RICHARD A. WALTON

Lecture in Inorganic Chemistry

Excited States of Transition Metal Complexes for Applications in Solar Energy and Biology



Claudia Turro received her B.S. with Honors in 1987 from Michigan State University. She worked with Daniel G. Nocera and George E. Leroi at Michigan State University and received her Ph.D. in 1992. She was awarded a Jane Coffin Childs Memorial Fund for Medical Research Postdoctoral Fellowship to conduct postdoctoral work at Columbia University with Nicholas J. Turro (no relation) from 1992 to 1995, and has been a faculty member at The Ohio State University since 1996. She received the Early CAREER Award by the National Science Foundation in 1998, the Arnold and Mabel Beckman Foundation Young Investigator Award in 1999, was named a 2010 Fellow of the American Chemical Society (ACS), and a 2012 Fellow of the American Association for the Advancement of Science. She was elected President of the Inter-American Photochemical Society (2012-14) and Chair of the ACS Division of Inorganic Chemistry (2016). She received the 2014 College of Arts and Sciences Susan M. Hartmann Mentoring and Leadership Award, the 2014 Award in Photochemistry from the American Photochemical Society, the 2016 Edward W. Morley Medal from the Cleveland Section of the ACS, the 2016 Award of the Columbus Section of the ACS, and the 2019 College of Arts and Sciences Harlan Hatcher Distinguished Faculty Award. Since 2016, she has been serving as Associate Editor for the Journal of the American Chemical Society. Professor Turro was elected a Member of the American Academy of Arts and Sciences in 2024 and a Member of the National Academy of Sciences in 2024.

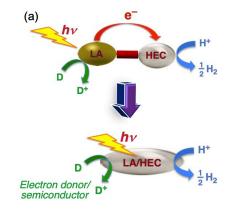
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Molecules that absorb low-energy visible and near-IR light use the energy provided by photons to access reactions not possible from their ground elecronic states. These excited state molecules can serve in applications that include sensors, imaging, photomedicine, and solar energy conversion and storage. The major portion of the presentation will focus on the latter.

The use of light to activate the action of a drug has become an important mode of cancer therapy because it is significantly less invasive an possesses reduced levels of systemic toxicity and related side effects to the patient compared to traditional treatment methods. Photoinduced ligand exchange is able to release drugs with spatiotemporal control which, together with the production of cytotoxic species, are able to act as more effective dual-activity agents. This new class of complexes will be presented, along with their activity towards biological targets and cancer cells.

The search for renewable, clean sources of energy is critical for the future of the planet. Harnessing sunlight and transforming its energy from abundant small molecules into storable clean fuels, such as hydrogen from water, has great potential to help meet the growing global demands, but remains a challenge. Systems for the production of solar fuels require strong light absorption that is well-matched to the solar spectrum, with excited states able to transfer electrons to catalysts that effect the desired transformation. Typically, a light absorber (LA) is combined with a hydrogen evolving catalyst (HEC) into functional LA-HEC architectures (Figure 1a). LAs currently used in these applications typically do not absorb beyond ~500 nm, such that a large fraction of photons that make up the solar spectrum are not utilized. In addition, multi-component LA-HEC platforms inherently lose energy through charge transfer steps. We have developed new Rh₂(II,II) complexes that that absorb light strongly throughout the visible region and into the near-IR. These compounds are able to undergo excited state redox processes, and some are able to act as single-molecule photocatalysts for the production of hydrogen with red and near-IR light (Figure 1b).



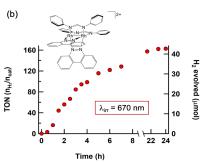


Figure 1. (a) Multi-component photocatalyst (PC) and its combination into a single molecule and (b) structure of Rh₂(II,II) single-molecule PC and H₂ evolution upon irradiation with red

One example of a single-molecule photocatalyst, cis-[Rh2(DPhF)2(bncn)2](BF4)2 (DPhF = N,N'diphenyl-formamidinate, bncn = benzo[c]cinnoline; 1), is shown in Figure 1b, along with the turnover numbers (TONs) for H₂ production upon irradiation with 670 nm light in the presence of acid and a sacrificial electron donor. The mechanism of photo- and electrocatalysis by 1 and related complexes will be discussed, which show that these bimetallic complexes are able to store two electrons upon the stepwise absorption of two low-energy photons to produce the catalytically-active doubly-reduced complex. Mechanistic aspects of the reduction of protons to H₂ by [1]²⁻ will be discussed, along with new systems for rhodium-free photocatalysis.





