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Review

Photoexcited radical anion super-reductants for solar fuels catalysis

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ABSTRACT

The catalytic transformation of carbon dioxide into fuels is one of the most important reactions for creating a sustainable, carbon-neutral energy economy. Given that the sun is the only plausible energy source that can accommodate the increased global energy demand without contributing to catastrophic climate change, it makes sense to use solar energy to drive this reaction, ideally using the largest possible portion of the solar spectrum. Over the past several years, we have explored the use of reduced rylenediimide chromophores, which absorb wavelengths ranging into the near-infrared, as strongly reducing photosensitizers capable of photosensitizing Re(diimine)$(CO)_3$L metal centers towards the binding and reduction of CO_2. We have explored the effects of varying the binding geometry, donor–acceptor redox potentials, and excitation wavelength on the kinetics of electron transfer from the reduced rylenediimide to the metal center. So far, we have achieved charge-separated lifetimes in electrocatalytically active complexes of 25 ns when illuminated with near-infrared light, and >250 ns when illuminated with blue light.

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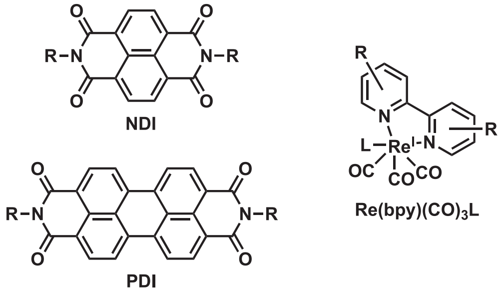
1. Introduction

1.1. Background

As we grapple with an increasingly chaotic climate fueled by rising global temperatures and CO_2 levels, the need for a sustainable, carbon-neutral source of fuels has become more and more apparent [1]. At the same time, global demand for energy is expected to increase over the coming decades, from around 14 TW in 2001 to 27 TW in 2050. The only renewable source of energy available to meet this demand is the light from the Sun [2]. While the efficiency of solar photovoltaic devices continues to improve [3], energy storage densities for electricity are still low compared to the energy stored in the chemical bonds of liquid fuels [2]. Consequently, we and many other researchers have sought to achieve the conversion of solar energy into stored chemical energy, an approach akin to the natural photosynthetic process and commonly referred to as artificial photosynthesis. Artificial photosynthetic systems use as their feedstocks the same inputs as natural photosynthesis, namely water as a source of reducing equivalents and carbon dioxide as the substrate to be reduced.

One of the key challenges in an artificial photosynthetic system is to reduce thermodynamically demanding substrates such as CO_2 using as much of the solar spectrum as possible. Typical electrocatalysts employed to reduce CO_2 function at potentials around -1.5 V vs SCE [4], a potential accessible using metalorganic chromophores that absorb at wavelengths shorter than 550 nm [5–9]. In addition, many of these highly reducing chromophores incorporate non-earth-abundant metals such as Ir [10,11], Pt [12], or Re [13]. There are reports of covalent assemblies of metalorganic chromophores with CO_2 reduction catalysts, the most widely researched of which are the $Ru(bpy)_3$–$Re(bpy)(CO)_3$ assemblies reported by Ishitani and co-workers [14], which achieve photocatalysis at wavelengths <500 nm. There has also been a report of a complex of an Ir^{III}(1-phenylisoquinoline)$_2$(bpy) complex attached to a $Re(bpy)(CO)_3$ catalyst, in which catalysis is achieved upon illumination at 480 nm [15]. Other assemblies that function at slightly longer wavelengths (<600 nm) incorporate zinc or magnesium porphyrins [16] or $Os^{III}(bpy)_3$ [17].

In contrast to metalorganic chromophores, purely organic chromophores that absorb in the visible region do not typically possess the excited-state reducing power required to photosensitize CO_2 reduction catalysts. However, it has been shown that certain organic chromophores, when reduced by one or two electrons, become powerful excited-state super-reductants that absorb long-wavelength visible and even near-infrared light while still exhibiting long enough lifetimes for use in donor–acceptor systems [18]. The use of a pre-reduced chromophore to transfer electrons to a CO_2 reduction catalyst has been previously demonstrated by Neumann and co-workers in a system in which a colorless polyoxometalate is reduced at mild potential in the presence of protons to generate an intensely absorbing chromophore [19]. The polyoxometalate is coordinated to a bimetallic CO_2 reduction catalyst, and photoexcitation of the reduced chromophore results in the transfer of two electrons and two protons to the catalyst, enabling binding and reduction of CO_2.



Scheme 1. Structures of naphthalenediimide (NDI), perylenediimide (PDI), and $Re(bpy)(CO)_3L$.

In our work, we have focused on the anions and dianions of rylenediimides (RDIs) as photoreductants. Structures of the rylenediimides used in this work are shown in Scheme 1. RDI anion chromophores were chosen on the basis of their relatively long excited-state lifetimes and the ease with which they can be incorporated synthetically into donor–acceptor assemblies, including metal centers capable of reducing CO_2. Chosen for our initial studies was the prototypical CO_2 reduction catalyst $Re(bpy)(CO)_3L$. This metal center was chosen for several reasons: first, its spectroscopic properties are well-understood, allowing for facile interpretation of our TA data; second, its ligand arrangement allows the chromophore to be attached to the metal center using a variety of geometries, allowing us to explore the effect of geometry on the rate and yield of charge separation; third, there is precedent for photodriving it as a catalyst using a covalently attached chromophore [17,20–24]. Finally, the complex is known to reduce CO_2 through a different set of pathways depending on whether the complex is reduced by one or two electrons before catalysis is initiated [25–28]. This property leaves open the possibility, which we have not yet explored extensively, of attaching multiple chromophores to the metal center and photodriving catalysis via the two-electron pathway.

We will begin this review by describing the properties, determined by ourselves and other groups, of the RDI anions and Re$(bpy)(CO)_3L$ complexes, shown in Scheme 1. First we will discuss their ground-state redox (Section 3.1) and optical (Section 3.2) properties. We will then discuss the excited-state spectroscopy of the RDI anions (Section 3.3) and some insights provided by high-level time-dependent density functional theory (TD-DFT) calculations on the excited state properties of PDI radical anion (Section 3.4) before beginning our discussion of RDI–Re(bpy) complexes.

Our initial studies involved direct attachment of the RDI chromophore to the Re(bpy) center, either through the bipyridine ligand, which will be discussed in Section 4.1.1, or through the pyridine ligand, which will be discussed in Section 4.2.1. A second generation of molecules comprised the same attachment geometries but with the addition of an intermediate electron acceptor. This intermediate acceptor was inserted in order to facilitate a longer lifetime of the final charge-separated state without compromising the rate of formation of that state. Those systems are discussed in Section 4.1.2 (bpy-linked) and 4.2.2 (py-linked).

During the course of these studies, we realized that there was also the potential to photodrive these systems in a completely different way, namely by using the Re → bpy MLCT state as the chromophore and the RDI anion as a covalently attached electron donor. The spin dynamics of this pathway proved unexpectedly rich and are discussed in Section 5.