



Collaboration between Experiment and Theory in Solar Fuels Research

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As the challenges in science increase in scope and interdisciplinarity, collaboration becomes increasingly important. Our groups have maintained close collaborations for solar fuels research over the past decade. Based on this experience, we discuss strategies for collaboration between experiment and theory including facilitation of effective communication and navigation of problems that arise. These strategies are illustrated by case studies of collaborative efforts in solar fuels research pertaining to interfacial electron transfer in dye-sensitized metal oxides and the design and mechanism of water-oxidation catalysts.

Key learning points

- (1) How to reflect on collaborative science and the role of investigators in a collaboration from the perspective of the philosophy of science.
- (2) Case studies to identify a collaborative framework based on previous research.
- (3) Tips for building a framework for a collaborative project, effective communication, and working productively with collaborators.

Introduction

With the rising level of atmospheric CO₂ and the difficulty of slowing the rise of average global temperature,¹ the development of solar energy technologies is needed to decrease dependence on carbon-based fuels.¹⁻⁵ Moreover, the development of cost-effective solar energy technologies is one of the grand challenges in modern scientific research. Finding solutions to such challenges often requires a broader perspective than can be found in a single research group. Collaborations, particularly among experimentalists and theorists, have become increasingly common.

Our collaboration and many others have concentrated on the development of renewable solar technologies for producing value-added chemical fuels referred to as “solar fuels.” The term solar fuels ranges from H₂, to methanol or ethanol, or even formic acid. They are formed in a manner related to that by which Photosystem II (PSII) generates reducing equivalents obtained from the conversion of water to oxygen.⁶ However, in the artificial photosynthetic systems discussed herein, the reducing equivalents generated by photocatalytic water oxidation are utilized to produce a solar fuel, such as H₂, rather than drive the biological production of NADPH in photosynthesis.

While much work has been done in this area, the design and understanding of artificial photosynthetic systems is likely to be more effective when experiments and theoretical calculations are combined in a collaborative framework. An atomistic-level understanding on both fronts facilitates the rational design of new catalysts, anchoring groups, semiconductors, and dyes for solar cell devices that may help push efficiencies closer to the level required for commercialization.

We examine frameworks for fostering collaboration, and provide insight into how researchers participate in the wider scientific inquiry, with an eye towards solving the grand challenges in science.

We discuss two case studies in the field that show how collaborations can occur in an either “concerted” or “stepwise” manner (and sometimes both). In the first case, we describe how experimentalists and theoreticians collaborated in a concerted fashion to design photosensitizers and to understand the mechanism of interfacial electron transfer (IET). In the second, we analyze the long-term, stepwise interplay between theory and experiment in understanding the mechanism of ruthenium-based water-oxidation catalysts.

In addition, we provide observations for successful collaborative science based on experience in collaborative solar fuels research. The goal of this tutorial is to allow recent progress in solar fuels research to demonstrate the value of collaboration and provide a framework for such interdisciplinary projects. We collect best practices for collaboration and show a logical progression of scientific understanding that has resulted from the interplay among all involved.

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The Philosophy of Collaboration

As practitioners of the scientific method, researchers are familiar with the process of making observations, developing a hypothesis, testing the hypothesis, and then analysing the results to either support or falsify the hypothesis. This hypothesis-based research paradigm⁷ (what philosophers of science call the “hypothetico-deductive model”⁸) more often than not also leads to serendipitous discoveries. Instead of supporting or falsifying the hypotheses at hand, such unanticipated discoveries may move research in an altogether different direction. In light of this situation, it is perhaps helpful to consider the three-phase process of scientific inquiry discussed by the philosopher Roy Bhaskar:⁹

- 1.) Observation of natural phenomena.
- 2.) Explaining the phenomena and verifying the explanations.
- 3.) Achieving a deeper understanding of the phenomena.

In practice, this three-phase process is equivalent to the scientific method with the added advantage that the process is understood to be cyclical, generating new research directions along the way. Significant for the purposes of this tutorial is that the three-phase process also provides a conceptual framework for discussing collaborative efforts in scientific problem solving.

Each step in the three-phase process can be accomplished by experimentalists or theoreticians. Sometimes the experimentalist identifies a natural phenomenon. They may then turn to a theoretician to help construct possible explanations for the phenomenon before returning to experiment to validate the explanations. Other times, a theoretician identifies a potential new material process or mechanism, and its potential benefits, and then turns to experimentalists to evaluate the new material through testing. Collaborations include these examples and many more, breaking most or all of these boundaries.

Defining Scientific Collaboration

It is useful to define what is meant by “collaboration.” Huebner, Kukla, and Winsberg¹⁰ single out several distinguishing aspects of collaboration. These are collaborations through space, over time, within or across research disciplines, and also the standards for assigning authorship. In this section, we consider the first three aspects of collaboration. We return to standards for assigning authorship below in “Tips for Successful Collaborative Research”.

Scientific collaboration is a pursuit involving different research teams at the same institution or different institutions (space constraints). The collaboration can take place over brief or long periods, with research teams either working in concert at each step, or in a stepwise manner (time constraints). In this respect, we propose that traditional understandings of “collaboration” can and should be extended to include activities such as engagement with the scientific literature and communication of results at conferences. As well as the fact that these activities aid progress in a field of research, such

activities can often lead to collaborations as they are traditionally understood (see the case of Sun and Ahlquist in the section on “Stepwise Collaboration” below). Extending the definition of collaboration in this way also emphasizes the significant fact that research is always carried out as part of a research community. Finally, we focus on theoreticians and experimentalists working on similar subject matter within the same research discipline (unidisciplinary constraints).

Two kinds of collaborations figure prominently in this review of solar fuels research. In the first case, experimentalists and theoreticians both tackle each step together simultaneously (concerted collaboration). We find that the field of IET fits this pattern in general.

Alternatively, one part of the team may discover a phenomenon and assert an explanation or mechanism. Then a counterpart supports or amends the original findings until a consensus is reached (stepwise collaboration). We find that the development of ruthenium-based water-oxidation catalysts (WOCs) fits this pattern. This kind of collaboration is a sequential approach. Results are communicated primarily through scientific articles or at conferences. In general, research progress tends to be slower compared to concerted collaboration, but illustrates an important synergy for experimentalists and theoreticians. Significantly, stepwise collaborations can be useful for initiating and fostering concerted collaborations.

Concerted Collaboration

Photosensitizer Design for Interfacial Electron Transfer

We recently investigated the IET dynamics of photosensitizers on dye-sensitized metal oxide (TiO₂ and SnO₂) electrodes using a variety of synthetic, electrochemical, spectroscopic, and computational techniques.^{11–17} These investigations were implemented within a collaboration between experimentalists and theoreticians working synchronously towards the goal of better understanding IET dynamics.

In the field of dye-sensitized solar cells (DSSCs) and water-splitting dye-sensitized photoelectrochemical cells (WS-DSPECs), the choice of dye is an important consideration and a principal challenge in molecular design.¹⁸ This choice is especially pertinent in WS-DSPECs, where the dye must not only efficiently inject an electron into the conduction band of a metal oxide and subsequently transfer a hole to a WOC, but must also be stable in an aqueous electrolyte under oxidative conditions.¹⁹ A common design strategy to mitigate this challenge is to change the anchoring group that binds the dye to the surface of the metal oxide.²⁰ The general view has always been that the anchoring group mediates the injection process and can be chosen to optimize IET.

In an early collaborative work, we studied the differences in electron injection from porphyrins bound axially to TiO₂ with a pyridyl linker employing differing anchoring groups. In this study carboxylate, phosphonate, acetylacetonate, hydroxamate, and boronic acid anchors were compared (see Figure 1).¹⁷ Time-resolved terahertz spectroscopy (TRTS)

measurements showed an apparent correlation between the total terahertz (THz) attenuation and the identity of the anchoring group. This phenomenon was explained theoretically by differences in the molecular conductance of the linker-anchors used. The molecular conductance of the linker-anchors was calculated using electronic structure methods and was found to track linearly with the observed maximum change in THz amplitude (*i.e.*, injection yield).

The experimental result relating THz attenuation and anchoring group fulfills the first step of identifying a phenomenon. This result led to the hypothesis that the anchoring group influences IET efficiency. We empirically scrutinized the linear correlation between the calculated conductance and change in THz amplitude, fulfilling the second step in the process of scientific inquiry. Finally, it was discovered that the molecular conductance of the anchor determines the electron injection efficiency. Therefore, a deeper understanding of the phenomenon of THz attenuation in this system was achieved through direct concerted collaborative effort between theory and experiment.

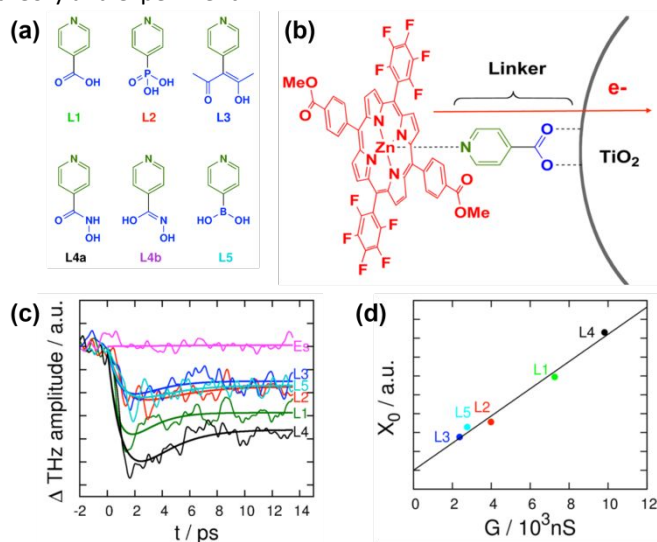


Figure 1. (a) Linker-anchors binding Zn-porphyrin to TiO_2 , (b) Proposed through-bond electron mechanism of axially-bound porphyrins. (c) TRTS measurements exhibiting differences in THz attenuation and (d) linear correlation between change in THz amplitude (X_0) and calculated conductance (G). Adapted with permission from Ref. 17. Copyright 2013 American Chemical Society

The three-phase schema for scientific inquiry is an inherently cyclical process that always leads to new questions. Therefore, we expanded our study by investigating IET in electrolyte rather than in air^{14, 17} and with the addition of a new anchoring group: the silatrane anchor.²¹ In addition, the linker and anchoring group were chemically bonded at a *meso* position rather than axially bonded as shown above.

The silatrane anchor is thought to be “insulating” like the phosphonate anchor,^{22, 23} so it should have poor electron injection efficiency based on the previously proposed mechanism. Experimentally, we found no discernable differences in IET dynamics among the four anchoring groups, and DFT calculations of the dyes showed that the orbitals responsible for electron transport were energetically

inaccessible. However, these calculations provided insight into the differences in the observed injection yields. Although the injection yield results followed a similar trend as previously reported for carboxylate, phosphonate, and hydroxamate,²⁴ the silatrane showed much higher injection yield than expected.¹⁵ Experimental injection yield results, the calculated energetically unfavorable transport orbitals, and previous work using vibrational sum-frequency generation spectroscopy²⁵ all suggested that injection likely occurs through-space rather than through-bond (see Figure 2) in electrolyte.¹⁵

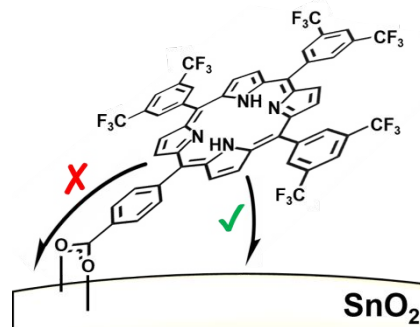


Figure 2. Proposed through-space injection mechanism for porphyrins bound to SnO_2 with the linker-anchor at the *meso* position in aqueous electrolyte.

Beginning with our previous understanding that IET was related to molecular conductance, we identified a new phenomenon pertaining to silatrane-anchor IET. This phenomenon was subjected to empirical scrutiny using DFT calculations and a new method of experimentally determining the injection yield that took into account both the relative differences in dye loading and the THz attenuation. Ultimately, we found that when the dye-sensitized metal oxide is bathed in electrolyte, the molecular conductance model was not sufficient and that IET is more likely to proceed through-space rather than through the linker-anchor (*i.e.*, through-bond). This result suggests that the anchoring group should be chosen based on chemical stability rather than perceived advantages in IET for operating porphyrin-sensitized WS-DSPECs in electrolyte.

Through a collaborative effort between experiment and theory, our understanding of IET from porphyrin sensitizers has evolved. Our collaboration resulted in a more complete picture that would be difficult to achieve with different research teams working sequentially. A prime example of the benefit of direct collaboration can be found by contrasting this work with previous all-experimental work from Brennan et al., which first suggested that the anchoring group does not affect performance in dye-sensitized solar cells.²² Although we were not the first to suggest that the anchoring group was an ineffective means of controlling performance, we were able to develop a much deeper understanding of the phenomenon in terms of molecular structure and dielectric environment (*i.e.*, electrolyte vs. air) through collaboration.

Other collaborations that have explored similar topics include the teams of Hammarström and Jacquemin on NiO -based dye-sensitized solar cells.²⁶⁻³⁰

Stepwise Collaboration

Ru Water-Oxidation Catalyst Design and Mechanism

Another important aspect of solar fuels research that we review here is the mechanistic understanding and rational design of WOCs. In the examples described below, experiment and theory collaborated largely in a stepwise fashion, with separate primarily experimental and primarily theoretical publications. We give illustrative case studies of how calculations and experiments helped to inform the development of certain ruthenium-based WOCs and strengthen the understanding of the relationship between the electronic structure of a catalyst and its mechanism.

The ruthenium-based water-oxidation catalyst $\text{Ru}(\text{bda})(\text{pic})_2$ (bda = 2,2'-bipyridine-6,6'-dicarboxylic acid, pic = 4-picoline) was reported by Sun and coworkers in 2009.³¹ At that time, the catalytic mechanism of non-aqua ruthenium WOCs was poorly understood. Seven-coordinate Ru intermediates had been proposed, but had not been experimentally or theoretically confirmed.³² From a precipitate obtained during a catalytic experiment, Sun and coworkers were able to isolate an uncommon dimeric seven-coordinate Ru(IV) complex. They verified that this complex was, in fact, active towards water oxidation, and thus could be an intermediate in the catalytic cycle. Kinetic measurements showed that catalysis was second order in Ru, which further indicated a binuclear catalytic process and served as the observation of a phenomenon.

By their very nature, catalytic intermediates in the water-oxidation process are difficult to observe using experimental methods.³³⁻³⁵ When a new catalyst is discovered, it can be nearly impossible to obtain a full mechanistic picture by experiment alone. To fulfill the step of explaining the phenomena, theory is often used to understand the electronic structure of the catalyst and to suggest a plausible catalytic cycle. In this process, theory provides complementary information to experimental results, and theoretical results are often communicated separately from experimental ones. Proposed mechanisms can then be tested against further experimental measurements or used to rationalize previous observations.

In the case of $\text{Ru}(\text{bda})(\text{pic})_2$, Privalov and coworkers proposed a binuclear mechanism involving the coupling of two formally Ru(V)=O intermediates,³⁶ based on the seven-coordinate intermediate isolated by Sun and coworkers. After a series of proton-coupled oxidation steps, they found a relatively low barrier for the formation of a peroxo intermediate and the subsequent release of O_2 . In collaboration, the Sun group measured the experimental potentials for oxidation of $\text{Ru}(\text{bda})(\text{pic})_2$ and found good agreement with the computed mechanism, providing empirical scrutiny. A deeper understanding of the catalytic pathway for the formation of O_2 was gained, which was then probed by further experimental studies.

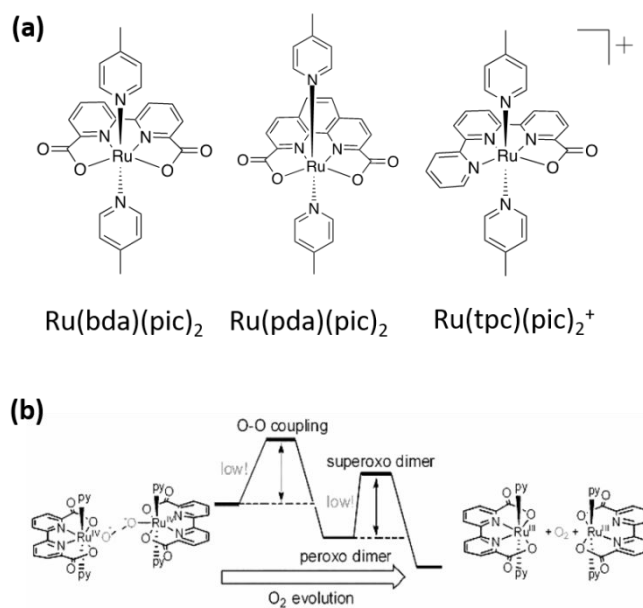


Figure 3. (a) Molecular structures of Ru complexes discussed in this tutorial. (b) The proposed bimolecular pathway for O_2 evolution by $\text{Ru}(\text{bda})(\text{pic})_2$, based on collaboration between Privalov and Sun. Adapted with permission from Ref. ³⁶. Copyright 2010 John Wiley and Sons.

Understanding Ru WOC Mechanisms: the Back-and-Forth

To further their study of ruthenium-based water oxidation, Sun and coworkers modified the catalyst's ligand backbone to understand what effects ligand identity would have on catalyst performance and mechanism.³⁷ To their surprise, when the bda backbone was replaced with the structurally similar but more rigid pda (pda = 1,10-phenanthroline-2,9-dicarboxylic acid), O_2 evolution was first-order in catalyst concentration, indicating a mononuclear, not binuclear, mechanism. Theoretical investigation proposed a water-nucleophilic attack (WNA) pathway that was consistent with electrochemical measurements and high resolution mass spectrometry studies. This observation posed the interesting question of why a minor ligand modification resulted in an entirely different catalytic mechanism.

Further computational studies by Kang and coworkers examined how ligand design could affect the barrier for binuclear (I2M) and mononuclear (WNA) mechanisms in a variety of Ru WOCs.³⁸ This work predicted that three factors, ligand sterics, net charge, and a "cis-effect" (carbene or phenyl *cis* to H^+ acceptor), could affect the relative barrier for the O-O bond formation step. These results suggested that ligand design could be used to promote one mechanism over the other. In another computational study, Ahlquist found that the activation energy of an I2M mechanism was related to the equilibrium between the monomer species and pre-reactive dimer. The barrier for formation of the dimer, they noted, would be affected by ligand sterics and net charge.³⁹

Recently, the prediction that net charge affects the catalytic pathway was examined experimentally and computationally in a concerted collaboration between Sun, Ahlquist, and coworkers.⁴⁰ By changing the ligand from the doubly anionic

bda to a singly anionic tpc (2,2':6',2''-terpyridine-6-carboxylate), it was shown that the Ru(tpc)L₂ complex catalyzed water oxidation via the mononuclear WNA pathway. DFT calculations indicated that lower formal charge and high spin density of the Ru(V)=O intermediate, both of which are affected by ligand design, were necessary for the binuclear pathway. The results of this collaboration provide valuable insight into how the ligand environment and electronic structure can affect the mechanism of water-oxidation catalysis. In this case study, initial results and mechanistic discussion occurred through stepwise collaboration and deeper understanding was obtained through concerted collaboration.

Through stepwise and concerted collaboration on the topic of Ru water-oxidation catalysts, a detailed mechanistic picture has emerged and an understanding has developed of the effects of ligand design on the mechanism of ruthenium-based water oxidation. Stepwise collaboration, as shown in the examples described above, has advantages in the field of water oxidation. The primary advantages are that it allows for more rapid publication on topics of interest and allows one to see how the work is received by the scientific community. In addition, separate experimental and theoretical publications provide the opportunity for more detailed study of a catalyst, whereas in a joint experimental-theoretical publication, some results may be excluded or de-emphasized for the sake of length and coherency of the narrative. While theoretical calculations could certainly provide deeper insight into many experimental results, the decision to pursue a concerted or stepwise collaboration may be based on factors such as whether such a collaboration has previously been established, urgency of results, and the desired type of publication (*e.g.*, communication or full paper). Stepwise collaboration may also lead to formal concerted collaborations, which may allow for more in-depth study of a phenomenon after initial experimental and/or computational results are published.

Other collaborations that have explored similar topics include Meyer, Baik, and Yang on the Ru "blue dimer",^{41, 42} Nocera and Lai on cobalt "hangman corroles",^{43, 44} and Llobet, Sala, and Batista on other single-site Ru WOCs.^{45, 46}

Tips for Successful Collaborative Science

Build a Framework

We began this tutorial by taking cues from work in the philosophy of science. When reflecting on collaborative science or planning future collaborations, a collaborative framework should be developed. This framework can be constructed by considering the aspects outlined above:¹⁰ will the collaboration take place between members of a single research team or between different research teams; what is the expected timeframe; does the research project require an interdisciplinary approach; what standards for first, co-first, secondary, and corresponding authorship will be used?

These aspects are by no means exhaustive. Other models for "team science" have been proposed,⁴⁷ and different types of collaborations may necessitate alternative frameworks. For

example, high levels of inter- or trans-disciplinarity have been shown to present significant challenges to scientific collaboration.⁴⁷ Therefore, collaborators may need to structure their framework in ways that will help surmount these challenges (for instance, preparing a longer timeframe). Nevertheless, a common framework among collaborators will benefit all parties.

One additional advantage of a collaborative framework is that investigators are able to assess their past collaborations and build on examples of past successes, as well as avoid potential missteps. In this tutorial, the examples of collaborations in solar fuels research were selected because they are believed to be particularly instructive, especially regarding collaborations between theory and experiment in solar fuels research. However, investigators should consider whether their own collaborations follow a different paradigm.

Communicate in Concrete Terms

The social character of science today makes communication a critical skill for researchers. In the context of collaboration, the situation is no less demanding. Collaborators working across disciplines should aid their colleagues in becoming familiar with the terms and tools of their respective trades. We recommend setting aside time at the beginning of the collaboration to define terms and establish essential background.

At the outset, collaborators should communicate in terms of concrete deliverables. Team members should have a clear idea of what they are expected to produce. Clarity can be ensured by setting unambiguous goals and timelines. This will give team members a better understanding of the role they should expect to play in the collaboration as a whole. In addition, by agreeing on clear goals and timelines ahead of time, collaborators will also steer clear of easily avoidable roadblocks. For instance, collaborators will have different levels of familiarity with any given experimental or theoretical method and the corresponding bottleneck processes or technical limitations. Therefore, every party involved should be open about these limitations, thoroughly explain their techniques in presentations, and be encouraged to ask about them.

A clearly delineated collaborative framework can also positively impact the sensitive subject of standards for authorship. In general, early agreement among collaborators about standards for authorship can help allay many anxieties that often later arise in the collaborative process. We strive to set standards for authorship that strike a balance between stability and flexibility: stable, so that once collaborators agree on standards for authorship, the "rules of the game" are not perceived to have changed unfairly later on, but flexible enough so unforeseeable developments over the course of the research project (*e.g.*, different journal requirements on authorship, additional collaborators joining projects already in progress) do not negatively impact collaborative relationships.

At the Energy Sciences Institute at Yale, lead authorship, for example, is commonly based on who initiates and leads the collaboration, whether experimentalist or theoretician. On the other hand, if the experimentalist and theoretician agree at the outset on shared intellectual responsibilities, or if over the

course of a project a consensus is reached among all collaborators that standards for lead authorship have been met by more than one party, then co-first authorship is assigned.

Finally, the frequency of communication tends to vary over the course of collaboration. Too often, the frequency of communication is high in the early stages, drops sharply in the middle, and races up again in the later stages, as deadlines loom or collaborators prepare manuscripts for submission (Figure 4, purple solid line). In our experience, this pattern leads to inefficient usage of time and lost productivity. In contrast, our research team communicates regularly throughout all stages of collaboration (Figure 4, green dashed line), which we think is key to a successful and efficient collaboration. Establishing expectations for communication at the earliest stages avoids communication drop-off that is often experienced during collaborations.

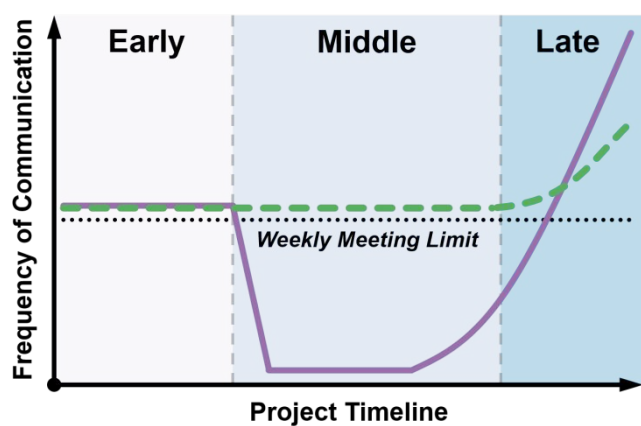


Figure 4. Frequency of communication over the course of collaboration, showing the recommendation (green dashed line) versus a possible reality (purple solid line). A weekly meeting is the suggested minimum for communication between collaborators.

Know the Limits

Collaborators should also be aware of the limitations when navigating between experimental and theoretical studies. For instance, collaborators should be mindful that the pace of research progress may be very different for theoreticians and experimentalists. Running computations on a chemical library might be accomplished in a few days or weeks; synthesizing a chemical library might require several weeks or months of work.

At least two more considerations are critical for facilitating the crossover. First, experimentalists and theoreticians should work closely together to design experiments and calculations in tandem such that they are closely comparable. For example, an experimentalist might use a redox couple that is theoretically convenient to compute, because of cancellation of systematic error.⁴⁸ For coordination complexes, this may require choosing a reference compound with the same metal and similar ligand framework to the compound of interest.

Second, for long-term investigations resulting in multiple publications, comprehensive supplementary information is essential as it is needed to reproduce the study and as a comparison for new results. Thus, every effort should be made

to make the supplementary information to research articles as complete as possible.⁴⁹

Conclusion and Outlook

Two types of collaborations have been identified: a concerted effort wherein the theoretical and experimental groups work together on the same project, and stepwise wherein the groups publish findings in response to each other. Our work on IET falls into the former category and work on Ru WOCs falls into the latter category. We recalled how these collaborations were successful and offered advice for successful collaborations going forward.

There appear to be new methods for collaboration between theorists and experimentalists just on the horizon. These methods reimagine the roles that traditionally saw experimentalists as the initiators of collaborations. Like synthetic chemists, theorists can now steer the design of molecules, which can save time, effort, and money. For example, machine learning has assisted in the interpretation of spectra⁵⁰ as well as in the design of new molecules.⁵¹ Another is the use of gradient-based methods in chemical space, which our groups have used for the inverse design of dyes for solar cells.⁵²

For those interested in learning more about tackling the challenges of collaboration, a useful resource is the National Academy of Science's "Enhancing the Effectiveness of Team Science."⁴⁷

Conflicts of interest

There are no conflicts to declare.

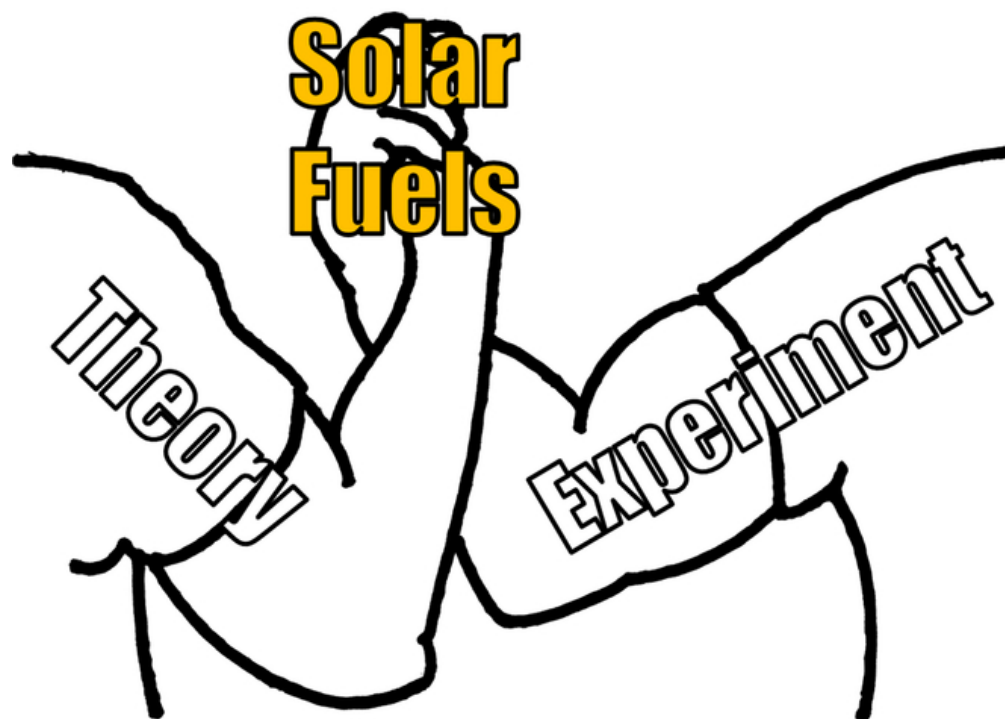
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