

McCamant Lab

Foundational Papers

Powering the planet: Chemical challenges in solar energy utilization

Nathan S. Lewis^{*†} and Daniel G. Nocera^{†‡}

^{}Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, CA 91125; and*

[‡]Department of Chemistry, Massachusetts Institute of Technology, Cambridge, MA 02139-4307

Edited by Edward I. Solomon, Stanford University, Stanford, CA, and approved August 11, 2006 (received for review May 25, 2006)

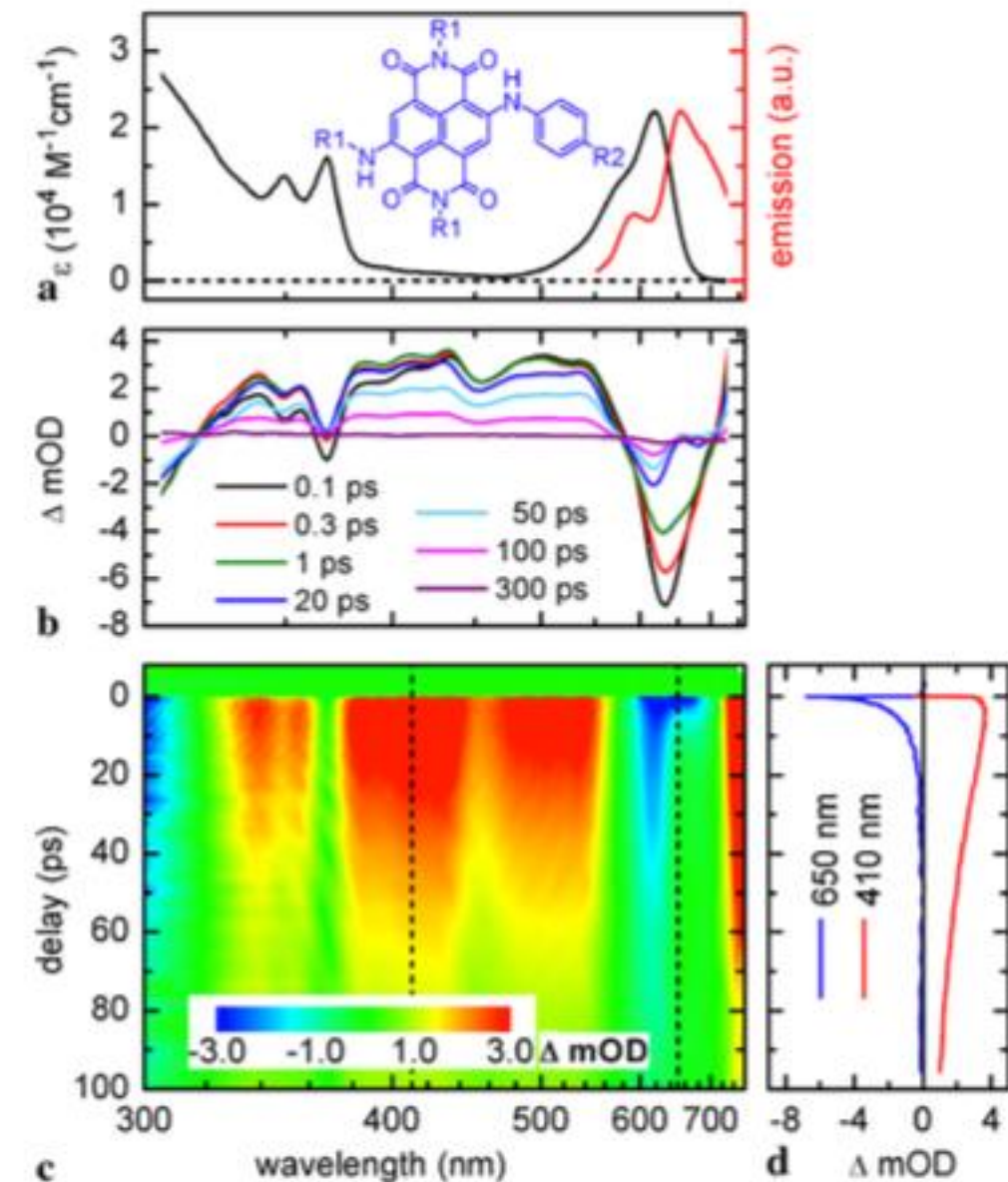
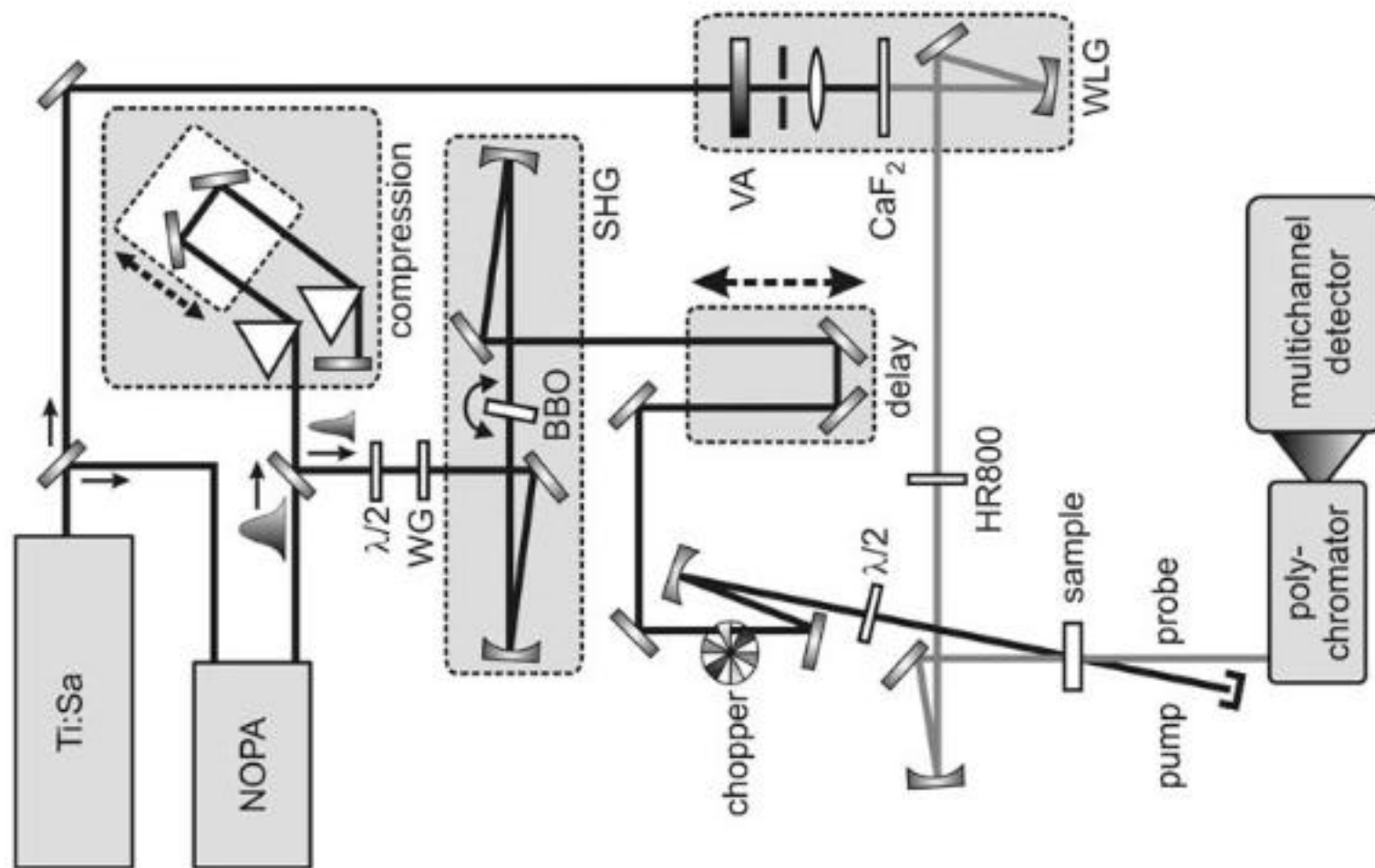
Global energy consumption is projected to increase, even in the face of substantial declines in energy intensity, at least 2-fold by midcentury relative to the present because of population and economic growth. This demand could be met, in principle, from fossil energy resources, particularly coal. However, the cumulative nature of CO₂ emissions in the atmosphere demands that holding atmospheric CO₂ levels to even twice their preanthropogenic values by midcentury will require invention, development, and deployment of schemes for carbon-neutral energy production on a scale commensurate with, or larger than, the entire present-day energy supply from all sources combined. Among renewable energy resources, solar energy is by far the largest exploitable resource, providing more energy in 1 hour to the earth than all of the energy consumed by humans in an entire year. In view of the intermittency of insolation, if solar energy is to be a major primary energy source, it must be stored and dispatched on demand to the end user. An especially attractive approach is to store solar-converted energy in the form of chemical bonds, i.e., in a photosynthetic process at a year-round average efficiency significantly higher than current plants or algae, to reduce land-area requirements. Scientific challenges involved with this process include schemes to capture and convert solar energy and then store the energy in the form of chemical bonds, producing oxygen from water and a reduced fuel such as hydrogen, methane, methanol, or other hydrocarbon species.

Lewis, N. S. and Nocera, D. G. "Powering the Planet: Chemical Challenges in Solar Energy Utilization" Proc. Natl. Acad. Sci. 2006, 103, 15729-15735

INVITED PAPER

Sub-50 fs broadband absorption spectroscopy with tunable excitation: putting the analysis of ultrafast molecular dynamics on solid ground

U. Megerle · I. Pugliesi · C. Schrieffer · C.F. Sailer · E. Riedle



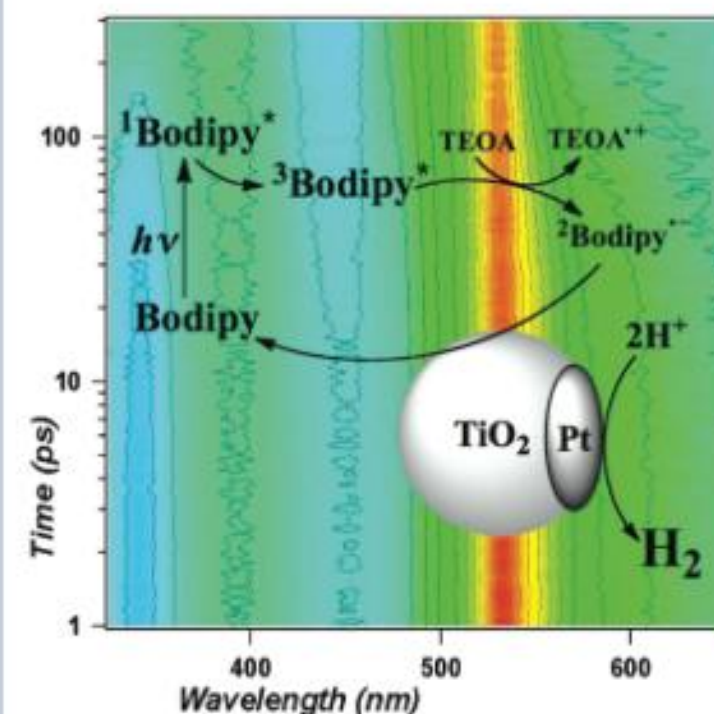
Intersystem Crossing in Halogenated Bodipy Chromophores Used for Solar Hydrogen Production

Randy Pat Sabatini, Theresa M. McCormick, Theodore Lazarides, Kristina C. Wilson, Richard Eisenberg,* and David W. McCamant*

Department of Chemistry, University of Rochester, Rochester, New York 14627, United States

ABSTRACT A series of halogenated boron-dipyrromethene (Bodipy) chromophores with potential applications in solar energy conversion were synthesized and characterized by steady state and ultrafast laser spectroscopy. The ultrafast dynamics of the chromophores were compared between a series containing H, Br, or I at the 2,6 positions of the Bodipy dye. The parent Bodipy has a fluorescent lifetime (τ_{fl}) of 3–5 ns, a fluorescence quantum yield (Φ_{fl}) of 0.56, and negligible triplet state yield. Bromination enhances the intersystem crossing (ISC) such that τ_{fl} and Φ_{fl} decrease to ~ 1.2 ns and 0.11, respectively, while iodination further accelerates ISC so that τ_{fl} is only ~ 130 ps and Φ_{fl} is 0.011. Transient absorption experiments lead to the observation of excited state absorption bands from the singlet (S_1) and triplet (T_1) states at ~ 345 and 447 nm, respectively, and characterization of ISC via the dynamics of these bands and the decay of S_1 stimulated emission.

SECTION Kinetics, Spectroscopy

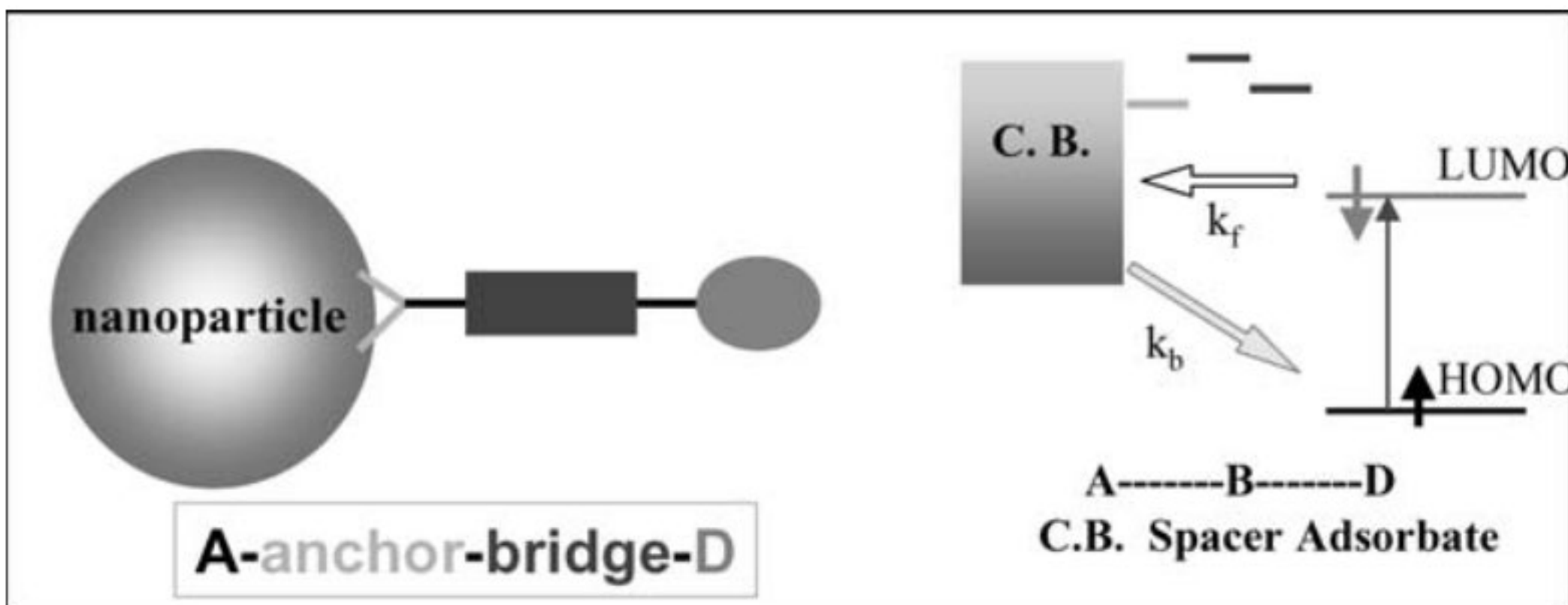


ULTRAFAST ELECTRON TRANSFER AT THE MOLECULE-SEMICONDUCTOR NANOPARTICLE INTERFACE

Neil A. Anderson and Tianquan Lian

Department of Chemistry, Emory University, Atlanta, Georgia 30322;

email: neil.anderson@nist.gov (see Acknowledgments), tlian@emory.edu



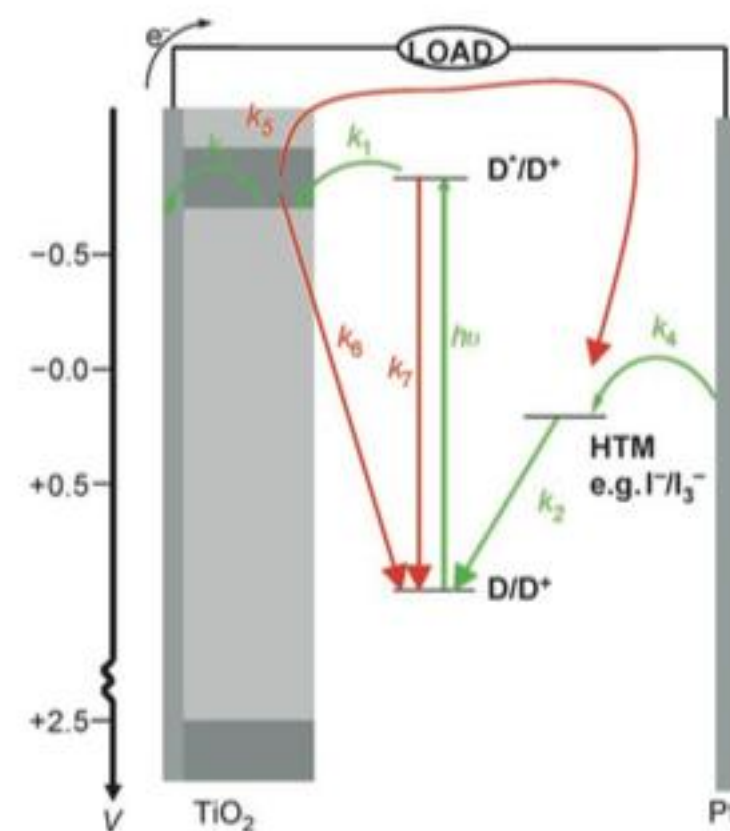
Optimizing Dyes for Dye-Sensitized Solar Cells

Neil Robertson*

Keywords:

dyes/pigments · energy conversion · redox chemistry ·
semiconductors · sensitizers

Dye-sensitized solar cells (DSSCs) have emerged as an important cheap photovoltaic technology. Charge separation is initiated at the dye, bound at the interface of an inorganic semiconductor and a hole-transport material. Careful design of the dye can minimize loss mechanisms and improve light harvesting. Mass application of DSSCs is currently limited by manufacturing complexity and long-term stability associated with the liquid redox electrolyte used in the most-efficient cells. In this Minireview, dye design is discussed in the context of novel alternatives to the standard liquid electrolyte. Rapid progress is being made in improving the efficiencies of such solid and quasi-solid DSSCs which promises cheap, efficient, and robust photovoltaic systems.



Sensitizing the Sensitizer: The Synthesis and Photophysical Study of Bodipy–Pt(II)(diimine)(dithiolate) Conjugates

Theodore Lazarides, Theresa M. McCormick, Kristina C. Wilson, Soohyun Lee, David W. McCamant,* and Richard Eisenberg*

Department of Chemistry, University of Rochester, Rochester, New York 14627, United States

Received August 5, 2010; E-mail: mcamant@chem.rochester.edu; eisenberg@chem.rochester.edu

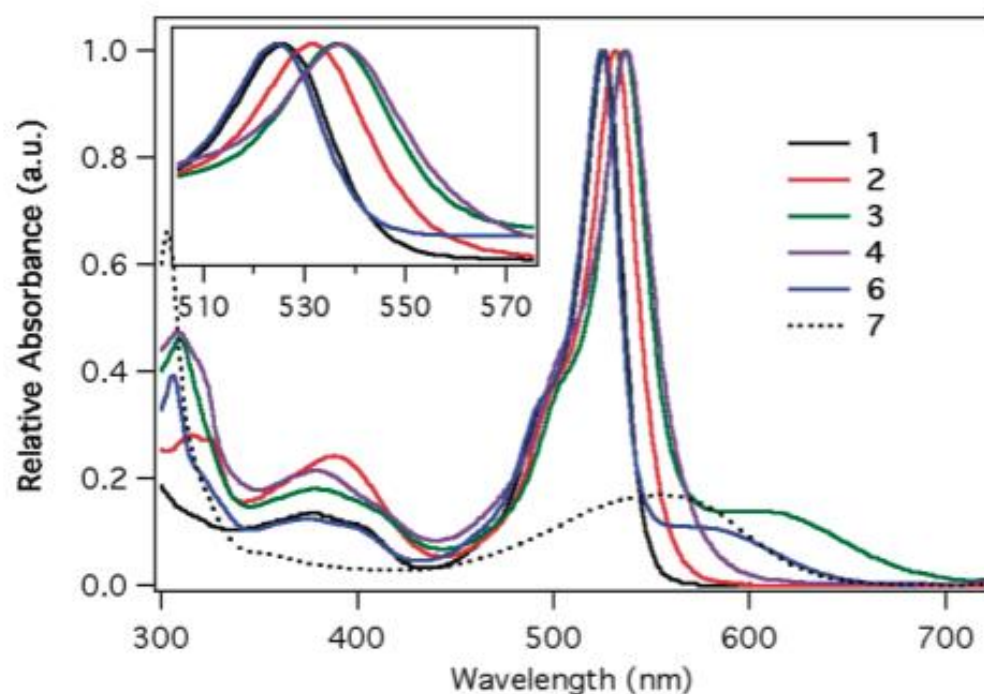
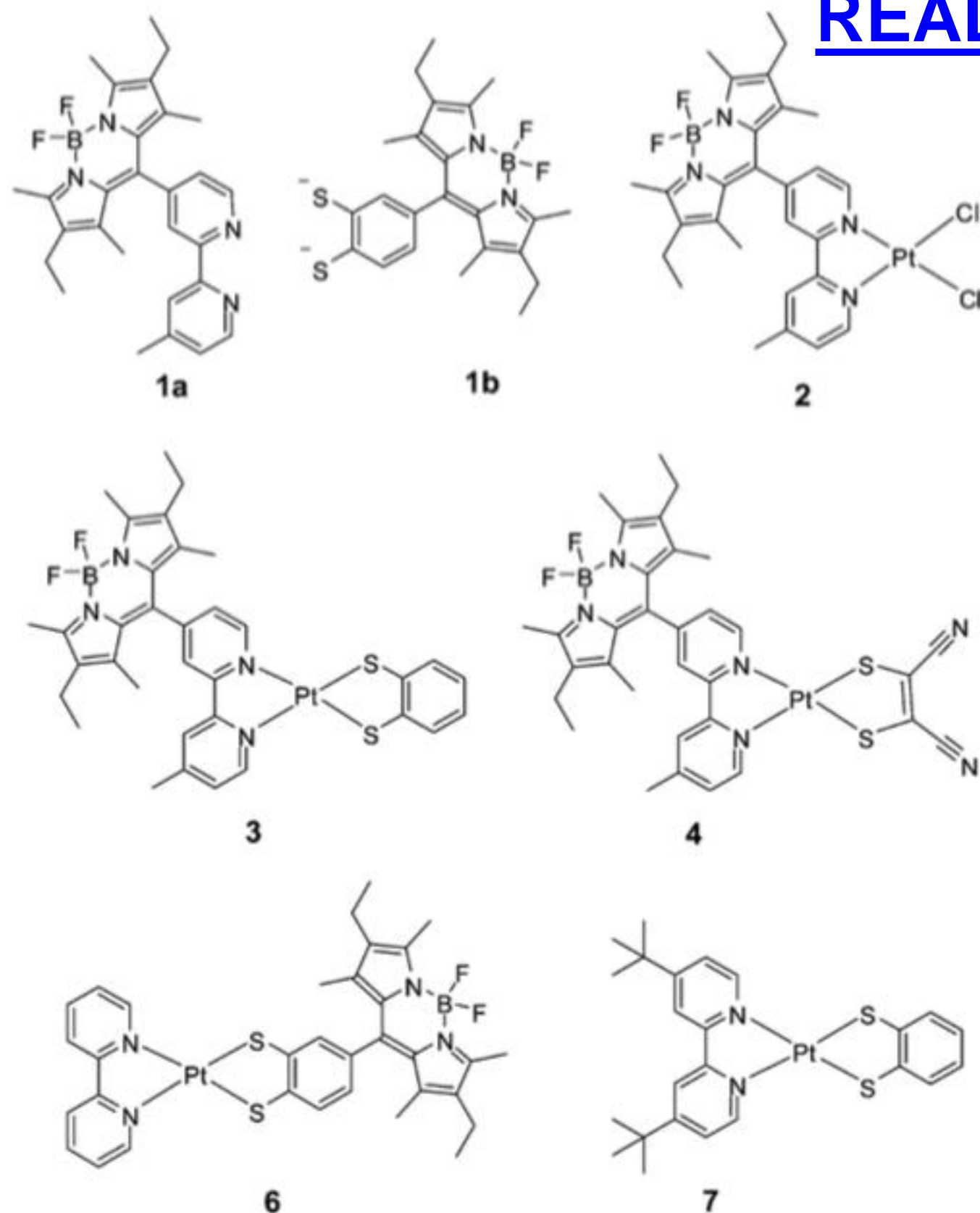


Figure 2. UV–vis absorption spectra of compounds **1a**, **2**, **3**, **4**, **6**, and **7** in dichloromethane. Spectra containing Bodipy have been normalized to give a maximum absorbance of 1. The spectrum of **7**, the Pt(bpy)(bdt) chromophore, has been scaled to make its intensity comparable to the other MMLL'CT absorption bands at ~ 600 nm. The inset shows an expanded region around the 530 nm Bodipy $\pi\pi^*$ absorption band.



Lazarides, T., McCormick, T. M., Wilson, K. C., Lee, S., McCamant, D. W. and Eisenberg, R. "Sensitizing the Sensitizer: The Synthesis and Photophysical Study of Bodipy–Pt(II)(Diimine)(Dithiolate) Conjugates" *J. Am. Chem. Soc.* 2010, 133, 350-364

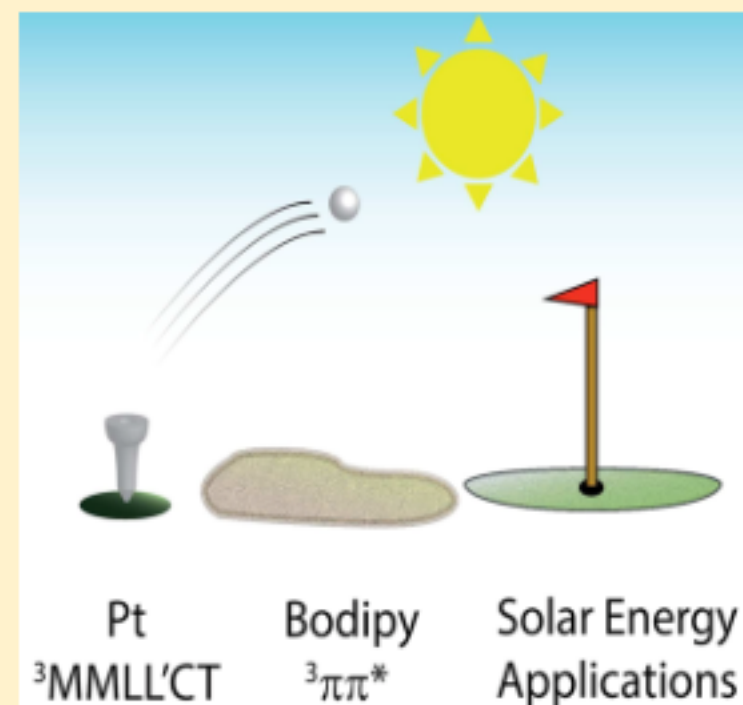
Deactivating Unproductive Pathways in Multichromophoric Sensitizers

Randy Pat Sabatini, Bo Zheng, Wen-Fu Fu,[†] Daniel J. Mark, Michael F. Mark, Emily Anne Hillenbrand, Richard Eisenberg,* and David W. McCamant*

Department of Chemistry, University of Rochester, Rochester, New York 14627, United States

S Supporting Information

ABSTRACT: The effects of solvent and substituents on a multichromophoric complex containing a boron-dipyrromethene (Bodipy) chromophore and Pt(bpy)(bdt) (bpy = 2,2'-bipyridine, bdt = 1,2-benzenedithiolate) were studied using steady-state absorption, emission, and ultrafast transient absorption spectroscopy. When the Bodipy molecule is connected to either the bpy or bdt in acetonitrile, excitation ultimately leads to the dyad undergoing triplet energy transfer (TEnT) from the redox-active Pt triplet mixed–metal–ligand–to–ligand' charge transfer ($^3\text{MML}'\text{CT}$) state to the Bodipy $^3\pi\pi^*$ state in 8 and 160 ps, respectively. This is disadvantageous for solar energy applications. Here, we investigate two methods to lower the energy of the $^3\text{MML}'\text{CT}$ state, thereby making TEnT unfavorable. By switching to a low dielectric constant solvent, we are able to extend the lifetime of the $^3\text{MML}'\text{CT}$ state to over 1 ns, the time frame of our experiment. Additionally, electron-withdrawing groups, such as carboxylate and phosphonate esters, on the bpy lower the energy of the $^3\text{MML}'\text{CT}$ state such that the photoexcited dyad remains in that state and avoids TEnT to the Bodipy $^3\pi\pi^*$ state. It is also shown that a single methylene spacer between the bpy and phosphonate ester is sufficient to eliminate this effect, raising the energy of the $^3\text{MML}'\text{CT}$ state and inducing relaxation to the $^3\pi\pi^*$.



Sabatini, R. P., Zheng, B., Fu, W.-F., Mark, D. J., Mark, M. F., Hillenbrand, E. A., Eisenberg, R. and McCamant, D. W. "Deactivating Unproductive Pathways in Multichromophoric Sensitizers" J. Phys. Chem. A 2014, 118, 10663-10672

Reductive Side of Water Splitting in Artificial Photosynthesis: New Homogeneous Photosystems of Great Activity and Mechanistic Insight

Theresa M. McCormick,[†] Brandon D. Calitree,[‡] Alexandra Orchard,[‡] Nadine D. Kraut,[‡]
Frank V. Bright,[‡] Michael R. Detty,^{*,‡} and Richard Eisenberg^{*,†}

Department of Chemistry, University of Rochester, Rochester, New York 14627, and Department of Chemistry, University at Buffalo The State University of New York, Buffalo, New York 14260-3000

Received July 8, 2010; E-mail: mdetty@buffalo.edu; eisenberg@chem.rochester.edu

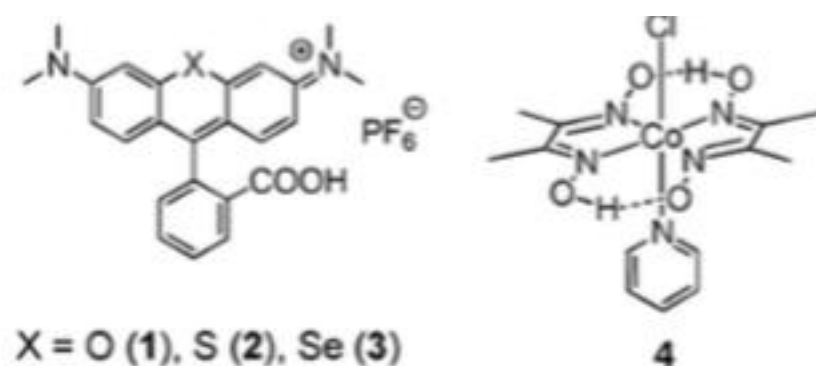


Figure 1. Structures of photosensitizers 1–3 and [Co^{III}(dmgH)₂(py)Cl] (4) (where dmgH = dimethylglyoximate, py = pyridine).

