibited a charge transfer character, in which the electronic charge migrated from the aniline to the acridinium moiety of the molecule upon excitation.
The standard potentials for the reduction and oxidation of the studied dyes were evaluated using cyclic voltammetry (Figure 4). All dyes (except for T-Acr\(^+\)) exhibited a reversible one-electron reduction process. The potential at which these reductions occurred tracked with cation stability. For instance, Et-Fl\(^+\) and 6O\(^+\) delocalized the positive charge through \(\pi\)-conjugation, while other cations (4O\(^+\), 2O\(^+\), Me2N-Acr\(^+\) and T-Acr\(^+\)) delocalized the charge via aromatic acridinium framework. Given that the aromatic cations are generally more stable than the conjugated ones, one would expect lower stability of Et-Fl\(^+\) and 6O\(^+\), and in turn these dyes should be more easily reduced than other cationic dyes, which was indeed observed. In the anodic range, the dyes that contained N-centers with lone electron pairs (such as Me2N-Acr\(^+\), T-Acr\(^+\) and 2O\(^+\)) underwent one-electron oxidation at less positive potentials (+1.2 to +1.5 V vs NHE) while other dyes were more difficult to oxidize (oxidation occurred at +1.8 to +2.1 V vs NHE).
Figure 4. Cyclic voltammograms of model compound dyes in the (A) anodic and (B) cathodic range: Pt working electrode, Pt counter electrode and nonaqueous Ag/AgCl reference electrode. Sweep rate: 100 mV/s; Electrolyte: 0.1 M TBAP, solvent: acetonitrile.

The standard reduction potentials were used to construct an energy diagram relative to the band energies of GaP (Figure 5). In the cases where the electrochemical behavior was chemically irreversible, the peak potentials were used instead of half wave potentials, which introduce an error as large as ~0.2 V in the estimated energies. The HOMO energies of all dyes were below the valence band of GaP, indicating that the excited dye can accept the electron from GaP. In the case of dyes that contain N-centers with lone electron pairs (Me2N-Acr+, T-Acr+ and 2O+), the driving force for electron transfer was relatively low (for example ΔG=−0.07 eV for T-Acr+). In addition, the LUMO energies of all dyes were below the conduction band, indicating that the excitation of GaP should lead to efficient electron transfer to the dye. Thus, the cationic dyes studied here are well suited for photoinduced electron transfer from GaP to the dye, under conditions of either dye or GaP excitation, which enables efficient coverage of visible range of the solar spectrum.
DYE SENSITIZATION. Since all model compounds exhibited favorable thermodynamics for dye-sensitized hole injection to GaP (Figure 4), their photoelectrochemical response was tested using p-GaP(111)A photoelectrodes biased at -0.4V vs. NHE and immersed in deaerated 1 M KCl (aq) with and without the model compound dyes (Figure 6). In the absence of model dyes, the photoresponse below 550 nm arises due to the excitation of GaP electrode itself. In the presence of dyes, the sub-bandgap response was expected to occur at wavelengths above 550 nm due to sensitization. Surprisingly, four dyes (6O⁻, 4O⁺, Me2N-Acr⁺ and T-Acr⁺) did not exhibit significantly different photocurrents as compared to the blank solution (Figures 6A, B, D and E), especially at wavelengths where the respective absorption of dyes was the strongest (Figure 1). In contrast, the 2O⁺ and Et-Fl⁺ dyes (Figure 6 C and F) elicited substantially higher photocurrents than the blank electrolyte. The internal quantum yields for these two dyes were evaluated assuming a monolayer coverage of the dye on the GaP surface and by accounting for the light- filtering effect of the dyes present in the solution. The values obtained were 17% for 2O⁺ and 25% for Et-Fl⁺, which were similar to the values previously reported for the GaP sensitization using monocationic dyes (for example, brilliant green: 25%; crystal violet: 42% and
ethyl violet: 20%). These internal quantum yield values were notably high, considering that the redox mediator was not present in the solution, but fully consistent with the advantage afforded by electrostatic suppression of deleterious back-charge transfer in dye-sensitization at photoelectrodes operating under strong depletion conditions.\textsuperscript{102}

![Graphs A, B, C, D, E, F](image)

Figure 6. External quantum yield measurements of etched p-GaP(111)A sensitized with cationic dyes (<50 µM) in nitrogen-purged 1 M KCl (colored squares) or without dye (gray diamonds). Colored circles represent transmittance of the corresponding dyes in solution.

The results of the sensitization experiment did not correlate with thermodynamics. For example, the driving force for electron transfer from p-GaP to 2O\(^+\) is \(\Delta G = -0.27\) eV, which is lower than for the 4O\(^+\) (\(\Delta G = -0.67\) eV) and 6O\(^+\) (\(\Delta G = -0.84\) eV). Another factor that can influence the charge injection efficiencies is the difference in adsorption affinities of dyes to the
p-GaP surface. However, the six dyes reported here were expected to have similar interaction with the surface: all model compounds were monocationic and did not possess appropriate functional groups for specific binding to Ga-centers of p-GaP(111)A. The third factor that can influence sensitization experiments is kinetic: if the excited-state lifetime of the dye is too short relative to the rate of charge injection, the sensitization photocurrent will not be observed. A further discussion of this effect will be provided in the following section.

The sensitized photocurrent responses for the 2O\(^+\) and Et-Fl\(^+\) dyes did not match the corresponding UV/Vis absorption spectra. In case of the 2O\(^+\) dye (Figure 5C), the sensitized photocurrent profile closely followed the absorption spectrum profile between 550 and 700 nm. Notably, offset in the wavelength corresponding to the maximum sub-bandgap external quantum yield (\(\lambda_{\text{max}}=630\) nm) from the wavelength of maximum absorbance of the dissolved dye (\(\lambda_{\text{max}}=616\) nm) indicated that the sensitization occurred by dye molecules that are physisorbed to the electrode surface.\(^{52}\) In the case of the Et-Fl\(^+\) dye (Figure 6F), the wavelength dependence of the sensitized photocurrent did not resemble the absorption spectrum: while Et-Fl\(^+\) absorbs at \(\lambda_{\text{max}}=550\) nm, the sensitized photocurrents extended beyond 700 nm. The photocurrent in the red part of the visible range could be due to excitation of GaP valence band electrons into the surface trap states, followed by their transfer to the LUMO orbital of Et-Fl\(^+\). Given that such trap-mediated photocurrent was not observed in the case of 2O\(^+\), the energy of a participating trap state would be situated in-between the LUMO levels of these two dyes (Figure 5). Alternatively, two other sources could contribute to the red shift of the sensitized spectrum. Spectral shifts relative to the absorption spectrum of Et-Fl\(^+\) in solution could be explained by aggregation on the surface of GaP. For example, J-aggregates are known to cause the red shift of the absorption spectra\(^{103}\) and were previously utilized as chromophores for sensitization of silver
nanoparticles, silver halide, TiO$_2$, and GaP. Separately, the neutral Et-Fl$^-$ radical could contribute to the photocurrent. Since the sensitization experiments were conducted in the absence of a redox mediator and under strong depletion conditions, the neutral Et-Fl$^-$ radicals formed upon photoreduction near the electrode surface may have a long lifetime. In addition, the Et-Fl$^-$ radical is known to be chemically stable, can absorb in the 500-700 nm range, and therefore could itself serve as a dye for another sensitization step.

The influence of surface chemistry on sensitization of various p-GaP electrodes by the 2O$^+$ dye was also studied (Figure 7). These three p-GaP electrode types differed in surface preparation but had nominally comparable bulk optoelectronic properties. As evident in Figure 7, both freshly etched p-GaP(111)A and p-GaP(111)B electrodes were readily sensitized by 2O$^+$ but the wavelength-dependences were different. As mentioned above, the profile for p-GaP(111)A surfaces nominally followed the absorption profile of the dye. However, the sensitized photocurrents of etched p-GaP(111)B were observed at much longer wavelengths than what was expected from light absorption by the dye, implying a strong sensitivity of the surface condition on the sensitization of p-GaP. To investigate whether such large shift occurred due to the formation of J-aggregates of 2O$^+$ on the semiconductor surface, the absorption spectrum of the dye adsorbed on GaP(111)B was collected (Figure 7C, green triangles). The adsorbed dye exhibits absorption that was 27 nm (0.09 eV) red-shifted relative to the absorption spectrum of the dye in solution, consistent both with the premises that the local dielectric experienced by the dye on the surface is substantially different than in solution or that the dye has aggregated. The maximum of the sensitized spectrum matched the absorption maximum of the physisorbed dye. However, the sensitized photocurrent observed at wavelengths above 720 nm cannot be assigned to J-aggregates and is more likely due to the sensitization of the trap states. This observation was
separately tested by sensitizing p-GaP(111)A electrodes that had first been modified with CH₃-groups through a Grignard reaction sequence. In this experiment (Figure 7B), the sensitization profile only slightly changed but the photocurrent magnitude increased significantly by almost a factor 3.

![Figure 7. External quantum yield measurements showing sensitization of 2O⁺ in 1 M KCl (colored squares) with (A) etched GaP(111)A, (B) CH₃-terminated GaP(111)A, and (C) etched GaP(111)B. Electrodes in blank solution are denoted by gray diamonds. Transmittance of the 2O⁺ in solution are denoted by green circles, while transmittance of the dye deposited on GaP(111)B is represented with green triangles.](image)

The dependence of the sensitization of p-GaP on the surface condition was itself unsurprising, as heterogeneous charge transfer at semiconductor electrodes is routinely sensitive to the presence of surface defects/traps. In the specific case of p-GaP, the electronic quality
of even freshly etched surfaces was poor and known to degrade rapidly over time.\textsuperscript{31, 44} The fact that sensitized photocurrents were even observed at native p-GaP surfaces with dyes that were, at best, randomly physisorbed pointed to the virtues of sensitization under strong depletion conditions.\textsuperscript{52} Still, the presented data showed that even with the limited options for surface passivation of p-GaP, the possibility exists to construct sensitized platforms with high internal quantum yields. If this aspect was preserved upon substantially increasing dye loading (e.g. through nanostructuring), then a pathway exists for designing sensitized p-GaP electrodes with near unity external quantum yields.

KINETICS. The sensitization results described above showed that only two dyes (Et-Fl$^+$ and 2O$^+$) exhibited efficient charge injection into GaP, despite the fact that the thermodynamics analysis predicted efficient injection from all model compounds. One possible explanation for such behavior was that most of the dyes exhibited short-lived excited-states and that the internal conversion to the ground state efficiently competed with the charge injection into p-GaP. To investigate the excited-state behavior of the model dyes, femtosecond pump-probe measurements were performed for dyes in solution. Transient absorption spectra of the model compounds (Figure 8) consisted of the negative features in the region of ground-state absorption (bleach bands) and fluorescence (stimulated emission bands, observed only in the case of 2O$^+$ and Et-Fl$^+$). The rest of the visible range was dominated by the positive signals that were assigned to the excited-state absorption bands. The spectral changes over varying probe delays showed that most of the dyes exhibit very fast excited-state deactivation. For example, 6O$^+$ lost its transient absorption signal within 20 ps after the excitation, confirming that the molecule fully relaxed to the S\textsubscript{0} state. Interestingly, the only two dyes that exhibit longer lifetimes (2O$^+$ and Et-Fl$^+$) were exactly the dyes that were found to efficiently sensitize GaP. These results suggested that the
charge injection from the “inefficient” dyes to GaP did not compete with the internal conversion, indicating that the rate of charge injection from these dyes to GaP did not occur on the sub-picosecond timescale under the employed conditions.

While a correlation between the excited-state lifetimes of the dyes in solution and the GaP sensitization efficiencies was observed here, we recognize other factors can also contribute strongly to the level of dye sensitization, depending on the conditions of the measurement. For example, the dyes studied here exhibited significant differences in charge recombination dynamics, consistent with the differences in the observed steady-state photocurrents. However, as expected for strong depletion conditions, the rate of charge recombination was likely very small under our experimental conditions. That is, the dependence of recombination by ‘back’ charge-transfer on the applied bias has been previously studied for dye-oxide systems.\textsuperscript{110-112} These studies showed that biasing the Fermi level away from the flat-band potential by only 300 mV leads to a 1000-fold decrease in the charge recombination rates. While similar studies have not yet been performed on hole injection into p-GaP per se, the effect of the applied bias (which is ~ 1.5 V more negative than the p-GaP flat-band potential) should be even more pronounced due to the large internal electric fields in GaP and the superior (relative to the majority of oxides) charge-carrier mobilities of single-crystalline GaP.\textsuperscript{52}

Furthermore, our attempt to evaluate the upper limit for the rates of interfacial charge injection from the solution-based excited-state lifetimes was based on the assumption that the lifetimes of the dye in solution and the dye adsorbed on GaP are similar. Such assumption is certainly limited: the adsorbed dyes are expected to have fewer degrees of freedom, which is likely to affect their rates of radiationless decay. Furthermore, the adsorbed dyes were in close proximity to each other, which could affect their energy levels and excited-state lifetimes due to
aggregation. Finally, the adsorbed dyes could undergo fast energy transfer until the “special” dye site was reached, from which the rate of interfacial charge transfer was fast. To obtain more meaningful results on these different mechanisms, the time-resolved experiments need to be conducted using dyes that are adsorbed on the GaP surface. Unfortunately, our pump-probe technique is not sufficiently sensitive to probe the monolayer of the dye on bulk GaP. To increase the dye coverage on GaP, our team is currently investigating the interfacial charge transfer in the dye/GaP nanowire systems, and this study will likely provide more insights into the factors that affect the dye sensitization of GaP.

Figure 8. Transient absorption spectra obtained at varying probe delays of model compound dyes in acetonitrile upon excitation at: (A) \( \lambda_{\text{exc}} = 525 \text{ nm} \) for 6O\(^+\); (B) \( \lambda_{\text{exc}} = 525 \text{ nm} \) for 4O\(^+\); (C) \( \lambda_{\text{exc}} = 615 \text{ nm} \) for 2O\(^+\); (D) \( \lambda_{\text{exc}} = 565 \text{ nm} \) for Me\(_2\)N-Acr\(^+\); (E) \( \lambda_{\text{exc}} = 600 \text{ nm} \) for T-Acr\(^+\); (F) \( \lambda_{\text{exc}} = 400 \text{ nm} \) for Et-Fl\(^+\). Dashed lines in each graph represent the ground-state absorption spectra of the dyes.
The kinetic trace for $6O^+$ (Figure 9) showed that the molecule decays to the ground state with a lifetime of only 3.3 ps. Such fast excited-state deactivation was observed for many other dyes in the triarylmethane family. As an example representative, malachite green ((Me$_2$NPh)$_2$PhC$^+$) was studied using time-resolved$^{113-115}$ and computational$^{116}$ methods. These studies indicated that the fast S$_1$/S$_0$ internal conversion started with the excited-state relaxation of the dye from the Franck-Condon point to the S$_1$ minimum by the rotations of the phenyl rings around the central C-C bonds. The S$_1$ minimum exhibited a twisted geometry in which two of the dihedral angles were close to 90°, while the third one was close to 0°. The energy of the S$_0$ state at this deformed geometry was large, thus causing the appearance of the conical intersection near the S$_1$ minimum, which was responsible for the fast excited-state deactivation of the dye. In analogy, we propose that the 3.3 ps decay in $6O^+$ occurs due to the same type of torsional motion of the aromatic rings. When going from $6O^+$ to $4O^+$ and $2O^+$, the bridging of the phenyl rings resulted in the restricted rotation of the aromatic rings, which in turn lead to an increase in the excited-state lifetimes: $4O^+$ exhibited a biexponential decay with 2.6 and 43 ps lifetimes, while $2O^+$ transients decayed with three lifetimes of 0.7 ps, 23 ps and 3.2 ns (Figure 8). These findings were in agreement with the reduced efficiency of internal conversion caused by the twisting of the aromatic rings.
Figure 9. Kinetic traces for model compounds in acetonitrile upon excitation at: $\lambda_{\text{exc}} = 400 \text{ nm}$ for Et-Fl$^+$; $\lambda_{\text{exc}} = 615 \text{ nm}$ for 2O$^+$; $\lambda_{\text{exc}} = 525 \text{ nm}$ for 6O$^+$; $\lambda_{\text{exc}} = 565 \text{ nm}$ for Me$_2$N-Acr$^+$; $\lambda_{\text{exc}} = 525 \text{ nm}$ for 4O$^+$; and $\lambda_{\text{exc}} = 600 \text{ nm}$ for T-Acr$^+$.

In the case of acridinium dyes Me$_2$N-Acr$^+$, T-Acr$^+$ and 4O$^+$, the excited-state decays were shorter than expected. For example, the singlet excited state of the phenyl-substituted acridinium ion (Ph-Acr$^+$) had a lifetime of $1\text{-}2 \text{ ns}$. When the phenyl group was replaced by better electron donors (such as mesityl, biphenyl or oligothiophenyl), the locally excited singlet states underwent fast intramolecular charge transfer to generate in either ground or excited charge-separated states. Charge-separated states usually exhibit long lifetimes and are readily detectable using time-resolved laser spectroscopy. The acridinium cations Me$_2$N-Acr$^+$ and T-Acr$^+$ exhibited the excited-state decays with lifetimes of 1 and 1.6 ps, which we assigned to the evolution of the locally-excited state to the charge transfer state. However, the charge
transfer state was either not detected at all (in the case of T-Acr\(^+\)) or was very short-lived (14.7 ps in the case of Me2N-Acr\(^+\)). These results suggested that the back electron transfer was very fast in these model compounds, thus preventing the efficient utilization of the charge-separated state in the GaP sensitization. Similar short-lived charge separated states were observed previously in acridinium cations containing strong electron donors, and the fast charge recombination was attributed to the fact that the back electron transfer occurs in the inverted Marcus region.\(^{120-121}\) To circumvent this fast deactivation, future acridinium-based dyes for GaP sensitization would need to exhibit higher thermodynamic driving force for the back electron transfer, so that the charge recombination occurs at the tail end of the inverted region, which would in turn lead to long-lived charge-separated states.

The flavin-based dye Et-Fl\(^+\) exhibited a singlet-excited state lifetime of 590 ps, which was relatively short relative to the typical fluorescent dyes whose lifetimes are in tens of nanoseconds. Nevertheless, Et-Fl\(^+\) efficiently sensitized GaP showing that the electron transfer from GaP to excited Et-Fl\(^+\) was quite fast. Even though the dye was not covalently attached to the semiconductor surface, the electronic communication between the dye and semiconductor was sufficient to promote interfacial charge transfer.

Clearly, dyes with short solution lifetime were the ones that did not sensitize etched p-GaP(111)A, indicating that the electron transfer from the semiconductor was not fast enough to compete. However, the lifetimes obtained in solution might not always reflect the lifetime of physisorbed dye. For example, crystal violet was previously shown to sensitize GaP with exceptionally high internal quantum yield (40\%),\(^{52}\) even though the solution-based lifetime experiments revealed the lifetime shorter than 10 ps.\(^{99}\) On the other hand, the Nile blue was shown to sensitize GaP with a lower quantum yield,\(^{53}\) even though its excited-state lifetime is
over 400 ps. In these examples, it was likely that the excited-state lifetimes of dyes in solution did not correlate with the lifetimes of dyes adsorbed on GaP, either because the formation of J-aggregates led to a noticeable perturbation of the molecular system, or because the rate of nonradiative decay was slower for adsorbed dye. Alternatively, the interfacial charge transfer rates might be significantly different for different dyes used, imposing different restrictions on the excited-state lifetimes that enabled sensitization. Additional time-resolved studies of dyes adsorbed on GaP are needed to discern these possible mechanisms.

The cumulative sensitized photocurrent responses and model dye lifetimes implied an upper limit on the hole injection rate from the dyes into p-GaP. Since the depletion condition of these p-GaP electrodes effectively eliminated ‘reverse’ hole transfer from the p-GaP back into the dye, the non-zero sensitized photocurrents at steady-state only arose when the hole injection rate from the dye into p-GaP outpaced all other deactivation pathways of the photoexcited dye. In this work, these pathways were not individually assessed. However, the measured dye lifetimes established the net time period available for a photoexcited dye to undergo hole transfer before it underwent deactivation. The data for 6O⁺, 2O⁺, Me₂N-Acr⁺, and T-Acr⁺ clearly showed that hole injection from the dyes did not occur on timescales of 10⁻¹¹ s or shorter. Similarly, the data for 2O⁺ and Et- Fl⁺ dyes implied that the rate of hole injection into p-GaP did occur on timescales of 10⁻¹⁰ s or longer. Correspondingly, the approximate rate constant of hole injection with this set of dyes was no greater than 10¹⁰ s⁻¹, in accord with the expectation of physisorbed dyes that were not strongly coupled electronically with p-GaP.

2.4 CONCLUSIONS

Charge transfer efficiencies in dye-sensitization processes are influenced by several
factors, such as the thermodynamics for the interfacial electron transfer, dye-adsorption affinities to the semiconductor surface and the excited-state kinetics of the dye. To explore the influence of these factors, we designed several triarylmethane, acridine and flavin dyes. All the dyes reported here exhibited the favorable thermodynamic properties for the electron transfer from p-GaP surface. These monocationic dyes were tailored in such fashion to have similar affinities for adsorption to the p-GaP surface like previously reported monocationic dyes with excellent internal quantum yields. Using time-resolved spectroscopy, we found that only dyes with relatively long-lived excited states elicited substantially higher photocurrents than the blank electrolyte. The results of these time-resolved experiments defined an upper-limit on the hole injection from the dye into p-GaP, of hundred picoseconds or higher. Future work on dyes that are covalently attached to GaP surface will provide more quantitative information on the kinetics of interfacial electron transfer.
3.1 INTRODUCTION

The hydride donating ability of a molecule is often described by its hydricity ($\Delta G_{H^+}$), which is defined as the Gibbs free energy for a hydride-ion release from the compound:

$$ R - H \rightarrow R^+ + H^- \quad \Delta G_{H^+} $$

The lower values of $\Delta G_{H^+}$ indicate better hydride donors, and this thermodynamic parameter provides valuable information on potential application of hydrides in fuel-forming reductions of protons and CO$_2$. Thus, the hydricities of a large number of metal-based hydrides have been broadly examined using computational and experimental methods.$^{123-125}$ Even though $\Delta G_{H^+}$ values depend on the solvent,$^{126-129}$ hydricities were often reported in acetonitrile, ranging from 25 – 120 kcal mol$^{-1}$. Only hydrides with hydricities below 76 kcal mol$^{-1}$ in acetonitrile are thermodynamically capable of proton reduction,$^{130-131}$ while $\Delta \Delta G_{H^+}$ below 44 kcal mol$^{-1}$ is needed for the reduction of CO$_2$ to formate.$^{132}$ These studies have shown several structural factors that influence the $\Delta G_{H^+}$ values of metal hydrides: (i) different metals significantly affect the hydricities of complexes. Metals with lower atomic number within the same row display greater hydride donor ability.$^{133}$ Meanwhile, metals in second and third rows in the same group are usually better hydride donors than the first-row metals; $^{123, 131, 134-135}$ (ii) the structural and electronic properties of the ligand can alter the hydricities as well: decrease in the ligand bite angle$^{135-137}$ and the presence of electron-donating substituents on the ligand result in the lowering of hydricities of metal
complexes;\textsuperscript{131, 138-139} (iii) the charge of the metal complex also alters the hydricites: the anionic complexes are generally stronger hydride donors than the corresponding neutral or positive analogs.\textsuperscript{140-142}

However, the thermodynamic hydricities have not been as extensively studied for the metal-free equivalents.\textsuperscript{142-147} Experimental values have been obtained only for a limited number of model compounds and it is found that the strongest hydride donors are NADH analogs ($\Delta G_{H^-}$ values are in the 59-70 kcal mol$^{-1}$ range),\textsuperscript{142} followed by hydroquinones ($\Delta G_{H^-} = 58-125$ kcal mol$^{-1}$)\textsuperscript{143-144} and triarylmethanes ($\Delta G_{H^-} = 75-120$ kcal mol$^{-1}$).\textsuperscript{145-147} Among these model compounds, it is found that hydricities can be lowered by introduction of electron-donating groups and by expanding the delocalization of the positive charge. Both factors improve the stability of cation $R^+$ formed upon the hydride transfer. Besides $\Delta G_{H^-}$, hydride donor abilities of organic hydrides are often characterized using two other parameters: the enthalpy change of the hydride release ($\Delta H_{H^-}$)\textsuperscript{148-149} and the hydride nucleophilicity ($N$).\textsuperscript{150-151} Even though these parameters are experimentally simpler to determine, certain disadvantages are associated with them: enthalpies often exhibit higher values (5-11 kcal mol$^{-1}$)\textsuperscript{142,152} and while they provide some thermodynamic insight, they disregard the entropic contribution. Similarly, the nucleophilicity $N$ provides the information on kinetic profiles of hydride transfer from model donors, but the parameter gives only indirect information about the activation free energy ($\Delta G^{\neq}$).
Scheme 5. Structure of biomimetic organic hydride donors: NADH analogs (BNAH, CN-BNAH, Me-MNAH, HEH), methylene tetrahydromethanopterin analogs (BIMH and CAFH), acridine (Ph-AcrH, Me2N-AcrH, T-AcrH, 4OH, 2OH, 3NH) and triaryl methane (6OH) derivatives.

In this study, we close the gap with metal-based hydride donors by providing calculated and experimental hydricities for model organic hydrides presented in Scheme 5. The model compounds studied here are: (i) analogs of the enzymatic cofactors NADH \(^{153}\) (BNAH, CN-BNAH, Me-MNAH and HEH); (ii) analogs of enzymatic methylene tetrahydromethanopterin H\(_4\)MPT\(^+\) \(^{154}\) (BIMH and CAFH); (iii) acridine derivatives (Ph-AcrH, Me2N-AcrH, T-AcrH, 4OH, 2OH, 3NH) and (iv) triaryl methane derivative (6OH). The hydricities are calculated for two solvents using density functional theory (DFT), while for the experimental values two methods were employed (“potential-pKa” or “equilibrium constant”). Our values showed a reasonable match between the theory and the experiment, and the obtained hydricities showed a strong dependence on structural and electronic properties of the model compounds. Finally, the hydricities of organic hydrides were contrasted with the metal-based equivalents and the similarities and differences are discussed.
3.2 COMPUTATIONAL AND EXPERIMENTAL SECTIONS

Geometry optimizations. All calculations were performed using Gaussian 09 package with the resources of the Ohio Supercomputer Center. The geometries of relevant species (R⁺, R⁻, and R-H) were optimized at the wb97X-D/6-311G(d) level of theory with the conductor-like polarizable continuum model (CPCM) for solvents (acetonitrile and dimethyl sulfoxide). The frequency calculation was performed to confirm the absence of imaginary frequencies. The output files from the frequency calculations provided the values thermal corrections to free energies (ΔG_{corr}^{sol}) for R⁺, R⁻, and R-H. The structures optimized at the wb97X-D/6-311G(d) level were then used to perform a single-point energy calculation at the wb97X-D/6-311++G(2df,p) and CPCM (ACN or DMSO) level and the electronic energies (ℰ_{0}^{sol}) of R⁺, R⁻ and R-H were obtained from these output files.

Hydricity calculations. The computational method was adopted from the previously published study. The hydricity of a model compound R-H (ΔG_{H⁻}) were obtained using the following reaction:

\[
R-H \rightarrow R^+ + H^- \quad \Delta G_{H^-} = G_{R^+} + G_{Hyd} - G_{R-H}
\]

The ΔG_{H⁻} values were derived from the calculated energies of R-H, R⁺ and the hydride ion:

\[
\Delta G_{H^-} = (\mathcal{E}_{0}^{sol} + \Delta G_{corr}^{sol} + \Delta G_{0 \rightarrow}^{*})_{R^+} + (\mathcal{E}_{0}^{gas} + \Delta G_{corr}^{gas} + \Delta G_{hyd}^{sol} + \Delta G_{0 \rightarrow}^{*})_{Hyd} - (\mathcal{E}_{0}^{sol} + \Delta G_{corr}^{sol} + \Delta G_{0 \rightarrow}^{*})_{R-H}
\]

where \mathcal{E}_{0}^{sol} and \mathcal{E}_{0}^{gas} represent electronic energies in solvated and gas-phases, ΔG_{corr}^{sol} and ΔG_{corr}^{gas} are thermal correction to the Gibbs free energy in solvated and gas-phases, ΔG_{hyd}^{sol} is solvation free energy for the hydride anion and ΔG_{0 \rightarrow}^{*} is a standard state correction (the value is
Electronic energies and thermal corrections to the Gibbs free energy were obtained as described in the geometry optimization section. To derive $G_{H\text{yd}}$, the electronic energy ($E_0^{\text{gas}} = -331.14 \text{ kcal/mol}$) and the thermal correction ($\Delta G_{\text{corr}}^{\text{gas}} = -6.28 \text{ kcal/mol}$) were obtained for gas-phase using the wB97X-D/6-31+G(d,p) level of theory. The solvation energy $\Delta G_{\text{sol}}^{\text{sol}}$ for $H^-$ was obtained from the thermochemical cycle connecting gas phase and solution phase one-electron reduction, as expressed in the following equation:

$$\Delta G_{\text{hyd}} = \Delta G_{(H/H^-)}^{\text{sol}} - \Delta G_{(H/H^-)}^{\text{gas}} + \Delta G_{(H)}^{\text{solv}},$$

where, $\Delta G_{(H/H^-)}^{\text{gas}}$ and $\Delta G_{(H/H^-)}^{\text{solv}}$ represent the Gibbs free energy changes for the one electron reduction of hydrogen atom in the gas phase and the solution, respectively. $\Delta G_{\text{gas}}(H/H^-)$ is the negative of the electron affinity of hydrogen atom ($\Delta G_{\text{gas}}(H/H^-) = -17.39 \text{ kcal/mol}$). $\Delta G_{(H/H^-)}^{\text{sol}}$ was obtained from the experimental one-electron potentials $E_0^{\text{H/H^-}}$: using $E_0^{\text{H/H^-}} = -0.60 \text{ V}$ and $-0.55 \text{ V}$ for acetonitrile and dimethyl sulfoxide, $\Delta G_{(H/H^-)}^{\text{sol}}$ values were estimated to be $-84.88 \text{ kcal/mol}$ and $-86.04 \text{ kcal/mol}$ for acetonitrile and dimethyl sulfoxide, respectively. $\Delta G_{(H)}^{\text{solv}}$ represents the solvation energy of hydrogen atom and this value was computed using CPCM/6-311++G(2df,p) and found to be $-0.1 \text{ kcal/mol}$ in both solvents. Using this procedure, the computed values for $G_{H\text{yd}}$ were $-404.8 \text{ kcal/mol}$ and $-406.0 \text{ kcal/mol}$ for acetonitrile and dimethyl sulfoxide, respectively.

Reduction potential calculations. The first ($E^0_{R+/R^-}$) and second ($E^0_{R^-/R^-}$) reduction potentials for our model compounds were derived from the calculated driving forces ($\Delta G_{R+/R^-}$ and $\Delta G_{R^-/R^-}$), as follows:
\[
\Delta G_{R^+/R} = (\mathcal{E}_0^\text{sol} + \Delta G_{\text{corr}}^\text{sol} + \Delta G_{a^{-}}^*)_R - (\mathcal{E}_0^\text{sol} + \Delta G_{\text{corr}}^\text{sol} + \Delta G_{a^{-}}^*)_{R^+}
\]

\[
\Delta G_{R/R^-} = (\mathcal{E}_0^\text{sol} + \Delta G_{\text{corr}}^\text{sol} + \Delta G_{a^{-}}^*)_{R^-} - (\mathcal{E}_0^\text{sol} + \Delta G_{\text{corr}}^\text{sol} + \Delta G_{a^{-}}^*)_R
\]

where electronic energies and thermal corrections were obtained as described in the geometry optimizations section. The obtained \( \Delta G \) values were then used to calculate the standard reduction potentials \( E = -\frac{\Delta G}{nF} \). The calculated values were referenced to NHE by subtracting 4.281 V from computed absolute potentials.\(^{160}\)

General methods. All chemicals were purchased from commercial suppliers and used without further purification. 1-Benzyl-1,4-dihydronicotinamide (BNAH) and 10-Methyl-9-phenylacridinium Perchlorate (Ph-Acr\(^+\)) were purchased from TCI America. Fluorene (FlH), triphenylmethane (TPM) and 4-benzhydryl-1,1′-biphenyl (BBP) were purchased from Sigma. NAD\(^+\) analogs (6O\(^+\), \(^{161}\)4O\(^+\), \(^{161}\)2O\(^+\), \(^{161}\)3N\(^+\), \(^{162}\)T-Acr\(^+\), \(^{161}\)Me2N-Acr\(^+\), \(^{161}\)BNA\(^+\), \(^{163}\)CN-BNA\(^+\), \(^{163}\)Me-MNA\(^+\), \(^{164}\)HE\(^+\), \(^{165}\)BIM\(^+\) and CAF\(^+\)), NADH analogs (6OH, \(^{168}\)2OH, \(^{79}\)Ph-AcrH, \(^{156}\)CN-BNAH, \(^{163}\)BIMH, \(^{166}\)CAFH\(^{167}\)) and indicators (9-phenylxanthene, XanH) were synthesized according to the previously published procedures. NMR spectra were recorded on a Bruker Avance III 500 MHz system. Steady-state UV/Vis absorption spectra were recorded on a Varian Cary 50 UV-Vis spectrophotometer.

\(N,N\)-dimethyl-4-(10-methyl-9,10-dihydroacridin-9-yl)aniline (Me2N-AcrH): Me2N-Acr\(^+\) (412 mg, 1 mmol) was dissolved in ethanol (5 mL) and cooled to 0\(^\circ\)C. Sodium borohydride (150 mg, 4 mmol, 4 eq) was then added, which resulted to color change to yellow. The reaction mixture was let to warm up to room temperature and stirring was continued for additional 4 hours. Resulting solution was filtered and washed with dichloromethane. The filtrate was extracted with dichloromethane, organic extracts were combined and solvent evaporated. The yellow oil was
dissolved in ethanol and the addition of water caused precipitation. The formed precipitated was filtered, washed with cold water and dried under vacuum to yield 115 g (37%) of pure product. 

\[^{1}\text{H}-\text{NMR (CD}\text{3CN, 500 MHz): 7.30-7.25 (4H, m), 7.05 (2H, d), 7.00-6.90 (4H, m), 6.60 (2H, d), 5.14 (1H, s), 3.41 (3H, s), 2.81 (6H, s).}\]

\[N, N-\text{dimethyl-4-}\text{-(10-methyl-9,10-dihydroacridin-9-yl)ethynylaniline (T-AcrH): T-Acr}^{+}\]

(120 mg, 0.27 mmol) was dissolved in 6 mL ethanol and cooled to 0°C. Sodium borohydride (62 mg, 1.62 mmol, 6 eq) was added and the stirring was continued for 2 hours. Over the course of time, deep blue colored disappeared. The reaction mixture was then filtered, filtrate disposed and precipitate washed with dichloromethane. Collected dichloromethane fraction was evaporated and 30 mg of brownish product (33%) was obtained. 

\[^{1}\text{H- NMR (CD}\text{3CN, 500 MHz): 7.67 (2H, d), 7.38 (2H, d), 7.33 (2H, t), 7.10-7.05 (4H, m), 6.73 (2H, d), 5.00 (1H, s), 3.46 (3H, s), 2.98 (6H, s).}\]

Cyclic voltammetry. Cyclic voltammetry was performed using a BASi epsilon potentiostat in a VC-2 voltammetry cell (Bioanalytical Systems) using platinum working electrode (1.6 mm diameter, MF-2013, Bioanalytical Systems), a nonaqueous Ag/Ag\(^{+}\) reference electrode (MF-2062, Bioanalytical Systems) and a platinum wire (MW-4130, Bio-analytical Systems) as a counter electrode. The spectroscopic grade solvent DMSO and the electrolyte tetrabutylammonium perchlorate (TBAP) were purchased from Sigma Aldrich and used as received. Fast scan rate cyclic voltammetry was performed using CHI 600 C potentiostat and platinum working electrode (CHI-107, CH instruments, 10 \(\mu\)m diameter). Electrochemical potentials reported here are referenced to normal hydrogen electrode (NHE), and conversion was achieved by adding 0.548 V to the experimental potentials.\(^{80}\)

Hydride transfer studies. The hydricities of some model compounds were obtained by
determining the equilibrium constant for the hydride transfer reaction with a hydride of known hydride affinity. The equilibrium concentration ratios of reactants and products were obtained using $^1$H NMR spectroscopy. The following steps were performed to ensure that the equilibrium was reached: the progress of the reaction was monitored until the integration of NMR peaks stopped changing. Then, an additional amount of one of the products was added and the reaction was monitored again until the equilibrium was reached. Deuterated acetonitrile and DMSO were used as solvents. All reaction mixtures were prepared in the glove box using dry reagents and air-tight NMR tubes.

Equilibrium of NADH and $2\text{OH}^+$: BNAH (3.8 mg, 0.0177 mmol) and $2\text{OH}^+$ (0.0081 g, 0.0175 mmol) were dissolved in 0.6 mL of deuterated acetonitrile or DMSO. The equilibrium constant was reached after 14 days in acetonitrile yielding $K_{eq}=9.61$ whereas the equilibrium was reached after 19 days in DMSO yielding $K_{eq}=1.68$. The hydricity of $2\text{OH}$ in acetonitrile was obtained from $K_{eq}$ and the reported hydricity of BNAH (59 Kcal/mol) as reference.$^{142}$ In case of DMSO, the hydricity of $2\text{OH}$ (58.3 Kcal/mol) was calculated by using potential-pKa method and the obtained value was used as reference to calculate the hydricity of BNAH in DMSO. The $2\text{OH}$ hydricity was 60 kcal/mol in acetonitrile and the hydricity of BNAH was 57.7 kcal/mol in DMSO.

Equilibrium of BNAH and $\text{HE}^+$: BNAH (3.8 mg, 0.0177 mmol) and $\text{HE}^+$ (0.0055 g, 0.0179 mmol) were dissolved in 0.6 mL deuterated acetonitrile or DMSO. In acetonitrile, the equilibrium was reached after 15 days, yielding $K_{eq}=87.52$. In DMSO, the equilibrium was reached after 49 days, yielding $K_{eq}=1.53$. The hydricity of HEH in acetonitrile was obtained from $K_{eq}$ and the reported hydricity of BNAH (59 Kcal/mol) as reference.$^{142}$ The hydricity of HEH in case of DMSO was obtained from $K_{eq}$ and hydricity of BNAH (57.7 Kcal/mol) as reference. The HEH hydricity was 61.5 kcal/mol in acetonitrile and 58.2 kcal/mol in DMSO.
pKa determination. The pKa values of the NADH analogs were determined using the indicator anion method in DMSO.\textsuperscript{169} Under inert atmosphere, indicators (InH) were added to a solution of potassium dimsyl (K\textsuperscript+CH\textsubscript{3}SOCH\textsubscript{2}\textsuperscript{−}) to generate the indicator anions (In\textsuperscript{−}). An excess of indicator solutions was added to the K\textsuperscript+CH\textsubscript{3}SOCH\textsubscript{2}\textsuperscript{−} to ensure the complete consumption of the base. The anion concentrations were determined using recorded absorbance and In\textsuperscript{−} extinction coefficients. Then, the colored In- solutions were quenched by addition of small aliquots of organic hydrides solutions in DMSO. The pKa values for the organic hydrides were determined using the known indicator pKa value and experimentally obtained equilibrium constants of the reactions between indicator anions and the hydrides. Indicators were chosen to be within two pKa units from the hydrides and indicator absorbed in visible spectrum where the other species were transparent.\textsuperscript{169}

The pKa values of indicators used in this study are:\textsuperscript{169} triphenylmethane (TPM, pKa = 30.6) for 4OH, diphenyldiphenylmethane (DPE, pKa = 29.4) for Me\textsubscript{2}N-AcrH, 9-phenylxanthene (XanH, pKa = 27.9) for Ph-AcrH and 6OH, fluorene (FlH, pKa = 22.6) for 2OH.

3.3 RESULTS AND DISCUSSION

Calculated Hydricities. The hydricities \( \Delta G_{H−} \) of model compounds R-H (eq 1) are calculated from the absolute Gibbs energies of reactant and product states in the appropriate solvation model:

\[
\Delta G_{H−} = G_{R+} + G_{hyd} - G_{R−H}
\] (2)

While the Gibbs energies of solvated R\textsuperscript{+} and R-H species can be calculated reasonably well
using the standard DFT methodology and solvation models, the calculation of absolute Gibbs free energy for the solvated hydride ion \( (G_{\text{hyd}}) \) represents a challenge. One way to overcome this drawback is to calculate the thermodynamic parameters for a hydride transfer reaction between \( \text{R-H} \) and a reference hydride acceptor (such as acridinium cation or \( p \)-benzoquinone) whose hydride affinity is known from the experiment. \(^{143, 170}\) Alternatively, the \( G_{\text{hyd}} \) value can be obtained as a fitting parameter from the experimental hydricities and calculated Gibbs energies \( G_{\text{R}^+} \) and \( G_{\text{R}^-\text{H}}. \(^{135, 171-173}\) Unfortunately, \( G_{\text{hyd}} \) values derived from these studies are not consistent (for example, \( G_{\text{hyd}} \) values in acetonitrile were reported to be \(-400.7 \text{ kcal/mol,}^{135} -404.7 \text{ kcal/mol}^{173}\) and \(-412.7 \text{ kcal/mol.}^{172}\)

In collaboration with the Krylov group, we previously calculated the hydricity of an acridine-based hydride donor and the obtained value was in excellent agreement with the experimental hydricity. \(^{156}\) In our approach, the absolute Gibbs energy \( G_{\text{hyd}} \) was obtained as the sum of the gas-phase energy \( G_{\text{hyd}}^{\text{gas}} \) and the solvent contribution \( \Delta G_{\text{hyd}}^{\text{sol}} \):

\[
G_{\text{hyd}} = G_{\text{hyd}}^{\text{gas}} + \Delta G_{\text{hyd}}^{\text{sol}}.
\]  

The gas phase energy \( G_{\text{hyd}}^{\text{gas}} \) was calculated using DFT, while the solvation energy \( \Delta G_{\text{hyd}}^{\text{sol}} \) was derived from the experimental one-electron reduction potential of hydrogen atom in a solvent of interest \(^{174}\) and the calculated gas-phase electron affinity of H-atom (as detailed in the computational section). The \( G_{\text{hyd}} \) values obtained in this way are \(-404.8 \text{ kcal/mol (in ACN)} \) and \(-406.0 \text{ kcal/mol (in DMSO).} \) In the current manuscript, this computational methodology was
utilized to calculate the hydricities of our model hydrides in two solvents (ACN and DMSO, Table 1).

Table 1. Calculated standard reduction potentials (vs. NHE) for $R^+/R^-$ and $R^-/R^-$, pKa values for RH and $\Delta G_{\text{H-}}$ for RH in different solvents.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$E_1$ ($R^+/R^-$)</th>
<th>$E_2$ ($R^-/R^-$)</th>
<th>pKa (RH)</th>
<th>$\Delta G_{\text{H-}}$(RH)</th>
<th>$\Delta G_{\text{H-}}$(RH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6OH</td>
<td>0.08</td>
<td>−1.27</td>
<td>30.4</td>
<td>84.1</td>
<td>85.8</td>
</tr>
<tr>
<td>4OH</td>
<td>−0.61</td>
<td>−1.48</td>
<td>37.6</td>
<td>73.2</td>
<td>75.1</td>
</tr>
<tr>
<td>PhAcrH</td>
<td>−0.25</td>
<td>−1.17</td>
<td>26.1</td>
<td>72.8</td>
<td>74.9</td>
</tr>
<tr>
<td>Me2N-AcrH</td>
<td>−0.30</td>
<td>−1.20</td>
<td>25.6</td>
<td>70.3</td>
<td>72.2</td>
</tr>
<tr>
<td>CN-BNAH</td>
<td>−0.69</td>
<td>−1.42</td>
<td>33.1</td>
<td>66.5</td>
<td>68.5</td>
</tr>
<tr>
<td>T-AcrH</td>
<td>−0.09</td>
<td>−1.02</td>
<td>14.9</td>
<td>64.7</td>
<td>66.6</td>
</tr>
<tr>
<td>2OH</td>
<td>−0.58</td>
<td>−1.40</td>
<td>27.0</td>
<td>61.1</td>
<td>62.9</td>
</tr>
<tr>
<td>HEH</td>
<td>−1.04</td>
<td>−1.50</td>
<td>36.0</td>
<td>60.6</td>
<td>62.5</td>
</tr>
<tr>
<td>BNAH</td>
<td>−0.94</td>
<td>−1.84</td>
<td>38.4</td>
<td>58.3</td>
<td>60.3</td>
</tr>
<tr>
<td>CaflH</td>
<td>−1.87</td>
<td>−1.65</td>
<td>45.8</td>
<td>51.3</td>
<td>53.2</td>
</tr>
<tr>
<td>Me-MNAH</td>
<td>−1.24</td>
<td>−1.63</td>
<td>34.1</td>
<td>50.3</td>
<td>52.2</td>
</tr>
<tr>
<td>BIMH</td>
<td>−1.51</td>
<td>−1.69</td>
<td>38.4</td>
<td>48.6</td>
<td>50.3</td>
</tr>
<tr>
<td>3NH</td>
<td>−1.07</td>
<td>−1.75</td>
<td>30.8</td>
<td>46.9</td>
<td>48.7</td>
</tr>
</tbody>
</table>

In the same collaboration, we calculated the standard reduction potential for the studied acridine-derivative in acetonitrile, which matched well with the experimentally obtained value.\(^{156}\)

Using this approach, we obtained the calculated values for first and second standard reduction potentials for studied R+ species ($E_1$ ($R^+/R^-$) and $E_2$ ($R^-/R^-$)) in dimethyl sulfoxide, presented in Table 1. The pKa values for the studied organic hydride donors in dimethyl sulfoxide were derived from calculated $\Delta G_{\text{H-}}$(RH), $E_1$ ($R^+/R^-$) and $E_2$ ($R^-/R^-$) using the following equation:

$$pK_a^{RH} = \frac{\Delta G_{\text{H-}} - 23.06 \left( E_{R^+/R}^0 + E_{R^-/R}^0 \right) - \Delta G_{\text{solvent}}^{H^+/H^-}}{1.364}$$
The calculated values for pKa are really inaccurate, since the very small changes in potential values lead to a large difference in pKa values. Despite that fact, the calculated values \( E_1 \) (\( R^+ / R^- \)), \( E_2 \) (\( R^- / R^- \)) and pKa are taken into account when experimental determinations were conducted.

Experimental Hydricities: To confirm calculated hydricity, two experimental approaches were utilized to determine the experimental hydricities of model compounds: the “potential-pKa” and “hydride transfer” methods. The “potential-pKa method” uses the relevant standard reduction potentials and pKa values to determine the hydricity of a model compound, as follows:

\[
R^+ + e^- \rightarrow R^- \quad \Delta G_{ET1} = -FE_{R^+ / R^-}^0 = -23.06 \ E_{R^+ / R^-}^0
\]

\[
R^- + e^- \rightarrow R^- \quad \Delta G_{ET2} = -FE_{R^- / R^-}^0 = -23.06 \ E_{R^- / R^-}^0
\]

\[
R^- + H^+ \rightarrow RH \quad \Delta G_{PT} = RT \ln K_a = -1.364 \ pK_a^{RH}
\]

\[
H^+ + 2e^- \rightarrow H^- \quad \Delta G_{DH/DMSO}^{H+/H^-} = 69.9 \ kcal/mol; \ \Delta G_{DH/ACN}^{H+/H^-} = 54.7 \ kcal/mol
\]

\[
RH \rightarrow R^+ + H^- \quad \Delta G_{H^-} = 23.06 \ (E_{R^+ / R^-}^0 + E_{R^- / R^-}^0) + 1.364 \ pK_a^{RH} + \Delta G_{DH/DMSO/ACN}^{H+/H^-}
\]

where \( \Delta G_{ET1} \) and \( \Delta G_{ET2} \) represent Gibbs free energy changes for first electron and second electron reduction of NAD\(^+\) analogs, calculated using their first and second standard reduction potential \( (E_{R^+ / R^-}^0 \text{ and } E_{R^- / R^-}^0, \text{ respectively}) \); \( \Delta G_{PT} \) represent a Gibbs free energy change for protonation of \( R^- \), calculated using the pKa values of NADH analogs \( (pK_a^{RH}) \); \( \Delta G_{DH/DMSO}^{H+/H^-} \) and \( \Delta G_{DH/ACN}^{H+/H^-} \) represent Gibbs free energy changes for two electron reduction of the proton in dimethyl sulfoxide and acetonitrile, respectively, using the derived potentials for proton reduction in these solvents; \( \Delta G_{H^-} \) represents hydricity of the studied NADH analog.
The “hydride transfer” method involves measuring of the equilibrium constant ($K_{HT}$) for a hydride transfer from a model hydride $R$-$H$ and a reference hydride acceptor ($A^+$) with known hydride affinity, as follows:

$$RH + A^+ \rightarrow R^+ + AH \quad \Delta G_{HT} = -RT \ln K_{HT}$$

$$AH \rightarrow A^+ + H^- \quad \Delta G_{H^-}(AH)$$

$$RH \rightarrow R^+ + H^- \quad \Delta G_{H^-}(RH) = \Delta G_{H^-}(AH) + \Delta G_{HT}$$

where $\Delta G_{HT}$ represents a Gibbs free energy change for the hydride transfer between examined and referent hydrides, calculated from experimentally obtained equilibrium constant for the hydride transfer, $K_{HT}$; $\Delta G_{H^-}(AH)$ and $\Delta G_{H^-}(RH)$ represent hydricities of the referent and examined hydrides.

Both of these approaches have drawbacks, which required the use of “potential-pKa method” for those model compounds that exhibited measurable reduction potentials and pKa values in DMSO. On the other hand, the “hydride transfer” method was used for the model compounds that reached the equilibrium point when reacted with the reference hydride acceptor.

Potential-pKa method. As mentioned above, this method is limited to the model compounds whose reduction potentials and pKa values can be determined in the solvent of interest. For example, the pKa of the model compound R-H can be experimentally determined only if R-H is more acidic than the solvent (for DMSO, pKa=35, which limits the pKa determination for compounds with pKa values lower than 32).\textsuperscript{176} 4OH, HEH, CN-BNAH, BNAH, CaffH, Me-MNAH and BIMH seemed like bad candidates, but it was not clear since the computational method for calculating pKa values was not very accurate. All compounds should be good candidates according to the calculated values, with BNAH, CaffH, BIMH, Me-MNAH and 3NH pushing the
limit of solvent electrochemical window. Guided by calculated parameters and method limitations mentioned beforehand, the hydricity could be determined for most of the model compounds using “potential-pKa method”.

Standard reduction potentials were obtained using cyclic voltammetry (Figure 10). Reversible electrochemical behavior was observed for the first reduction step of $6O^+$ and most acridine-based models (Ph-Acr$^+$, Me$_2$N-Acr$^+$, 4O$^+$, 2O$^+$ and 3N$^+$) at low sweep rates (such as 100 mV/s), indicating stable radicals (Table 2). On the other hand, the first reduction potentials of pyridinium (CN-BNA$^+$, HE$^+$, BNA$^+$ and ME-BNA$^+$) and imidazolium (BIM$^+$ and CAF$^+$) models appear at more negative potentials and display irreversible peaks. Similar result has been reported and has been assigned to the dimerization of the radicals.\textsuperscript{178-181} The lower reactivity of acridine-based radicals and chemical reversibility over the pyridine-based structures is probably due to higher delocalization of the unpaired spin in the acridine-based radicals.\textsuperscript{179} However, the reduction of T-Acr$^+$ becomes chemically reversible at high scan rates (2 kV/s, Figure 10), even though it is an acridine-derivative. The origin of the chemical irreversibility has not been explored further, but it is interesting to note that the reduction of the neutral acridine-based analog to form the radical anion is chemically reversible even at 100 mV/s.\textsuperscript{182} The chemical irreversibility of imidazolium radicals has been previously attributed to either their dimerization\textsuperscript{181} or to the loss of H-atom and formation of carbene analogs.\textsuperscript{181, 183-185} While the one-electron reduced CAF$^+$ can form carbene analogs by a loss of a hydrogen atom from the carbon located between two N centers, it is not clear whether BIM$^+$ can undergo similar chemistry by a loss of phenyl radical. The chemical reversibility for the one-electron reduction of pyridinium and imidazolium models could not be achieved (scan rates up to 10 kV/s were investigated), which prevented us from obtaining the standard reduction potentials for these processes and using the “potential-pKa” methods to determine their hydricities.
Figure 10. Cyclic voltammograms of model compound (cations) in the cathodic range: Pt working electrode, Pt counter electrode, and nonaqueous Ag/AgNO₃ reference electrode. Sweep rate, 0.1 V/s (3N⁺, CN-BNA⁺, HE⁺, BNA⁺, Me-MBNA⁺, BIM⁺ and CAF⁺), 25 V/s (6O⁺, T-Acr⁻, Me2N-Acr⁺, 2O⁺), 2 kV/s (T-Acr⁺), 100 V/s (Ph-Acr⁺, 4O⁺); electrolyte: 0.1 M TBAP in DMSO. The second reduction peak of T-Acr⁺ was obtained from the oxidation of T-Acr⁻ which was formed by the deprotonation of TAc-H in the presence of dimsyl ion (pKa = 35).¹⁷⁶

The second reduction peaks were obtained only for NAD⁺ analogs whose first reduction peaks were reversible (6O⁺, Ph-Acr⁺, Me2N-Acr⁺, 4O⁺, 2O⁺ and 3N⁺, Table 2). For low scan rates (100 mV/s), second reduction peaks were irreversible, likely due to the protonation of the generated anion to form NADH analogs. Consistent with this assignment is the fact that the reactivity of NAD⁻ anions correlates well with experimentally obtained pKa values of the corresponding R-H analogs. For example, the second reduction peak of 6O⁺ becomes reversible at relatively low scan rates (25 V/s), which is consistent with relatively low basicity of 6O⁻ anion (the pKa of 6OH is 26.9, see text below). On the other hand, the reversibility for 4O⁺ requires the scan rates of 100 V/s and the pKa of 4OH is 30.3 (Table 2). The second reduction peak was not detected
in the case of T-Acr\(^-\), because of the sluggish electron transfer kinetics of this process at high scan rates that were needed to achieve the reversibility of the first reduction peak (2 kV/s). Instead, the standard reduction potential for this process was obtained by electrochemical oxidation of T-Acr\(^-\) anion, formed by the deprotonation of T-AcrH (Figure 1). Similar experiments were attempted on CN-BNAH, HEH, BNAH, Me-BNAH, BIMH and CAFH, but these compounds couldn’t be deprotonated because of acidities lower than solvent.

Table 2. Experimentally obtained \(E^0_{R^+/R^-}\), \(E^0_{R^-/R^-}\) and \(pK_{aR}^{RH}\) of NADH model compounds for obtaining experimental \(\Delta G_{H^-}\) values using “potential-pKa” method in dimethyl-sulfoxide.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Solvent</th>
<th>(E^0_{R^+/R^-}) (V vs NHE)</th>
<th>(E^0_{R^-/R^-}) (V vs NHE)</th>
<th>(pK_{aR}^{RH})</th>
<th>(\Delta G_{H^-}) (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>6OH</td>
<td>DMSO</td>
<td>+0.24</td>
<td>-1.24</td>
<td>26.9</td>
<td>83.5</td>
</tr>
<tr>
<td>4OH</td>
<td>DMSO</td>
<td>-0.38</td>
<td>-1.41</td>
<td>30.4</td>
<td>70.2</td>
</tr>
<tr>
<td>PhAcrH</td>
<td>DMSO</td>
<td>-0.29</td>
<td>-1.23</td>
<td>28.3</td>
<td>73.5</td>
</tr>
<tr>
<td>Me(_2)N-AcrH</td>
<td>DMSO</td>
<td>-0.30</td>
<td>-1.42</td>
<td>29.2</td>
<td>70.1</td>
</tr>
<tr>
<td>T-AcrH</td>
<td>DMSO</td>
<td>-0.22</td>
<td>-1.07</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2OH</td>
<td>DMSO</td>
<td>-0.50</td>
<td>-1.39</td>
<td>23.4</td>
<td>58.2</td>
</tr>
<tr>
<td>3NH</td>
<td>DMSO</td>
<td>-0.80</td>
<td>-1.62</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The pKa values for R-H analogs in dimethyl sulfoxide were obtained using the method by Bordwell.\(^{176}\) The method involves the spectroscopic titration of the colored indicator anion of known acidity with the acid of unknown acidity. To achieve high accuracy, the indicators were
chosen to be within 2 pKa values from the determining R-H analog and the indicator anion absorbed well in the region where other species didn’t absorb. Using this approach, we obtained the pKa values for 6OH, 4OH, PhAcrH, Me2N-AcrH and 2OH (Table 2).

Hydride-transfer method. The hydride-transfer method was used to determine hydricities for organic hydride donors whose hydricity could not be acquired using the previous method. The relevant equilibrium constants were obtained using NMR spectroscopy in two different solvents, dimethyl sulfoxide and acetonitrile. A quantifiable equilibrium constant can be achieved if the hydricities of two hydrides differ up to ~3 kcal/mol, which corresponds to 1:10 ratio of the equilibrated concentrations. Furthermore, it is necessary to ensure that the equilibrium has been reached, either by determining the equilibrium constants for forward and backward reactions or by addition of the products to equilibrated system and measure the constant again. This approach was utilized by Dubois to obtain the hydricity values of NADH-analogs (BNAH and CN-BNAH) in acetonitrile, using the metal-based hydride donors as references.

The organic hydride donors with the hydricity determined using “potential-pKa” method in this work were also used as referent hydride acceptors.

The reaction between NADH and 2O\(^+\) went cleanly at room temperature over the course of 14 days in acetonitrile. An equilibrium constant of 9.61 was calculated for the reaction by integration of \(^1\)H NMR spectrum. Using the obtained free energy for hydride transfer (-1.3 kcal/mol) and the previously reported hydricity of NADH in acetonitrile (\(\Delta G_{H^+} = 59\) kcal/mol),
we obtain $\Delta G_{H^-} = 60.3$ kcal/mol as a hydricity of 2OH in acetonitrile. Similarly, the hydricity of HEH in acetonitrile, NADH and HEH in dimethyl sulfoxide were obtained (Table 3).

Unfortunately, the attempts to apply this method on other model compounds resulted in side reactions and couldn’t provide the hydricity values.

Table 3. The hydricity values ($\Delta G_{H^-}$) obtained using “hydride-transfer” method in dimethylsulfoxide and acetonitrile.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta G_{H^-}$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>DMSO</td>
</tr>
<tr>
<td>CN-NADH</td>
<td>63</td>
</tr>
<tr>
<td>HEH</td>
<td>58.0</td>
</tr>
<tr>
<td>2OH</td>
<td>58.2</td>
</tr>
<tr>
<td>BNAH</td>
<td>57.5</td>
</tr>
</tbody>
</table>

The experimental hydricity values obtained in this work, using “potential-pKa” and “hydride-transfer” methods, showed a generally good agreement with the calculated values. The results obtained using the first method displayed slightly lower values than calculated (less than 3 kcal/mol). Similarly, the experimental hydricities obtained from the equilibrium constants for hydride transfer exhibited values of 2 kcal/mol less than the calculation. Overall, the hydride donor abilities were improved slightly going from acetonitrile to dimethyl sulfoxide (by ~2 kcal/mol), which was also predicted by calculations. Such trend can be explained by the small differences in their dielectric constants ($\varepsilon$(DMSO) = 47 vs $\varepsilon$(ACN) = 38),$^{186}$ which results in slightly better solvation of formed charged species ($R^+$ and $H^-$) and it is expected to be even more improved when water is used as a solvent ($\varepsilon$(H$_2$O) = 79).$^{186}$ A similar solvent trend has been observed for the Ni-based hydride, whose hydricites were obtained in acetonitrile ($\Delta G_{H^-}$= 
57.4 kcal/mol), dimethyl sulfoxide (ΔG_H^+ = 55.5 kcal/mol) and water (ΔG_H^+ = 30.0 kcal/mol).\textsuperscript{126}

Structure-property relationship. The stabilization of the forming cation, R^+, leads to an improvement in the hydride donor ability. Therefore, the hydricity of a molecule R-H is significantly dependent on its structure and how well the formed positive charge can be stabilized. Hydricities obtained for the model compound studied here span in 47 – 84 kcal/mol range. Among them, several interesting points can be raised regarding the structure of the model organic hydride donors. In general, benzimidazole structures proved to be the strongest hydride donors, followed by NADH-analogous structures, acridine-derivatives and triarylmethanes.

The high hydride donor ability of imidazole derivatices derivatives (BIMH and CAFH) can be credited to the specific conformation and an anomeric effect, where neighboring nitrogen centers donate their lone pairs to the antibonding orbital of the C-H bond, stabilizing the cation R^+ (Scheme 2c). Also, the aromatization of formed R^+ further facilitates the hydride release. Similar effect of aromatization being a main driving force was observed for NADH-analogs (BNAH, CN-BNAH, Me-MNAH and HEH) and acridine-derivatives (Ph-AcrH, Me2N-AcrH, T-AcrH, 4OH, 2OH, 3NH). The greater hydricity values of NADH-analogs over acridine-analogs can be attributed to the higher aromaticity of a pyridine ring over acridine.\textsuperscript{170} The triarylmethane model compound 6OH lacks in planarity, and therefore the formed 6O^+ is not aromatic. As a consequence, it was found to be the weakest hydride donor in this study, which is consistent with the hydricities obtained for a series of triarylmethanes (usually above > 80 kcal/mol).\textsuperscript{145,147}

Besides aromatization, the formed positive charge can be stabilized through the inductive effect. The presence of the electron-donating groups in the molecule significantly increases the stability of the cation lowering the hydricity of the molecule. Correspondingly, the electron-withdrawing groups decrease the hydride-donating ability of the organic hydrides. This effect can be
observed for the NADH-analogs: methyl group in Me-MNAH ($\Delta G_{H_2} = 50$ kcal/mol), amide group in BNAH ($\Delta G_{H_2} = 59$ kcal/mol), and cyano group in CN-BNAH ($\Delta G_{H_2} = 63$ kcal/mol). Similarly, the hydricity of Me2N-AcrH ($\Delta G_{H_2} = 70.1$ kcal/mol) was improved in comparison to the derivative without donating group (PhAcrH, $\Delta G_{H_2} = 73.5$ kcal/mol).

Comparison with metal-based hydrides. The model compounds studied here displayed hydricity values in 47 - 85 kcal/mol range, which is similar to a majority of metal-based hydrides. While the polarization of the M-H bond facilitates the hydride release (electronegativity of metals are close or less than electronegativity of hydrogen atom), the driving force for hydride release for metal-free hydrides is the structural stabilization of the product (electronegativity of carbon is higher that of hydrogen atom). As mentioned above, the structure-property relationship can be explained through anomeric, aromatization and inductive effects. (Figure 11) In case of their metal-analogs, two factors mainly affect the hydride donor ability: the metal present in the complex and the bite angle of the ligand (Figure 11). Metals with lower atomic number within the same row display greater hydride donor ability. Meanwhile, metals in second and third rows of transitional metals are significantly better hydride donors than the first-row metals. In case of the ligand bite angle, the geometry of the complex represents an important factor that affects hydricity. Specifically, it has been found that the increased tetrahedral distortion improves the hydride donor ability: a decrease in the ligand bite angle result in the lowering of hydricities of metal complexes.
Even though the hydricities of metal-free hydrides and metal-based hydrides follow different structure-property relationships, some interesting correlations regarding the reduction potentials can be drawn. Linear correlations between free energy for hydride release with relevant first reduction potentials (metal-free, $R^+/R^-$ and metal-based, $M^{2+}/M^+$) indicate that free energies for homolytic $R$-$H$ and $M$-$H$ bond dissociations (bond dissociation energy, BDE) only somewhat differ within the series (Figure 12a). The BDE energies of the metal hydrides were found to be slightly lower than for the metal-free hydrides, indicating the more favorable hydrogen atom release from metal-analogs. The slopes for both correlations are very close to theoretical values ($nF = 23.06$), and they show that first reduction potentials for $E(R^+/R^-)$ are uniformly shifted for $\sim -0.5$ V from the first reduction potentials for $(M^{2+}/M^+)$. 

Figure 11. Structure-property relationships for metal-free and metal-base hydride donors.
Figure 12. a) Correlation between $E_1$ (metal-free, $R^+/R^-$ and metal-based, $M^{2+}/M^+$) and $\Delta G_{\text{H}}$ of R-H and M-H. b) Correlation between $E_2$ (metal-free, $R^+/R^-$ and metal-based, $M^+/M^0$) and $\Delta G_{\text{H}}$ of R-H and M-H. c) Correlation between free energies for second electron transfer (related to $E_2$) and proton transfer (related to pKa of R-H and M-H). All potentials were referenced to NHE.

Such trends were not observed in correlations between the second reduction potentials (metal-free, $R^+/R^-$ and metal-based, $M^+/M^0$) and $\Delta G_{\text{H}}$ of R-H and M-H (Figure 12b). The second reduction potential values were significantly shifted in case of metal-free hydrides ($\sim$ -1.0 V). The correlation between free energies for second electron transfer (related to $E_2$) and proton transfer (related to pKa of R-H and M-H) showed that organic hydrides are weaker bases (higher pKa) and the second electron reduction ($R^+/R^-$) require more negative potentials (Figure 12c). In the case of metals, the second reduction potentials are very close to the first reduction potentials ($< 0.5$ V),
while the differences in reduction potentials for organic hydrides are drastically higher (~ 1.0 V). The reduction potentials of conjugated hydride donors (R\(^+\)) indicate the feasibility of the closing the catalytic cycle and converting R\(^+\) back to R-H. Unfortunately, the large negative values for reduction potentials for R\(^+\) hinder their potential application in catalysis.

3.4 CONCLUSIONS

Thermodynamic hydricities were determined computationally and experimentally in dimethyl sulfoxide and acetonitrile for a series of metal-free hydride donors. The hydride donor ability for organic hydrides is greatly influenced by the structural properties of a molecule and can be drastically improved due to the anomeric effect, the effect of aromatization of the forming positive charge and by the presence of electron-donating groups. The obtained hydricities span a 47 – 85 kcal/mol range, similarly to the majority of metal-based hydrides. Unlike the metal- analogs, the metal free analogs studied here exhibit the large negative potentials for E\(_1\) (R\(^+\)/R\(^-\)) and E\(_2\) (R/R\(^-\)). As a consequence, the possible application of these metal-free hydride donors in catalysis is hindered because of the difficulty to close the catalytic cycle. Future work should focus on how to lower the reduction potentials of NADH analogs in order to improve their catalytic ability in solar fuel forming reactions.
CHAPTER 4. SUMMARY AND FUTURE OUTLOOK

The current need for alternative energy sources has lead the scientific world to sunlight and its capability to deliver enough energy for mankind’s demand. Due to the temporal and special inconsistency in solar irradiance, energy from the sun needs to be chemically stored in the form of fuels. Our approach is to construct an efficient photoelectrochemical solar cell using earth-abundant materials. The proposed system contains bio-inspired metal-free hydride donors (NADH analogs) suitable for fuel forming reductions and a p-type semiconductor that serve as a light harvester and source of electrons. In this study, we investigated the capability of a p-GaP semiconductor to photochemically reduce the NAD\(^+\) analogs. Also, we determined the hydride donor ability of NADH analogs that is important for fuel forming reductions.

The initial work on the photoreduction of NAD\(^+\) analogs with p-GaP surface was based on investigating the factors that influence the charge transfer efficiencies to the model NAD\(^+\) analogs: thermodynamics for the interfacial electron transfer, dye-adsorption affinities to the semiconductor surface and the excited-state kinetics of the dye. While the NAD\(^+\) analog exhibited the favorable thermodynamic properties, only the compounds with the excited state lifetimes above 600 ps displayed a successful electron transfer.

The hydride donor abilities (hydricity) have been determined computationally and experimentally for a series of metal-free NADH analogs. They are greatly influenced by the structural properties of a molecule and can be enhanced due to the anomeric effect, aromatization effect by the presence of electron-donating groups. All model compounds displayed a favorable strength for proton reduction. While they proved to be in the same range as for metal-based analogs, significantly higher values for reduction potentials of the conjugated hydride acceptors
hinder their application in catalysis.

Future work will focus on the lowering the reduction potentials of the conjugated acceptors by implementing the structural motifs that improve hydricity of NADH analogs into a large delocalized system, such as graphene quantum dots (Figure 13a). Furthermore, the hydride transfer reactions from NADH analogs to proton and CO$_2$ will be tested in order to evaluate their applicability in fuel forming reactions (Figure 13b). Finally, the overall performance of proposed system will be tested in a photoelectrochemical solar cell setup (Figure 13c).

Figure 13. Future efforts towards designing an efficient photoelectrochemical cell include: a) lowering the reduction potentials to facilitate the closure of the catalytic cycle; b) analysis of the activity of NADH analogs in fuel forming reactions; c) testing the performance on a photoelectrochemical cell.
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