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Chemically regulating Rh(I)-Bodipy photoredox switches†

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A. M. Lifschitz,[a] R. M. Young,[ab] J. Mendez-Arroyo,[a] V. V. Roznyatovskiy,[ab] C. M. McGuirk,[a] M. R. Wasielewski[ab] and C. A. Mirkin*[a]

The ability of Rh(I) centers to undergo photoinduced electron transfer from discrete metal orbitals to Bodipy fluorophores is mediated through reversible coordination chemistry.

Rh(III) coordination complexes have been extensively utilized as strong photo-oxidants in broad areas of chemistry, such as photoredox catalysis and materials for photovoltaic cells.[1] While the generation of photo-oxidized Rh species can also have important implications in organometallic and catalytic transformations,[2] the role of monometallic Rh(I) complexes as photo-reductants remains largely unexplored.[3] Typically, monometallic Rh(I) complexes are unable to directly undergo the electronic transitions in solution that efficiently transfer charge from the metal in ways that can be exploited for redox chemistry.[4] However, the ability to modulate the oxidation of Rh(I) by an ancillary photoactive species *via* simple coordination transformations could be exploited for the generation of novel molecular switches for photoredox processes with important applications in renewable energy and catalytic processes.

Rh(I) complexes are a powerful platform in the Weak-Link Approach (WLA), a methodology for the synthesis of supramolecular constructs that can be toggled between active states through modulation of the coordination chemistry of hemilabile ligands at d^8 metal nodes.[5] Upon coordination to small analytes, Rh(I) serves as a structural regulator to guide distances and orientations between functional moieties embedded in the supramolecular structure, resulting in molecular switches capable of sensing, signal amplification, and control of catalytic activity.[6] By exploiting high-lying, metal-centered orbitals to engage in photoredox interactions within the supramolecular environment, a further degree of control over photoactive WLA structures could be achieved. Herein we show that Rh(I) coordination complexes incorporating Bodipy moieties can be used to switch Bodipy's fluorescence on and off by modulating the ability of the metal center to undergo photoinduced electron transfer (PeT) to the fluorophore. The inclusion of Bodipy as the electron acceptor provides us with a straightforward spectroscopic handle for the PeT process.[7] Thus, we are able to achieve coordination chemistry-based control of PeT from a discrete d_{z^2} Rh(I) orbital to Bodipy by either controlling the oxidation potential of the metal center, yielding a switch in which PeT is disabled *via* ligand chelation (Fig. 1A); or by affecting the Bodipy's redox potential, resulting in a system in which PeT is triggered by ligand chelation (Fig. 1B). As a whole, the Bodipy-WLA platform enables the kinetically fast formation of photo-oxidized Rh species that decay slowly in time, thus offering both an easily accessible platform for highly relevant photoredox transformations and a novel means to control photoredox switches.

To modulate the ability of Rh(I) to undergo photo-oxidation based on its redox potential, we first synthesized a pair of complexes in which the charge of the first coordination sphere is varied. Thus, semiopen Rh(I) complex **1** incorporating Bodipy-functionalized hemilabile ligand **S3** (see Fig. S1, ESI†) was assembled *via*

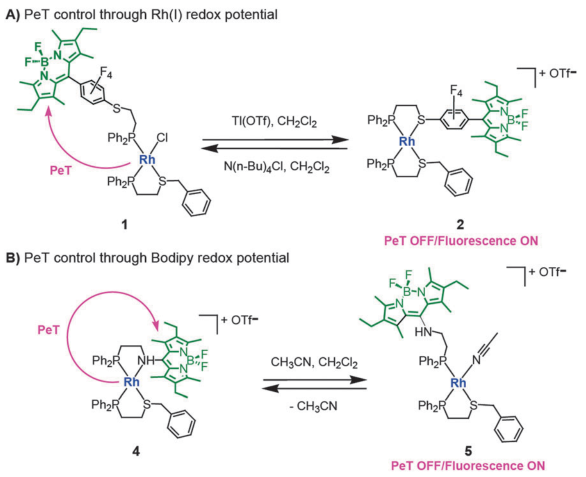

Fig. 1 Modulation of PeT through coordination-based control of redox potentials.

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[a] *Department of Chemistry and International Institute for Nanotechnology, Northwestern University, 2145 Sheridan Road, Evanston, Illinois 60208, USA. E-mail: chadnano@northwestern.edu*

[b] *Argonne-Northwestern Solar Energy Research (ANSER) Center, Northwestern University, Evanston, Illinois 60208, USA*

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Table 1 Spectral and electrochemical data

Complex	λ_{max} abs (nm)	λ_{max} em (nm)	QY fluo. em	Bodipy E_a (V)	Rh E_a (V)
1	544	571	0.089	0.65	0.039
2	547	569	0.48	0.71	—
4	465/528	520	0.047	0.70	0.456
5	463	519	0.34	0.42	0.747

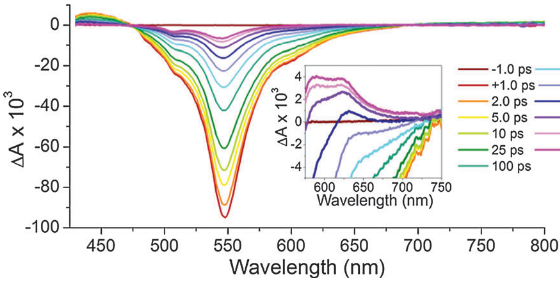

Fig. 2 Transient absorption spectra of **1** in CH_2Cl_2 (λ_{ex} = 505 nm). Inset: zoom-in of transient absorption from the Bodipy anion.

standard WLA procedures[6] and reversibly converted to closed complex **2** upon abstraction of a coordinated chloride. This transformation effectively changes the charge of the Rh(I) first coordination sphere from neutral to positive. The Bodipy is appended to the hemilabile coordinating moiety through a perfluorinated phenyl bridge that does not allow for ground-state interactions with the Rh(I). This particular ligand design precludes significant changes in the inductive contributions to the Bodipy frontier orbitals upon coordination changes.[8] As a result, the introduction and abstraction of chloride can be used to change the oxidation potential of the metal center while retaining the redox properties of Bodipy (Table 1).

Ground-state computational and electrochemical analyses are useful for assessing potential excited state interactions in Bodipy systems, since the fluorophore displays relatively small Stokes shifts and thus we can expect the energetics of both its ground- and excited-states to be similar. In our system, DFT calculations of complexes **1** and **2** show that the coordination of chloride results in the destabilization of the metal d_{z^2} orbital energy level to the degree that it lies in between the Bodipy-centered frontier orbitals (see Computational section, ESI†). Conversely, displacement of chloride by the Bodipy-ligand thioether depletes the electron density of Rh(I) and lowers the energy level of the d_{z^2} orbital so that it now lies below the Bodipy-centered HOMO. The computational results are clearly projected onto the electrochemical behavior of complexes **1** and **2**. As expected, the Bodipy-centered redox processes are largely unaffected by the coordination chemistry of Rh(I) (Table 1). On the other hand, an irreversible Rh-centered oxidation process is observed at 39 mV for neutral complex **1** at a lower potential than the Bodipy oxidation. This anodic wave disappears upon abstraction of chloride in **2**, supporting computational modelling of the effects of coordination on the energy level of the Rh(I)-centered d_{z^2} orbital. Comparison with Bodipy ligand **S3** as well as with Rh(I) complexes **S1** and **S2**, which mimic the coordination environment of **1** and **2**, respectively, but do not incorporate a Bodipy moiety, supports the assignment of the anodic wave at 39 mV to Rh(I) oxidation (see ESI†).

The absorption peaks corresponding to the Bodipy-centered π–π* and n–π* transitions are very similar in complexes **1** and **2**, supporting the lack of ground state interaction between Bodipy and Rh(I) (see Fig. S5, ESI†). On the other hand, the transient absorption (TA) spectrum of **1** shows that absorption is followed by fast formation of a Bodipy radical anion species band at 600 nm (Fig. 2), accompanied by a reduction in fluorescence quantum yield (QY) to 8.9% (compared to 91% of the free ligand).[8a] A similar radical Bodipy anion band is also observed upon controlled-potential, bulk electrolysis of the Bodipy ligand at −1.6 V, thus providing unequivocal spectral evidence of the PeT process (see Fig. S15, ESI†). Closed complex **2**, on the other hand, displays a QY that is 5.3 times higher (48%), and no bands corresponding to reduced Bodipy species can be found in its TA spectrum. Interestingly, the weak Rh–S interaction in the perfluorinated Bodipy ligand precludes significant stabilization of the *meso*-centered LUMO, so that PeT to the perfluorinated phenyl spacer does not occur significantly. Indeed, computational modelling of **2** shows that the LUMO is spread throughout the Bodipy and the *meso* substituent, suggesting that the energy of the two π systems is very similar.

The on–off PeT switch comprised by **1** and **2** provides the basis for the design of a reverse off–on switch. That is, if one is to enable PeT from Rh(I) in a WLA coordination complex in which a Bodipy ligand is chelated to the metal centre and disable PeT when the ligand is partially displaced, then neutral coordination spheres should be avoided. In doing so, it can be ensured that partial displacement of the of the Bodipy ligand results in a Rh(I) centre that cannot be oxidized at lower potentials than the Bodipy moiety itself. Furthermore, since the coordination changes effected by the displacement of a neutral Bodipy ligand by another neutral coordinating species are not expected to have a major effect on the oxidation potential of Rh(I), then coordination changes should target the oxidation potential of the Bodipy to control PeT. We can achieve this by designing a novel Bodipy ligand **3** in which a phosphinoalkylamine coordinating moiety is directly attached to the Bodipy core, thereby allowing for control of the Bodipy ground state energetics through coordination chemistry (Fig. 3, inset).

Amino-functionalization of the Bodipy 8-position has recently attracted much attention.[9] The effects of amino coordination on sterically hindered 8-amino Bodipys, however, has not yet been explored. We found that incorporation of ligand **3** into closed complex **4** results in a red-shift of the Bodipy absorption, suggesting that the fluorophore's HOMO–LUMO energy levels can be modulated through metal cation coordination (Fig. 3). Formation of semiopen complex **5** *via* reaction with acetonitrile reconstitutes the original absorption features of ligand **3**. Since semiopen complex **5** is

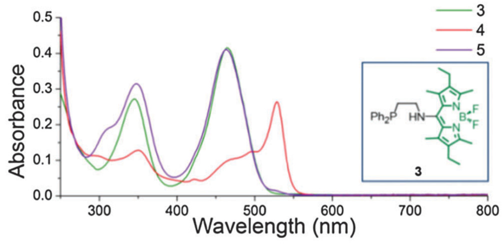

Fig. 3 Absorption spectra of ligand **3** and its Rh(I) complexes.

generated through displacement with a neutral coordinating species, quenching through PeT from the Rh(I) is not possible as in the case of **1**; the fluorescence QY thus increases from 4.7% in **4** to 34% in **5** (Table 1). These spectral effects are also accompanied by a large decrease in the absorption cross-section in **4**, resulting in a fluorescence intensity switching ratio between the two complexes of 27.4. Interestingly, the sharp feature on the absorption spectrum of **4** at 528 nm leads to very low fluorescence emission and it does not appear in the fluorescence excitation spectrum (see ESI†), suggesting that the peak in question corresponds to a charge transfer transition and that the Bodipy π–π* band is centered at 465 nm.

The absorption and fluorescence behavior of complexes **4** and **5** can be explained through computational modelling of their ground-state, orbital energy levels. In these studies, closed complex **4** displays a Rh(I) d_{z}^{2} HOMO flanked by the Bodipy frontier orbitals, suggesting that the low fluorescence QY may partly result from PeT from Rh(I) to the fluorophore. Furthermore, while the Bodipy-centered HOMO displays a characteristic nodal plane on the *meso* position, the Bodipy-centered LUMO shows significant contribution from the Rh–N coordination bond, thus providing a potential explanation for the charge transfer band in the absorption spectrum of **4**. On the other hand, semiopen complex **5** displays HOMO and LUMO orbitals fully centered on the Bodipy moiety with several metal-centered occupied orbitals laying at lower energy levels.

The computational modelling of **4** and **5** is validated by the complexes' spectroelectrochemical behaviour. The Rh-centered oxidation events occur at potentials lower than Bodipy-centered processes in closed complex **4**, while the opposite is observed in semiopen complex **5** (Table 1). Model complexes **S4** and **S5** that mimic the coordination environment of **4** and **5**, respectively, but that do not incorporate Bodipy moieties were also synthesized and characterized *via* cyclic voltammetry to corroborate the nature of the redox processes discussed above (see ESI†). Accordingly, TA spectra of **4** show the growth of a broad feature at lower energies than the ground state following Bodipy excitation, which we can assign to overlapping triplet excited Bodipy and Bodipy radical anion bands, the latter resulting from PeT from the Rh(I) center (Fig. 4). This feature is red-shifted relative to the Bodipy anion absorption observed through spectroelectrochemical characterization of ligand **3** (see Fig. S16, ESI†), likely as a result of coordination to Rh(I). However, no such features are observed in the TA spectra of **5**, supporting the idea that a reverse PeT switch can be accessed with novel ligand **3**.

The design of photoredox switches based on Rh(I) has the advantage that PeT from the metal center is an inherently fast process capable of competing with other slower electron and energy transfer mechanisms. Thus, the use of Rh(I) as a photo-reductant can allow for control of photocatalytic and photoredox systems by enabling fast energy funnelling pathways upon simple coordination changes. This approach stands in stark contrast with previous methodologies for the control of active WLA systems, since in this case the rational tuning of redox potentials rather than the use of defined, and often unpredictable, supramolecular architectures is necessary to assure switchability. Furthermore, the interaction between Rh(I) and excited Bodipy moieties can affect the energetics of redox and organometallic transformations based on the metal, thus posing new venues to expand the already prominent capabilities of Rh(I) in the field of catalysis. The use of Bodipy is an excellent complement for Rh(I) photoredox systems since the fluorophore's redox and photophysical properties can also be rationally addressed, as we have demonstrated in the development and successful use of novel 8-amino Bodipy ligand **3**. Overall, through the exploitation of Rh(I) as a photoreductant unit, we have introduced a new paradigm for the development of molecular switches, sensors and photo-mediated catalytic processes.

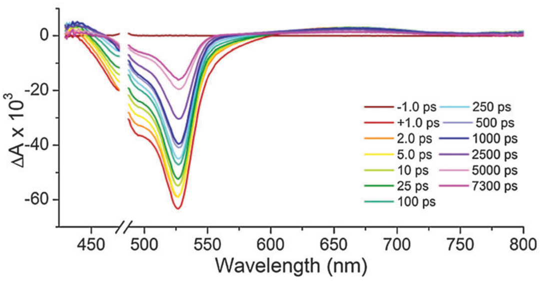

Fig. 4 Transient absorption spectra of **4** in CH_2Cl_2 (λ_{ex} = 477 nm).

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