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Unsymmetrical Dirhodium Single Molecule Photocatalysts for H₂ Production with Low Energy Light

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New axially blocked unsymmetrical dirhodium complexes photocatalyze the production of H₂ under red light irradiation with a turnover number (TON) of 23 ± 3 in the presence of acid and a sacrificial donor. The presence multiple metal/ligand-to-ligand charge transfer transitions improves their absorption of light into the near-IR.

The quest for more efficient carbon-neutral fuels and renewable energy sources is of paramount importance for addressing the challenges of increasing global energy demands.¹⁻⁶ Over the last several decades, solar energy applications, such as dye-sensitized solar cells (DSSCs)⁷⁻¹¹ and artificial photosynthesis systems,¹²⁻¹⁶ have made great progress to begin addressing this challenge. Traditional homogeneous artificial photocatalytic systems mimic the natural photosystem II reaction center, which features separate chlorophyll derivative light absorbing units as the photosensitizer (PS) coupled to a catalytic center (CAT),¹⁷ and often employ an electron donor (ED) and electron relay (ER) molecules to effect charge separation.

Conventional multicomponent systems for hydrogen generation feature Ru(II) and Ir(III) complexes as the PS,¹⁸⁻²⁶ combined with Co,¹⁸⁻²⁰ Fe,²¹⁻²³ or Ni²⁴ units as the CAT, and require photoinduced electron transfer from PS to CAT to drive a reaction. Therefore, the efficiency of catalysis is largely dependent on the charge transfer steps making covalently linked macromolecular assemblies an attractive alternative.²⁷⁻²⁹ These tethered systems typically involve multi-step synthesis, making them difficult to scale for practical use. In addition, heterogeneous assemblies with PS-CAT interactions at specific distances and orientations are essential for maximizing electron transfer and minimizing charge recombination. Such precision, however, is difficult to maintain at the surfaces of

semiconductors and in supramolecular systems. Consequently, the design of single molecule photocatalysts can aid in the development of more efficient photoinduced H₂ production.

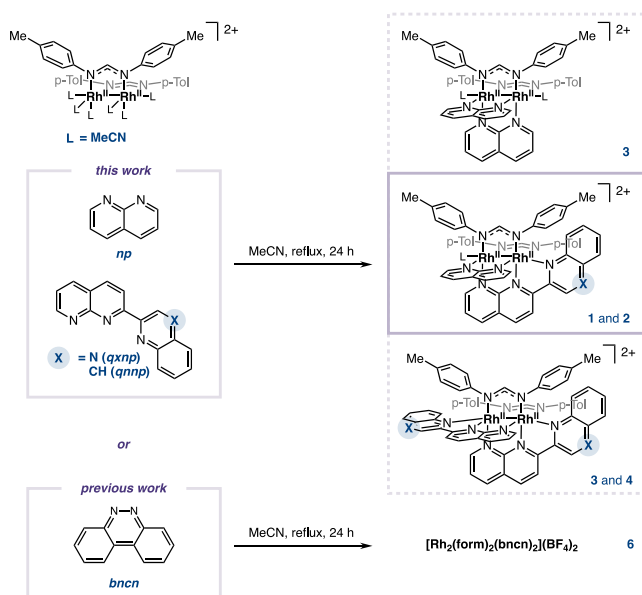
Dirhodium complexes are excellent candidates for photocatalysis since they display panchromatic absorption profiles, are known to catalyze proton reduction, and are water and air stable. The Nocera group reported several two-electron mixed-valence dirhodium complexes in which the catalytic center and the sensitizer are combined in the same unit.³⁰⁻³⁴ For example, Rh₂^{0,II}(tfepma)₂(CNAd)₂Cl₂ (tfepma = CH₃N[P(OCH₂CF₃)₂]₂, CNAd = 1-adamantylisocyanide) produces H₂ upon irradiation with a TON of 7 after 144 hours of UV irradiation (λ_{irr} > 305 nm).³⁵ This compound, however, does not absorb beyond 550 nm and is sensitive to moisture and oxygen. Recently, our groups developed air-stable, axially-blocked panchromatic dirhodium complexes sensitizers, *cis*-[Rh₂(DTolF)₂(npCOO)₂] (DTolF = *p*-ditolylformamidinate, npCOO⁻ = 2-carboxylate-1,8-naphthyridine) and *cis*-[Rh₂(DTolF)₂(qnp)₂][BF₄]₂ (qnp = 2-(quinolin-2-yl)-1,8-naphthyridine),^{36,37} that exhibit relatively long-lived ³ML-LCT (triplet metal/ligand-to-ligand charge transfer) excited states.

These longer lifetimes are attributed to the axial coordination that results in an increase in energy of the Rh₂(σ*) orbital and, consequently, a higher energy ³MC (metal-centered) excited state, making the latter less accessible for fast non-radiative decay and allowing them to serve as panchromatic PSs in multi-component photocatalytic hydrogen evolution systems.³⁸ These molecules, however, are not catalytically active due to the blocked axial sites which render the bimetallic core inaccessible for substrate binding, a situation that was remedied by preparing *cis*-[Rh₂(form)₂(bncn)₂](BF₄)₂ (form = diphenylformamidinate, bncn = benzo[*c*]cinnoline) with open axial sites. This molecule features a shorter Rh–Rh bond afforded by the bncn bridging ligands, which also raises the energy of the Rh₂(σ*) orbital.³⁹ Particularly, *cis*-[Rh₂(form)₂(bncn)₂](BF₄)₂ is a single-molecule photocatalyst that produces H₂ with a TON = 170 ± 5 in acidic

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Scheme 1 Synthetic scheme for the synthesis of **1** and **2** as well as the previously published compound **6**.³⁹

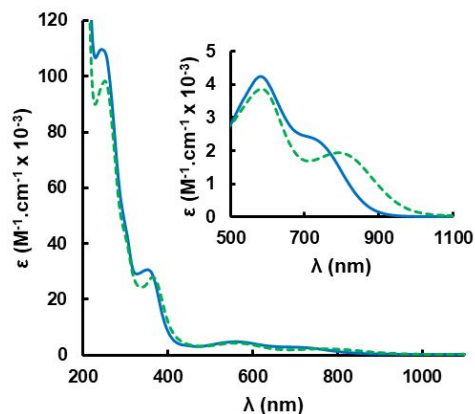
solution upon red light irradiation, 670 nm, as well as with 735 nm irradiation.

The present work focuses on a new design for panchromatic single-molecule photocatalysts that involves the use of unsymmetrical bridging ligands. The dirhodium compounds $\text{cis-}[\text{Rh}_2(\text{DTolF})_2(\text{L})(\text{np})][\text{BF}_4]_2$ ($\text{np} = 1,8\text{-naphthyridine}$; Scheme 1), where $\text{L} = \text{qxnp}$ (2-(1,8-naphthyridin-2-yl)quinoxaline) (**1**) and qnnp (**2**), were prepared which feature one axial site blocked by a π -accepting ligand, while the other axial site remains available for substrate binding required for photocatalytic hydrogen production (Figures S1 and S2). The properties of **1** and **2** are compared to those of the previously reported compounds $\text{cis-}[\text{Rh}_2(\text{DTolF})_2(\text{np})_2][\text{BF}_4]_2$ (**3**), $\text{cis-}[\text{Rh}_2(\text{DTolF})_2(\text{qxnp})_2][\text{BF}_4]_2$ (**4**), and $\text{cis-}[\text{Rh}_2(\text{DTolF})_2(\text{qnnp})_2][\text{BF}_4]_2$ (**5**), shown in Scheme 1.^{37, 40}

Complexes **1** and **2** exhibit a one-electron reversible oxidation couple at +0.82 and +0.80 V vs Ag/AgCl, respectively (Table 1, Figure S3), assigned to the removal of an electron from the highest occupied molecular orbital (HOMO) of $\text{Rh}_2(\delta^*)/\text{DTolF}$ character, as reported for related dirhodium formamidinate complexes.^{36, 37, 39} In addition, a reversible one-electron reduction was observed for **1** and **2** at -0.60 and -0.69 V vs Ag/AgCl, assigned to the reduction of the qxnp and qnnp ligands, respectively. These complexes are more easily reduced than **3**, consistent with more extended π -systems and greater electron-withdrawing character for the qxnp and qnnp ligands in **1** and **2** as compared to the np ligand in **3**. A cathodic scan in the presence of acetic acid (Figures S4 and S5) revealed that the complexes are catalytically active, producing H_2 at potentials more negative than -1.2 V vs Ag/AgCl. This activity of **1** and **2** is attributed to the presence of an open axial position, in contrast to the fully blocked complexes **4** and **5** which do not exhibit an electrocatalytic current under similar experimental conditions.

The steady state absorption of **1** and **2** is strong throughout the ultraviolet to visible ranges and extends into the near-IR region (Figure 1, Table 1). The complexes exhibit ligand-

centered $\pi\pi^*$ transitions at 252 nm, also observed in the 256 – 259 nm range in **4** and **5** (Table 1), consistent with the absorption of the free ligands in solution.³⁷ The features at 365 and 352 nm for **1** and **2**, respectively, are likely to be Rh_2 -to-ligand in character since they are red-shifted compared to the absorption at 300 nm in **3**, as expected given the more positive ligand reduction potentials for these complexes. In the case of **1**, the broad absorption bands at 584 nm and 790 nm are assigned to $\text{Rh}_2/\text{DTolF} \rightarrow \text{np}$ and $\text{Rh}_2/\text{DTolF} \rightarrow \text{qxnp}$ $^1\text{ML-LCT}$ transitions, respectively, which are slightly red-shifted relative to the peaks observed for the corresponding symmetric complexes, at 566 nm for **3** and at 758 nm for **4**.³⁷ A similar



assignment can be made for the bands at 582 nm and 712 nm for **2**.

Fig. 1 Electronic absorption spectra for **1** (green, dashed) and **2** (blue, solid).

Density Functional Theory (DFT) calculations show that the HOMOs of **1–5** are $\text{DTolF}(\pi^*)/\text{Rh}_2(\delta^*)$ in character, consistent with related formamidinate-bridged dirhodium complexes (Figures S6 – S8 and Tables S1 – S4).⁴¹ Interestingly, in the presence of acid, a slight blue-shift of the $^1\text{ML-LCT}$ band is observed for **1** and **2** (Figure S9). Titrations of **1** and **2** with tosylic acid, TsOH, followed by electronic absorption spectroscopy reveal a 1:1 protonation stoichiometry with each complex (Figure S10). In addition, Time Dependent DFT (TD-DFT) calculations (Figures S11 and S12) and ^1H NMR acid titrations (Figures S13 and S14) indicate that protonation occurs at the N atom of the formamidinate ligand *trans* to the axial blocking ligand. This protonation, however, does not lead to ligand dissociation on the timescale of days.

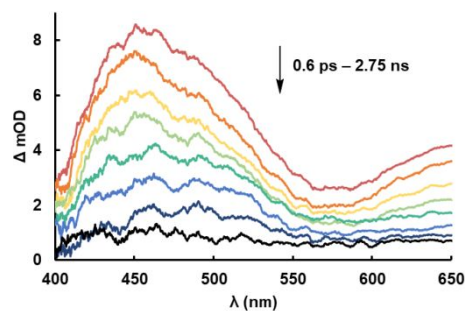


Fig. 2 fsTA spectra of **1** recorded 0.6, 2.1, 4.3, 5.3, 18, 68, 911, and 2753 ps after the excitation pulse ($\lambda_{\text{exc}} = 720$ nm, 2.5 μJ , IRF = 85 fs) in CH_3CN ; black trace at -20 ps.

Table 1 Electronic Absorption Maxima with Molar Absorptivities, Reduction Potentials, Singlet (τ_1) and Triplet (τ_2) Lifetimes for **1** – **5** in CH₃CN.

Complex	$\lambda_{\text{abs}} / \text{nm}$ ($\epsilon / \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$)	$E_{1/2} / \text{V}^a$	τ_1 / ps	τ_2 / ns
1	252 (98), 365 (29), 584 (3.9), 790 (1.9)	+0.82, -0.60	6 ^b	1.5 ^b
2	252 (109), 352 (31), 582 (4.3), 712 (2.4)	+0.80, -0.69	10 ^b	4 ^c
3^d	235 (55), 300 (25), 436 (1.8), 566 (3.6)	+0.87, -0.94	14	0.64
4^d	259 (83), 369(32), 554 (2.2), 758 (3.2)	+1.08, -0.43	8	7
5^d	256 (90.4), 366 (32), 583 (2.5), 704 (3.4)	+0.99, -0.62	8	7

^avs Ag/AgCl, 0.1 M Bu₄NPF₆. ^bFrom transient experiments at 298 K ($\lambda_{\text{exc}} = 720 \text{ nm}$, 2.5 μJ , IRF = 85 fs); error $\sim 10\%$. ^cFrom transient absorption experiments at 298 K ($\lambda_{\text{exc}} = 650 \text{ nm}$, 5 μJ , IRF = 6 ns); error $\sim 1 \text{ ns}$. ^dFrom ref. 34.

A broad positive signal was observed from 400 to 675 nm with a maximum at $\sim 450 \text{ nm}$ and a lower intensity feature at $\sim 670 \text{ nm}$ in the femtosecond transient absorption (fsTA) spectrum for **1** (Figure 2). It is evident from the low intensity of the signal at $\sim 580 \text{ nm}$ that the ground state bleach overlaps with positive excited state absorption in this spectral range. The signal at 450 nm can be fitted to a biexponential decay with lifetimes of $\tau_1 = 5.6 \text{ ps}$ (68%) and $\tau_2 \sim 1.5 \text{ ns}$ (32%) assigned to the ¹ML-LCT and ³ML-LCT excited states, respectively. Complex **2** also exhibits a broad absorption at 470 nm attributed to the ¹ML-LCT state with $\tau = 10 \text{ ps}$ (Figure S15), similar to the symmetric analogs **4** and **5**.³⁷ The nanosecond transient absorption spectra (nsTA, Figure S16) resemble those collected at 911 ps for **1** and at $\sim 2.7 \text{ ns}$ for **2** in the fsTA experiments, Figures 2 and S17, respectively. The decay of the signal of **2** at 470 nm decays with a lifetime of $\sim 4 \text{ ns}$ (Figure S17 and Figure S18 for **1**), assigned to the decay of the ³ML-LCT state. The shorter triplet lifetimes of **1** and **2** compared to their fully blocked symmetric analogues **4** and **5**, $\sim 7 \text{ ns}$,³⁷ is attributed to lower energy ³MC states in the former compounds arising from the presence of one open axial site, thus facilitating excited state deactivation.

Complexes **1** and **2** undergo bimolecular photoinduced electron transfer with the reversible electron donor *p*-phenylenediamine (*p*-PD, $E_{1/2}(p\text{-PD}^{+/0}) = +0.28 \text{ V vs Ag/AgCl}$)³⁷ upon 650 nm excitation, resulting in nsTA spectra consistent with a *p*-PD radical cation superimposed with that of the reduced dirhodium complex (Figure S19), which recombine with a time constant of $\sim 35 \mu\text{s}$.³⁷ Therefore, albeit shorter-lived ³ML-LCT excited states relative to the symmetric analogues **4** and **5**, complexes **1** and **2** are able to undergo bimolecular charge transfer with low energy red excitation.

Given the recent report of photocatalytic H₂ production by *cis*-[Rh₂(form)₂(bnch)₂](BF₄)₂ (**6**),³⁹ it was hypothesized that **1** and **2** may also act as single-molecule photocatalysts. Upon irradiation with 655 nm, **1** and **2** generate H₂ in DMF upon in the presence of 0.1 M TsOH as the proton source and 1-benzyl-1,4-dihydropyridinamide (0.12 M; BNAH, $E_{\text{ox}} = +0.62 \text{ V vs Ag/AgCl}$) as the sacrificial electron donor (Table S5).³⁹ A turnover number (TON) of ~ 23 was measured for **2** after 24 h of irradiation. This

value, along with the use of low energy visible light, represents a notable improvement over Rh₂^{0,II}(tfepma)₂(CN^tBu)₂Cl₂.³⁵

A lower TON of ~ 2 was observed for **1** under the same conditions which is attributed to the shorter ³ML-LCT lifetime compared to **2**, reducing its ability to participate in electron transfer reactions hindering the production of H₂. Complexes **3** – **5** were irradiated under similar conditions but no H₂ was detected. Additional control experiments revealed that H₂ production by **2** requires light, BNAH, a 5 – 10 ns lifetime, and TsOH. Moreover, the fact that **4** and **5** are not photocatalytic, points at the need of an open axial site for reactivity. It is noted that **2** is not as active as the recently reported photocatalyst **6**, owing to its shorter triplet lifetime, lower excited state driving force, the presence of only one active open site for catalysis, and lower oscillator strength at the irradiation wavelength. Nevertheless, the structural modification of the unsymmetrical complexes constitutes a promising route to the design of a single-molecule photocatalysts.

In contrast with **6**, protonation of **1** and **2** in the ground state was observed. The fsTA and nsTA spectra of the fully protonated compounds **1** and **2** exhibit similar ¹ML-LCT and ³ML-LCT spectral features and lifetimes compared to those in the absence of acid (Figures S20 and S21), indicating that protonation at the formamidinate bridging ligand does not disturb the excited state properties of the complexes.

The chemically prepared proposed intermediates [**1**]¹⁻ and [**2**]¹⁻ are dark green in color and, in the presence of acid, they generate the purple protonated compounds with release of H₂ (Figures S19 and S22). The turnover number of H₂ produced per dirhodium complex is ~ 0.4 as shown in Table S6, suggesting a mechanism where two protonated complexes may react to produce one molecule of H₂ and to fully regenerate the Rh(II,II) complex, as depicted in Figure 3, although we cannot rule out other possible pathways at this time.

In summary, two new unsymmetrical dirhodium complexes *cis*-[Rh₂(DTolF)₂(qxnnp)(np)][BF₄]₂ (**1**) and *cis*-[Rh₂(DTolF)₂(qnnp)(np)][BF₄]₂ (**2**) are capable of photocatalytic H₂ production upon irradiation with low energy visible light. This work underscores the fact that a careful choice of ligands for the dirhodium core can lead to lifetimes suitable for electron transfer reactions while allowing the one of the metals to be

accessed by H^+ for H_2 production. More broadly, this new approach aimed at installing two different acceptors in the coordination sphere opens unexplored possibilities for the design of new unsymmetrical dirhodium complexes as photocatalytic systems for H_2 production.

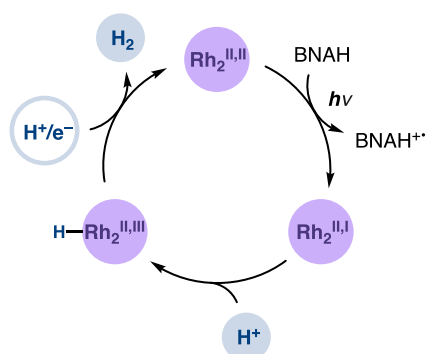


Fig. 3 Schematic representation of the H_2 production by **1** and **2** (see Fig. S25 for additional details).

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Conflicts of interest

There are no conflicts to declare.

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New asymmetric dirhodium complexes for photocatalytic H₂ production with red light

