Published in final edited form as:

J Chem Phys. 2016 September 14; 145(10): 104310. doi:10.1063/1.4962254.

Computational Characterization of Competing Energy and Electron Transfer States in Bimetallic Donor-Acceptor Systems for Photocatalytic Conversion

Lisa A. Fredin^{a,*} and Petter Persson^b

^aChemical Informatics Research Group, Chemical Sciences Division, Material Measurement Laboratory, National Institute of Standards and Technology, 100 Bureau Drive, Mailstop 8320, Gaithersburg, MD

^bChemistry Department, Theoretical Chemistry Division, Lund University, Box 124, SE-22100 Lund, Sweden

Abstract

The rapidly growing interest in photocatalytic systems for direct solar fuel production, such as hydrogen generation from water splitting is grounded in the unique opportunity to achieve charge separation in molecular systems provided by electron transfer processes. In general, both photoinduced and catalytic processes involve complicated dynamics that depend on both structural and electronic effects. Here the excited state landscape of metal centered light harvester-catalyst pairs is explored using density functional theory (DFT) calculations. In weakly bound systems, the interplay between structural and electronic factors involved can be constructed from the various mononuclear relaxed excited states. For this study, supramolecular states of electron transfer and excitation energy transfer character have been constructed from constituent full optimizations of multiple charge/spin states for a set of three Ru-based light harvesters and nine transition metal catalysts (based on Ru, Rh, Re, Pd, and Co) in terms of energy, structure, and electronic properties. The complete set of combined charge-spin states for each donor-acceptor system provides information about the competition of excited state energy transfer states with the catalytically active electron transfer states, enabling the identification of the most promising candidates for photocatalytic applications from this perspective.

Keywords

quantum chemistry; density functional theory; donor-acceptor; excited state evolution; supramolecular systems; photochemistry; charge separation; electron transfer; excited state energy transfer

*Corresponding Author: lisa.fredin@nist.gov.

Supporting Information. Additional computational details including the spin densities, electronic structure diagrams, and the complete list of TD-DFT calculated transitions.

Introduction

There is rapidly growing interest in photocatalytic systems for direct solar fuel production, such as carbon dioxide reduction and oxygen and hydrogen generation from water splitting.^{1–5} Model systems have been formed by linking regions to perform each desired function, for example a Ru(II) light harvesting core linked to a catalytic center (e.g. Co(III)). Covalently linked bimetallic complexes have been used extensively to experimentally investigate electron transfer properties of donor (D)-acceptor (A) systems^{6–7} including studies of bridged Ru(II)-Co(III) systems^{8–10} as well as theoretical intermolecular electron transfer studies.^{11–12} The complicated excited state dynamics which depend on both structural and electronic effects are frequently further complicated by solvent interactions and/or coupling between the electronic and nuclear processes, making these processes difficult to study.^{13–14} However, advances in time-resolved optical spectroscopy down to femtosecond time-scales relevant for many photoinduced electron transfer processes^{4, 15} combined with theoretical calculations of key electronic factors, e.g. electronic coupling strengths, have provided significant insight into important processes such as long-range electron transfer in supramolecular and heterogeneous donor-bridge-acceptor systems.^{4, 16–26} In addition, recent advances in time-resolved X-ray spectroscopy give the first experimental handle to probe the photoinduced structural evolution of transition metal complexes.^{27–29}

The thermodynamics and kinetics of electron transfer, energy transfer, charge recombination, and other dynamical processes determine the observed states of a dyad system. Combined with the catalytic activity and stability of the catalyst center, this competition determines the overall usefulness of photoinduced catalysis. In an ideal bimetallic catalysis system, the initial excitation of the light harvester results in electron transfer and then the catalyst is in its catalytically active form ($^2A^-$, as all the catalysts are defined here) to promote formation of products. Competing with this desired path is relaxation to lower energy donor excited states (D^*_{thermal} and triplet metal-to-ligand charge transfer or 3MLCT_D , and metal centered or 3MCD), excited state energy transfer to form excited acceptors ($A^*, ^3A$), or electron transfer to catalytically inactive states ($^4A^-$). In addition, intersystem crossings (ISCs) between these states compete with the recombination between the two centers to reform the initial ground state. Many of these dynamical processes are being investigated using both time-resolved techniques and theory.^{4, 16–30} For photoelectrochemical applications such as the catalysis in solar fuel applications one can expect that slower catalytic kinetics rather than the ultrafast initial kinetics is rate determining in most cases so that ascertaining the systems which display suitable thermodynamic stability of the final catalytically active state is critical.

Quantum chemistry, in particular with density functional theory (DFT) and time-dependent DFT (TD-DFT), has made accurate calculations of ground and excited state properties of a wide range of large molecular systems, including transition metal complexes, possible.^{31–35} Specifically, quantum chemical calculations of the electron transfer (ET) and excitation energy transfer (EET) potential energy surfaces beyond the initially excited Franck-Condon region provided a more comprehensive theoretical understanding of the possible structural evolution accompanying photoinduced electronic processes for prototype light-harvesting

transition metal complexes.^{36–41} Many model photoactive D-A dyad systems comprised of one light harvesting Ru-complex^{37–38, 42–44} coupled to a model Co-center^{45–50} have been investigated. Donor-acceptor interactions have been widely studied and range from very weak to very strong, as nicely illustrated in the series of unbound (Ru|Co), weakly bound (Ru–Co), and tightly bound (Ru=Co) supramolecular Ru(II)-Co(III) systems studied by us and others.^{10, 12} ET kinetics of many (D|A) unbound systems consisting of two transition metal centers in solution have also been extensively studied as a classic example of Marcus⁵¹ type ET. In linked D-A systems, the chemical nature of the linker group is of key importance, and there have been numerous investigations of D-A interactions with different linker groups from early work by Newton and others.¹⁴ In tightly bound systems, there can be strong mixing effects like those captured in both the experiment and calculations of Ru=Co⁵² and in other related types of D-A systems such as strong interfacial interaction in some dye-sensitized titania systems.^{21, 53–54} We recently employed DFT to show that efficient light absorption of visible light by the Ru-chromophore provides the necessary energy to drive a cascade of excited state processes that include photoinduced electron transfer from Ru(II) to Co(III) to form a charge separated Ru(III)–Co(II) state.¹²

For weak D-A interactions involving e.g. saturated hydrocarbon linker groups used as molecular bridges in the common donor-bridge-acceptor (D-B-A) fashion,⁵⁵ modeling the donor and acceptor units as decoupled is generally applicable and a very good model to a first approximation, since the weakly bound interaction can be captured as a weak perturbation of the independent D and A states where the D-A interaction strength decays exponentially with D-A separation. This was also clearly seen in our recent study where a non-interacting unbound system (Ru|Co), where each center was relaxed separately, was able to reproduce the excited state landscape of the combined weakly bound (Ru–Co)¹⁰ complex.¹² Thus, in weakly bound systems, a first order approximation of the interplay between structural and electronic factors involved can be constructed from the various mononuclear relaxed excited states. Here we construct these states for a wide set of metal centered catalysts that display different local coordination but have a similar degree of reorganization around the metal center.

These extensive sets of calculations provide critical insight into the competition between EET and ET in the complicated excited state evolution in these systems. Here we investigate the driving force for photoinduced processes in bimetallic dyads by constructing supramolecular states of excitation and charge transfer character in terms of energy, structure, and electronic properties. This study focuses on spin unrestricted optimizations of the ground state and excited states of three common Ru(II) light harvester donors (Chart 1) and nine experimental Ru, Rh, Re, Pd, or Co centered catalyst acceptors (Chart 2) using the well benchmarked PBE0 hybrid functional and a triple- ζ basis set, 6-31G(d,p), for the light atoms, N, H, O, Cl, and Br, and the Stuttgart/Dresden, SDD(ECP), for the metals, Ru, Rh, Re, Pd, and Co, with an acetonitrile complete polarizable media solvent (PCM).

Results

Here we have chosen three well studied Ru(II)-light harvesters (naming and Chemdraw structures also in Table S1), [Ru(bpy)₂(dimethyl-bpy)]²⁺ where bpy=2,2'-bipyridine called

BPY,⁵⁶ cis-bis(isothiocyanato)bis(2,2'-bipyridyl-4,4'-dicarboxylato) ruthenium(II) called **N3**,⁵⁷ and $[\text{Ru}(\text{dqp})_2]^{2+}$ where dqp =2,6-bis(8-quinolynyl)-pyridine called **DQP**^{41–43} (Chart 1). Each of these is well tested experimentally and known to produce relatively long-lived excited states with enough energy to be transferred to other metal centers or the conduction band of TiO_2 . In addition, nine experimentally studied catalysts (Chart 2) with a variety of metal centers, catalyzed reactions, reaction rates, mechanisms, and spectral coverage were chosen (naming and ChemDraw structures also in Table S1). These include catalysts of carbon dioxide reduction: $\text{trans}(\text{Cl})\text{-Ru}(\text{bpy})(\text{CO})_2\text{Cl}_2$ or **Ru**⁵⁸ and $\text{Re}(4,4'\text{-dimethyl-bpy})(\text{CO})_3\text{Br}$ or **Re**.⁵⁹ Catalysts used for hydrogen production or proton reduction catalysts: a cobalt–salen complex, 6,6'-((1E,1'E)-(ethane-1,2-diylbis(azanylylidene))bis(methanylylidene))bis-(2,4-ditert-butylphenol)cobalt(III) or **Co1**⁶⁰ and $[\text{Co}^{\text{III}}(\text{Cp}^*)(\text{bpy})(\text{OH})]^{2+}$ where $\text{Cp}^* = \eta^5\text{-pentamethylcyclopentadienyl}$ or **Co2**.⁶¹ Catalysts used for oxygen production: $[\text{Rh}^{\text{III}}(\text{dmbpy})_2\text{Cl}_2]^+$ where $\text{dmbpy} = 4,4'\text{-dimethyl-2,2'-bipyridine}$ or **Rh**,⁶² $(2,5\text{-dpp})\text{PdCl}_2$ with 2,5-di(pyridine-2-yl)pyrazine or **Pd1**,⁶³ $(2,6\text{-dpp})\text{PdCl}_2$ with 2,6-di(pyridine-2-yl)pyrazine or **Pd2**,⁶⁴ $[\text{Co}^{\text{III}}(\text{CR})\text{Cl}_2]^+$ where $\text{CR} = 2,12\text{-dimethyl-3,7,11,17-tetra-azabicyclo}(11.3.1)\text{-heptadeca-1(17),2,11,13,15-pentaene}$ or **Co3**,⁶⁵ and 5-[4-(5-carboxyl-2,7-di-tert-butyl-9,9-dimethylxanthene)]-10,15,20-tris(pentafluorophenyl)porphyrinatocobalt(I) or **Co4**.⁶⁶

As expected, the Ru donors have metal-to-ligand charge transfer (MLCT) absorption bands in the 350–700 nm range and a ligand $\pi\text{-}\pi^*$ band ~300 nm (Figure 1) and the catalysts (Figure 1b) have more broadly spread absorption, most having absorption in the 200–400 nm range. The absorption spectra of most of the catalysts are such that the Ru-MLCT band of each complex could be individually excited. However, exciting the MLCT of each light harvester would mostly likely also result in some excited state population for **Re**, **Co1**, and **Co4**, which have broad absorption at wavelengths longer than 380 nm, possibly leading to different pathways in the excited state dynamics.

For each light harvesting donor the fully symmetry unrestricted relaxed ground state (singlet), and excited state triplets, MLCT and metal centered (MC), as well as the doublet and quartet oxidized forms have been optimized (Figure S1). Each metal centered catalyst has been fully relaxed to its singlet and triplet, as well as reduced doublet and quartet states (Figure S2). The optimizations are symmetry unrestricted to account for Jahn-Teller effects and allow the geometric changes to be mapped with the electronic changes across various symmetries. In order to investigate the manifold of low-energy excited states relevant following photoexcitation theoretically, a set of the 6 most common photoinduced charge/spin electron or energy transfer states were constructed for each dye-catalyst combination. The charge/spin state of each site and the overall spin state are indicated by the notation $m^3[m^1\text{D}(\text{Q1})|m^2\text{A}(\text{Q2})]$ where m_1 , m_2 , and m_3 are the multiplicity of the Ru light harvester or D, the metal catalyst center or A, and the overall complex, respectively, and Q1 and Q2 are the charge on the D and A sites, respectively. These charge/spin states are shown in a Jablonski like diagram (exemplified in Figure 2 for **[BPY|Co3]**) where the horizontal lines represent the sum of the calculated energies of the two states. For example, a system singlet can be constructed from the light harvester (**BPY**) ground state (GS) singlet and the catalyst (**Co3**) ground state both having energy of zero giving a total energy of zero, or from

the TDDFT calculated excited state singlet of the **BPY** and the ground state of **Co3** with an energy of 2.77 eV. Ru light-harvesting complexes form two possible triplets: metal-to-ligand charge transfer, either the initial ISC triplet at the GS geometry ($^3\text{Ru(II)}/^1\text{Ru(II)}$) and the $^3\text{MLCT}$ minimum ($^3\text{MLCTRu(II)}$), and the ^3MC ($^3\text{MCRu(II)}$) combined with the GS of the catalyst give an overall bimetallic triplet. Other types of triplets and quintets can be formed through excited state energy transfer (EET, red) or electron transfer (ET, orange or green, which is catalytically active). EET results in a triplet on the catalyst ($^3\text{Co(II)}$ for **Co3**) whereas ET results in a reduced cobalt (Co(I) for **Co3**) either a quartet or doublet. Combinations result in two triplets, formed by a singlet-triplet and doublet-doublet, and two quintets, formed by combinations of a quartet and a doublet. The doublet-doublet triplet and one of the quintets contain the low energy ($^2\text{Co(I)}$) catalytically active form. The active quintet is often very high in energy due to the high energy $^4\text{Ru(III)}$. These constructed states are approximate states of a weakly bound system. The reorganization around the metal centers used here are at most 0.7 Å which is the same order of magnitude for the model Ru–Co systems where the unbound states reproduced the weakly bound system.¹² The unbound constructions also allow multiple states of the same spin to be characterized, permitting both the ET and EET triplet of each system to be determined.

To demonstrate the competing electron or energy transfer pathways for each catalyst we begin by constructing bimetallic dimers with each of the catalyst acceptors and a single donor, *e.g.* the BPY benchmark light-harvesting complex (Figure 3 and S3). In Ru light harvesting complexes, the initial singlet excitation is quickly converted in fs timescales to a $^3\text{MLCT}$ state. The lifetime of this $^3\text{MLCT}$ determines the timescale for subsequent charge or energy transfers. The format of Figure 3 highlights the systems with driving force to form either ET or EET states below the $^3\text{MLCTRu(II)}$ grey line. BPY has enough excited state energy to form the EET state for the **[BPY|Rh]**, **[BPY|Re]**, **[BPY|Pd1]**, and **[BPY|Co4]** systems and also the ET state for the **[BPY|Pd2]**, **[BPY|Co1]**, **[BPY|Co2]**, and **[BPY|Co3]** systems. In order to preform catalysis with the second metal center, the catalytically active state needs to not be deactivated into a lower energy excited state or through back electron transfer to reform the initial complex. Thus systems where that the electron transfer state is the most thermodynamically stable state are preferable, like **[BPY|Co1]**.

In addition to **BPY** two other dyes that are often used as benchmark systems have been investigated: **N3** and **DQP**. The **N3** dye is one of the best performing Ru dyes for dye-sensitized solar cells since its energy alignment allows for fast efficient transfer of electrons from both the excited state singlet and triplet into the conduction band of TiO_2 .^{67–68} However, **N3** has a similar $^3\text{MLCT}/^3\text{MC}$ balance as **BPY** (Figure 4) so the largest effect on the constructed systems is the difference in energies of the oxidized states of **N3** and **BPY**, supported by the measured oxidation potential of **N3**.⁵⁷

In Figure 4 we compare the linear and bent ligand Pd catalysts (**Pd1** and **Pd2** respectively). In the linear case **[N3|Pd1]**, both the initially excited state donor singlet and the triplet MC state have enough driving force to form the catalytically active charge separated state $^1/3[{}^2\text{Ru(III)}|^2\text{Pd(I)}]$, however the EET state is the most stable. The linear ligand (**Pd1**) doublet has a delocalized spin across the whole ligand like the $^3\text{Pd(II)}$ state (Figure S2) and fairly small geometric changes between the reduced doublet and the excited state triplet

indicating possible interconversion pathways between the doublet and triplet. Therefore, even if the doublet is initially formed, the lowest energy EET catalytically inactive $^3\text{Pd(II)}$ state is the most likely thermodynamic product. However, for the bent ligand **[N3|Pd2]**, the ET state $1/3[{}^2\text{Ru(III)}|{}^2\text{Pd(I)}]$ is the most thermodynamically stable state and can be formed from any of the donor excited states. The bent ligand (**Pd2**) promotes a $^2\text{Pd(I)}$ metal and monodentate ligand centered state where there are larger geometric changes from the ground state, possibly geometrically isolating the catalyst in this minimum (Figure S2). Thus even though the EET also has some driving force for formation in the bent system, from either the hot vertical singlet and triplet donor excitations or from the triplet MC state, the most likely product of photoexcitation is the thermodynamically stable ET catalytically active form, making this system a good candidate for photoinduced catalysis. These differences in electronic and geometric structure explain the experimental observation that no hydrogen was generated by a **[BPY|Pd1]** like complex,⁶³ whereas a Ru center associated with **Pd2** has electron transfer to the Pd in ~ 150 ps (and recombination ~ 120 ps).⁶⁴

DQP has an impressive microsecond excited state lifetime and shows particular promise for dyad formation, due to its structural propensity to form linear arrays.^{42–43} Its extremely octahedral coordination geometry leads to larger ligand field splitting destabilizing the ^3MC with respect to the $^3\text{MLCT}$, and increasing the $^3\text{MLCT}$ lifetime into the microsecond regime. However, the calculated $^3\text{MLCT}$ energy of **DQP** is similar to **BPY** and **N3** so the constructed states have similar driving forces for either ET or EET. Figure 5 shows two alternative cases for **DQP** systems. Systems like **[DQP|Rh]** can form the ET active system only by electron transfer from the higher energy unrelaxed excited states like $^1\text{Ru(II)}^*$. As we have observed previously,¹² the doublets of each complex undergo more geometric change from the ground state than the excited state triplet MLCTs, indicating that this ET state might be observable in experiments even though there are lower energy triplets.¹² By utilizing symmetry unrestricted optimizations, these calculations allow each of the spin states to adopt whatever geometry stabilizes the spin best. Thus for systems of particular interest, more extensive geometry vs. energy excited state landscape searches can be used to explore the potential energy surfaces and compliment experimental X-ray and optical studies of photoinduced pathways in donor-acceptor systems. Systems like **[DQP|Co2]** (Figure 5) which have multiple states that are very similar in energy; two stable ET states $1/3[{}^2\text{Ru(III)}|{}^2\text{Co(II)}]$ and $3/5[{}^2\text{Ru(III)}|{}^4\text{Co(II)}]$ at $\sim 1\text{eV}$ and a lower energy EET state; are particularly interesting candidates for further investigation. Which state will be the final observed state would have to be explored through further geometric-electronic structure construction of potential energy surfaces to map the competing energy and electron transfer surfaces and their crossings helping to identify suitable systems for emerging possibilities to perform more computationally expensive dynamic simulations of excited state processes.⁶⁹

Finally, to understand the effect of different donors Figure 6 shows the four excited Ru states expected to contribute to charge separation or energy transfer (the vertical $^1\text{Ru(II)}^*$ and $^3\text{Ru(II)}/^1\text{Ru(II)}$, and the relaxed $^3\text{MLCTRu(II)}$ and $^3\text{MCRu(II)}$), as well as three charge separation states (formed from combinations of ^2D , ^4D , ^2A , ^4A) and the EET state of **Pd2** with each dye. Because **BPY** has enough driving force from any of its excited states ($^1\text{Ru(II)}^*$, $^3\text{Ru(II)}/^1\text{Ru(II)}$, $^3\text{MLCTRu(II)}$, or $^3\text{MCRu(II)}$) to form the ET and EET states in this

system, **DQP**, which has slightly lower energies for each of these states, just leads to more energy lost during ET or EET. The largest difference in the donors is the balance of the charge separated ET vs. the EET that is shifted in **N3** due to its unique oxidation potential.

Discussion

Here we examined the competing energy and electron transfer states from dyads formed from nine experimental carbon dioxide reduction or oxygen or hydrogen production catalysts and three well-studied Ru(II) light harvesters. Stable low energy excited state energy transfer states, like those seen in Ru(II)-Co(III) model systems,¹² form the majority of the thermodynamically stable states for these systems. In addition, for many of the systems most of the excited state energy is lost during energy or electron transfer, with < 0.5 eV remaining from the about 2 eV excitation. Finally, a couple of promising catalytic systems can be identified where photoexcitation is expected to result in thermodynamically stable charge transfer to bring about a catalytically active acceptor, e.g. [D|Pd2] and to some extent [D|Co1] systems for oxygen or hydrogen production, respectively.

In addition to providing a broad basis for comparative analysis and screening, these calculations highlight some particularly important aspects for the investigated type of photocatalytic donor-acceptor systems. Firstly, the calculations show that optimizing both the donor and acceptor sites separately allows for the formation of several combined D-A states of sufficiently low energy to be accessible following the initial donor photoexcitation, and they can be characterized and compared theoretically even if not all such combined states are easily accessible experimentally. The separate optimizations provide evidence for a competition between the formation of low-energy electron and excitation energy transfer states. The presence of EET as the final (lowest energy) activated state might at first sight appear surprising considering that most of the catalytically active acceptor sites only absorb light at significantly higher energies compared to the light-harvesting donor sites (Figure 1). The calculations, however, show the importance of structural relaxations to form relaxed excited acceptor states (i.e. D-A*) with easily accessible low energies (Figures 2–5), similar to *e.g.* light-induced excited state spin trapping (LIESST) states for several mononuclear transition metal complexes with weak to moderate ligand field strengths (*e.g.* [D|Pd1]). Given the lack of acceptor absorption, the competitive formation of such EET states over the formation of the desired ET states that form the catalytically active reduced acceptor site might therefore be easily overlooked without the presented computational characterization of the full set of combined D-A states. While many of potential photosensitizer-catalyst combinations are likely to display interesting and complicated early photoinduced dynamics involving a range of excited D*, ET, and EET states, the rate determining catalytic kinetics dictate that whether the thermodynamic product is catalytically active is critical. Thus, quantum chemistry can be used to identify the few cases that are potentially interesting for real photocatalytic applications. Once promising donor-acceptor pairs have been identified optimizations of bound supramolecular systems could be used to investigate the interactions between units.

Secondly, the calculations demonstrate the importance of combining suitable donor and acceptor properties to form photocatalytic D-A complexes that promote the photo-induced

formation of the desired catalytically active state in a non-trivial manner. In particular, photocatalysis has more competing pathways compared to using the catalytic acceptor parts by themselves in an electrocatalytic fashion that only involves electrochemical reduction of the acceptor but no electronic excitations. On one hand, the energy balance between the different reduced acceptor states is effectively governed by the formation of a catalytically active ET state alone (similar to electrocatalysis). However, the desired energy and spin state for the investigated D-A systems using typical ruthenium dyes, such as the ones investigated here, have a clear energetic preference for a low-spin oxidized final state due to the energetics of the dye. This could, however, conceivably be modified for D-A systems featuring more complicated donor photophysics with alternative low-energy spin states for the oxidized donor. On the other hand, these calculations show that the important balance between ET and EET that governs which will be the lowest energy activated D-A state can be influenced not only by the choice of acceptor (*e.g.* [N3|Pd1] vs. [N3|Pd2]), but also by the choice of a suitable donor complex as the total energy balance between the ET ($E_{\text{ET}}(\text{D}^+-\text{A}^-) = E_{\text{red}}^{\text{A}} - E_{\text{ox}}^{\text{D}}$) and EET ($E_{\text{EET}}(\text{D-A}^*) = E_{\text{ex}}^{\text{A}}$) states in the D-A system is influenced also by the tuning of the ground state oxidation potential of the donor as can be seen in the comparison between the BPY and N3 systems (*e.g.* [BPY|Pd2] vs. [N3|Pd2]).

Conclusion

Bound photoinduced catalytic complexes are expensive to make and study experimentally. However, weakly bound, donor-acceptor systems of Ru-light harvesters and experimentally studied catalysts can be constructed from the fully relaxed excited states of the individual sites, saving computational cost and allowing systems to be considered in a mix-and-match fashion. Here we presented the thermodynamics of the competing electron and energy transfer states that might result from initial photoexcitation of a donor. We are able to characterize all of the possible energy and electron transfer states in weakly interacting photosensitizer-catalyst dimer systems by optimizing the donor and acceptor separately. This provides identification of the most interesting combinations of photosensitizers and catalysts in a computationally efficient way, and thus also provides guidance to single out the D-A combinations where it will be interesting to proceed in future work with more elaborate computational investigations of explicitly bound supramolecular potential energy surfaces and the dynamics after the initial excited state to provide a more detailed picture of the excited state decay pathways.

Three key factors to which state, energy or electron transfer, wins out in a system emerge. First, metal centers that have low energy high spin forms like Co provide many low energy competing states, including excited state energy transfer (with low energy triplets) and thermodynamically stable high spin (quartet) electron transfer states, which are useful for applications like luminescent solar concentrators.⁷⁰ Other metals, like Pd studied here, might be more conducive to forming the catalytically active state through electron transfer. Second, ideal light harvesters would have maximum spectral coverage (N3), structural aspects like readily forming vectoral arrays (DQP), and driving force to preform energy or electron transfer. While current Ru(II) harvesters have some of these characteristics, the methods used to extend lifetimes of tridentate complexes have often decreased the ³MLCT excited state energy, reducing the driving force for charge separation via electron transfer. This can

be seen in the limited number of dyads whose ET (green) state is below the $^3\text{MLCT}$ excited state energies (in Figure 1), making some of the most common light-harvesters less than ideal. And lastly, acceptors that have less spectral coverage below 350 nm provide the opportunity to selectively excite the light harvesting site, directing the initial excited state evolution toward photoinduced processes.

This method of constructing donor-acceptor systems allows theoretical chemists to characterize the balance of electron and energy transfer states of photoexcited donor-acceptor pairs, pin-pointing promising pairs for photoinduced electron and energy transfer in weakly bound systems. Analyzing the possible dyads formed from these known catalysts, the $[\text{D}|\text{Pd}2]$ and $[\text{D}|\text{Co}1]$ systems are good candidates for photoinduced oxygen or hydrogen production as the most thermodynamically stable form is the designed charge separated catalytically active form.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

We acknowledge our funding support as well as supercomputing facilities support from the NSC, LUNARC, and NIST-Raritan.

Funding Sources

This work was supported by the Crafoord Foundation, the Swedish Research Council, the Swedish Energy Agency (Energimyndigheten), and the Knut and Alice Wallenberg Foundation. LAF acknowledges funding from the NIST-NRC fellowship program.

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Figure 1.
Calculated absorption spectra of the 3 Ru(II) light harvesters (A) and all nine catalysts (B)
PBE0/6-31G(d,p)[N,H,O,Cl,Br]SDD(ECP)[Ru]/PCM(MeCN) FWHM=0.3.

Figure 2.

The singlet (S_0), triplet (T_1), and quintet (Q_1) **[BPY|Co3]** constructed bimetallic states, where the electron transfer states (ET) that form catalytically active catalysts are green, other ET states are orange, and excited energy transfer (EET) states are red. The energy of each state is the sum of the calculated energies of each individual state. PBE0/6-31G(d,p) [N,H,O,Cl,Br] SDD(ECP)[Ru,Rh,Re,Pd,Co]/PCM(MeCN); $m^3[m^1D(Q_1)|m^2A(Q_2)]$ where m_1 , m_2 , and m_3 are the multiplicity of the Ru light harvester, the metal catalyst center, and the overall complex, respectively, and Q_1 and Q_2 are the charge on the D and A sites, respectively.

Figure 3.

[BPY|A] constructed bimetallic states of the form $m^3[m^1D(Q1)|m^2A(Q2)]$ below 2.73 eV $^3MLCT_{Ru(II)}$ injection energy (all states in Figure S3), where the electron transfer states (ET) that form catalytically active catalysts are green, other ET states are orange, and excited energy transfer (EET) states are red, PBE0/6-31G(d,p)[N,H,O,Cl,Br]SDD(ECP) [Ru,Rh,Re,Pd,Co]/PCM(MeCN).

Figure 4.

The singlet (S₀), triplet (T₁), and quintet (Q₁) [N3|A] constructed bimetallic states of the form $m^3[m^1D(Q_1)|m^2A(Q_2)]$ for the 2 Pd catalysts, where the electron transfer states (ET) that form catalytically active catalysts are green, other ET states are orange, and excited energy transfer (EET) states are red, PBE0/6-31G(d,p)[N,H,O,Cl,Br]SDD(ECP) [Ru,Rh,Re,Pd,Co]/PCM(MeCN).

Figure 5.

The singlet (S₀), triplet (T₁), and quintet (Q₁) [DQP|A] constructed bimetallic states of the form $m^3[m^1D(Q_1)m^2A(Q_2)]$ for 2 representative catalysts, where the electron transfer states (ET) that form catalytically active catalysts are green, other ET states are orange, and excited energy transfer (EET) states are red, PBE0/6-31G(d,p)[N,H,O,Cl,Br]SDD(ECP) [Ru,Rh,Re,Pd, Co]/PCM(MeCN).

Figure 6.

The singlet (S_0), triplet (T_1), and quintet (Q_1) [D|Pd₂] constructed bimetallic states of the form $m^3[m^1D(Q_1)]m^2A(Q_2)$, where the electron transfer states (ET) that form catalytically active catalysts are green, other ET states are orange, and excited energy transfer (EET) states are red, PBE0/6-31G(d,p)[N,H,O,Cl,Br]SDD(ECP)[Ru,Rh,Re,Pd,Co]/PCM(MeCN).

Chart 1.

Optimized singlet structures of the 3 Ru-light harvesters where Ru is turquoise, N is dark blue, O is red, S is yellow, C is grey, and H is white (naming also in Table S1).

Chart 2.

Optimized singlet ground state structures of the 10 catalytic centers where Ru is turquoise, Rh is dark green, Re is dark blue, Pd is orange, and Co is bright blue, Br is pink, Cl is green, F is light blue, N is dark blue, O is red, S is yellow, C is grey, and H is white (naming also in Table S1).