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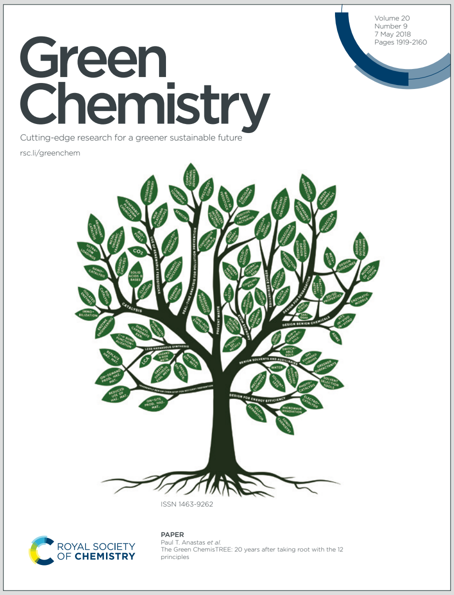

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How the sustainable solvent water unleashes the photoredox catalytic potential of ruthenium polypyridyl complexes for pinacol couplings[†]

By Robert Naumann and Martin Goez[*]

Abstract: *By complementing laser flash photolysis with product studies in visible-LED driven syntheses, we show that the one-electron reduced forms OER of tris(2,2′-bipyridine)ruthenium(II) and its more reactive derivative with 4,4′-dimethylated ligands exhibit a reductive power greater by 0.2 eV in water than in acetonitrile; and that this difference allows the reduction of carbonyl compounds, and thus pinacol couplings, in aqueous medium via ruthenium-based photoredox catalysis as an alternative to using more expensive and less photostable higher-energy complexes (e.g., of iridium). Ascorbate serves as sacrificial donor to access OER. SDS micelles or cyclodextrins as carriers help overcome solubility problems of less hydrophilic substrates, and more reactive water-soluble substrates can even be coupled at neutral pH, such that the mild conditions make the process fully sustainable.*

1 Introduction

Tris(2,2′-bipyridine)ruthenium(II), RuBpy, enjoys outstanding popularity in visible-light photoredox catalysis[1–4] owing to its long-term photostability, the favourable absorption properties of its ground state GS, the quantitative formation of its long-lived metal-to-ligand charge-transfer excited state MLCT, and the feasibility of quenching MLCT both oxidatively and reductively.[5] The intrinsic persistence of its one-electron reduced form OER would make it ideal for the reductive activation of substrates on all counts, were that persistence not accompanied by an insufficient reducing power: the standard potential $E^{\ominus}\big(\mathrm{GS/OER}\big)$ in acetonitrile or dimethylformamide is only $-1.05\,\mathrm{V}$ (*i.e.*, $-1.29\,\mathrm{V}$ *vs.* SCE),[5] and it is a general tenet that RuBpy and its derivatives are, therefore, unsuitable for catalyzing more demanding transformations such as pinacol couplings.[4,6–10] Herein, we show that the simple expedient of changing the solvent to water — tantamount to performing the reaction in a sustainable medium — suffices to overcome that limitation.

Despite an early study by Creutz and Sutin,[11] which indicated a noticeably more negative $E^{\ominus}\big(\mathrm{GS/OER}\big)$ for RuBpy in water, and subsequent evidence by Pac *et al.* that OER is capable of reducing pinacol precursors in methanol,[12] the accepted view seems to be that polar solvents, be they protic or aprotic, do not influence $E^{\ominus}\big(\mathrm{GS/OER}\big)$.[13] Consequently, instead of modifying the reductive power through the solvent, current efforts in the field of pinacol couplings have focused on much more expensive iridium,[7,8,10] rhodium,[14] and platinum complexes,[15] or tailor-made organic dyes.[6,16]

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[†] Supporting Information available: materials and methods; mechanistic details and control experiments; NMR spectra of the coupling products; other reaction types. See DOI: ...

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We substantiate the practicability of our alternative approach both by photokinetic studies on short timescales and by preparative illuminations, employing RuBpy and its more reactive derivative with 4,4′-dimethyl bipyridine ligands, RuDmb. As we will demonstrate, pinacol couplings through aqueous photoredox catalysis with these complexes are also feasible for micelle-solubilized or cyclodextrin-encapsulated substrates, hence not restricted to water-soluble precursors. To keep this report concise, we refer extensively to the Supporting Information (SI), which contains all experimental details and more involved analyses.

2 Results and discussions

The electrochemical window of water disfavours direct measurements of $E^{\ominus}(\mathrm{GS}/\mathrm{OER})$, but no such problem arises with indirect determinations that utilize the dependence of the kinetics on the thermodynamic driving force $\Delta G^{\ominus}$. The long-established Rehm–Weller equation,[17]

$$k_\mathrm{q} = \frac{k_\mathrm{d}}{1 + k'_{-\mathrm{d}}\left[\exp\left(\Delta G^{\ominus}\right) + \exp\left(\frac{\Delta G^{\ominus}}{2} + \sqrt{\left(\frac{\Delta G^{\ominus}}{2}\right)^2 + \left(\frac{\lambda}{4}\right)^2}\right)\right]} \quad (1)$$

connects the second-order rate constant k_q of an electron-transfer quenching process to $\Delta G^{\ominus}$ as the dominant controlling variable. The molecule-specific, but broadly class-characteristic, reorganization energies λ act as modifiers, and the quantities k_d and $k'_{-\mathrm{d}}$ are diffusion-related quasi-constants. In Equation 1, all energies are relative to the thermal energy RT; and $\Delta G^{\ominus}$ contains the electrochemical potentials for reducing GS and oxidizing the quencher, as well as the energy difference E^* between GS and MLCT, whereas Coulombic work terms are negligible in our case. (For auxiliary formulas and parameter estimates pertinent to this work, see SI–2.1.2).

Equation 1, or a variant thereof, features prominently in many analyses of quenching experiments on ruthenium polypyridyl complexes.[11,13,18–22] In aqueous solution, the popular[13,19–22] quenching of MLCT by phenolates ArO^- is a near-ideal model reaction on the following grounds: (i) its mechanism is a purely dynamic (SI–2.1.1) electron transfer,[19] hence Equation 1 is applicable without modifications; (ii) substitution, preferably in the 4-position only, alters the redox potential $E^{\ominus}(\mathrm{ArO}^\bullet/\mathrm{ArO}^-)$ over a wide range but leaves the quencher size and shape practically unchanged, hence decouples the variable $\Delta G^{\ominus}$ from the approximately constant quantities λ, k_d and $k'_{-\mathrm{d}}$; (iii) phenolate oxidation in water is reversible, hence $E^{\ominus}(\mathrm{ArO}^\bullet/\mathrm{ArO}^-)$ can be specified without imposing a major uncertainty on $\Delta G^{\ominus}$.

Conspicuous discrepancies between literature values of k_q for these systems under conditions reportedly identical (and the same as herein)[19,20,22] prompted us to base our determinations of $E^{\ominus}(\mathrm{GS}/\mathrm{OER})$ in water on a reinvestigation. The main plot of Figure 1 displays the result for a series of mostly 4-substituted phenolates as quenchers of the MLCT states of RuBpy and RuDmb. Details on our measurements of k_q can be found in SI–2.1.1.

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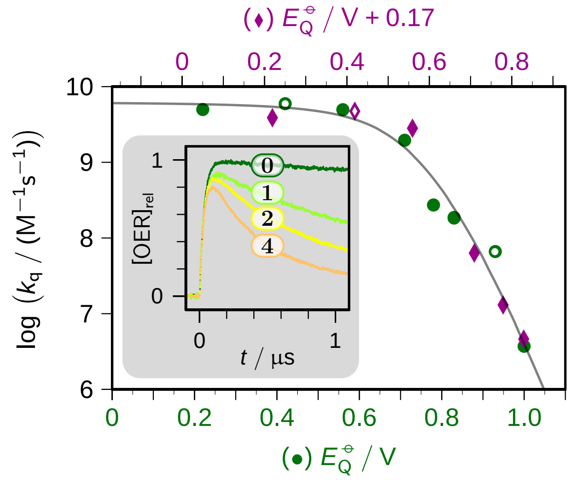

Figure 1: Kinetic determination of the OER standard potentials, and demonstration of the increased reducing power of OER in water. Main graph, log-lin plot of the rate constants k_q of reductively quenching the MLCT excited state by phenolates Q as functions of the phenolate standard potentials $E^\ominus_Q$. Filled and open symbols, 4- and 2-substituted phenolates; RuBpy, green, circles, $E^\ominus_Q$ on the lower axis; RuDmb, violet, diamonds, $E^\ominus_Q$ (increased by 0.17 V) on the upper axis. Inset, decay of OER (generated from 50 μM RuBpy and 5 mM Asc^{2-} by a 532 nm laser flash of duration 5 ns and intensity 389 mJ cm^{-2} at time t = 0; and observed through the absorbance at 505 nm) in the presence of anisaldehyde AnCHO (concentration in mM given as label on each trace); OER traces normalized to the maximum concentration (21 μM) without the aldehyde.

With $E^\ominus(ArO^\bullet/ArO^-)$ as the independent variable instead of $\Delta G^\ominus$, the data are horizontally shifted by a constant, complex-specific amount, which is the sum of E^* and the desired $E^\ominus(GS/OER)$. By the same token, shifting the data set of one complex relative to that of the other superimposes them. As the Figure illustrates, both data sets are describable by the same fit curve when the relative shift is +0.17 V for RuDmb.

The best-fit results can be summed up as follows (SI–2.1.2). Apart from the horizontal shift, the curve shape and maximum height can be reproduced with many different combinations of λ, k_d, and k'_{-d}, because these parameters are strongly correlated in the function of Equation 1, and are not independently available with sufficient precision. For any set $\{\lambda, k_d, k'_{-d}\}$ fulfilling that task, however, the best-fit absolute horizontal shift is almost the same: the driving force $\Delta G^\ominus$ becomes zero for $E^\ominus(ArO^\bullet/ArO^-)$ equal to 0.82 ± 0.006 V; and the fits cannot accommodate a less positive value. With E^* amounting to 2.12 eV for RuBpy and 2.06 eV for RuDmb,[23] this puts $E^\ominus(GS/OER)$ at -1.30 V and -1.41 V (-1.54 V and -1.65 V *vs.* SCE). Hence, OER of both complexes is more difficult to access — tantamount to being a more powerful reductant — in water than in acetonitrile, by at least 0.2 eV.

This boost by the solvent proves to be a game changer for the reduction of carbonyl compounds to their radical anions, the key step in pinacol couplings through photoredox catalysis: whereas OER of RuBpy does not react at all with benzaldehyde PhCHO in acetonitrile (SI–2.2.2),[6,7,9,10] it rapidly reduces PhCHO and even the significantly more electron-rich anisaldehyde AnCHO in homogeneous aqueous solution (rate constants, $3.7 \times 10^9\ M^{-1}s^{-1}$ and $6.0 \times 10^8\ M^{-1}s^{-1}$; SI–2.2.1.1). On a μs timescale, the inset of Figure 1 furnishes direct proof of this successful activation of AnCHO by RuBpy in water.

Owing to the higher energy of OER, a more powerful reductive quencher of MLCT has to be employed: whereas, *e.g.*, the aliphatic amine DABCO is well suited for accessing OER of RuBpy in acetonitrile (SI–2.2.2), it no longer quenches MLCT in water (SI–2.1.3). For the

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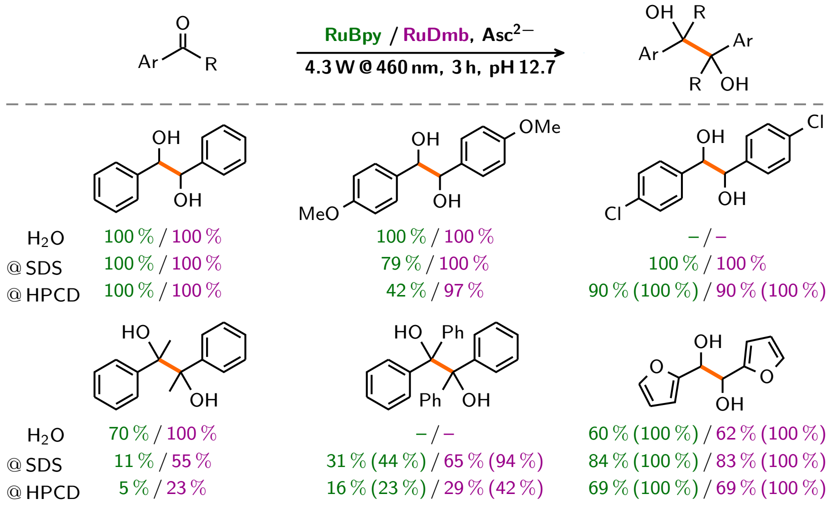
syntheses of this work, the ascorbate dianion Asc^{2-}, and at high concentrations even the monoanion $HAsc^{-}$, provided a sustainable answer with the further advantages of yielding a very unreactive electron-transfer by-product, the ascorbyl radical $Asc^{\bullet-}$; of allowing an easy separation of the pinacol products from residual Asc^{2-} or $HAsc^{-}$ by extraction with ether; and of scavenging dissolved oxygen, which makes the catalytic system very robust. Preparative examples with LED illumination have been collected in Schemes 1 and 2, and the NMR spectra of the products can be found in SI–3.



Scheme 1: LED-induced pinacol couplings in basic aqueous media (10 mM substrates, 0.1 mM ruthenium photoredox catalysts RuBpy or RuDmb , 100 mM sacrificial donor Asc^{2-}) with yields prior to workup, values in parentheses (only when side products are formed) specifying substrate consumption, and "–" denoting insufficient solubility without SDS micelles or (2-hydroxypropyl)-β-cyclodextrin HPCD.

It might be thought that the insufficient solubility of many organic substrates severely narrows the applicability of a water-based photoredox catalytic system. However, that problem can be greatly alleviated by enclosing such substrates in water-soluble carriers; and the pinacol couplings of 4-chlorobenzaldehyde or benzophenone, successful with either SDS micelles or — again sustainable — (2-hydroxypropyl)-β-cyclodextrin HPCD as carriers but impossible without them, demonstrate both the feasibility and the necessity of that modified approach. Substrates equally transformable in water alone, such as PhCHO or AnCHO, intercept OER orders of magnitude more slowly when employed in the presence of SDS or HPCD (SI–2.2.1). Yet, this merely exerts a moderate influence on the pinacol yields at end point because the only reaction competing with the substrate reduction is the recombination of OER and $Asc^{\bullet-}$, which is both self-braking (through being a second-order process)[24] and innocuous (through recovering the catalyst, and thus at worst wasting photons).

With SDS (SI–2.2.1.2), the decelerated reduction of the substrate might partially be due to a medium-induced lower OER energy because the cationic OER is localized in the Stern layer of the anionic micelle instead of in the aqueous bulk,[25] but the adverse effect on the interception rate is compensated to some degree by a much longer intrinsic persistence of OER.[24] In no case did we observe effects pointing to micellar assistance through enforced proximity. The kinetics of PhCHO @ HPCD or AnCHO @ HPCD (SI–2.2.1.3) indicate negligible radical anion formation across the cyclodextrin–water interface; rather, reduction in the

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aqueous bulk seems to dominate, with the cyclodextrin functioning as a reservoir that keeps up the equilibrium concentration of the carbonyl compound in the aqueous phase on the timescale of preparative illumination.

It has long been known that photochemical decomposition of ruthenium polypyridyl complexes involves thermally activated crossover from the polar MLCT to a less polar dd excited state, which then undergoes ligand dissociation and substitution.[26] Hence, strong MLCT quenching wards off the crossover through competition; solvents of higher dielectric constant decrease the crossover rate through increasing the MLCT–dd energy gap; and solvents or anions with lower coordinating tendency mitigate the subsequent effects at the dd stage. Aqueous Asc^{2-} is highly efficient in the first respect, as we have repeatedly shown;[23,24,27,28] and the sustainable solvent water clearly satisfies the second and third condition much better than typical nonaqueous solvents do.

Replacing RuBpy by RuDmb retains all the advantages of a ruthenium-based catalyst, in particular the stability and attractive cost, but steps up the reductive power of OER by about 0.1 eV. As can be seen in Scheme 1, this increases the pinacol yields throughout, with impressive improvements by factors between 2 and 5 for the less easily activated substrates.

OER is photoionizable with blue light, and we have already reported on the RuBpy/Asc^{2-} and RuDmb/Asc^{2-} systems in SDS micelles as LED-driven catalytic sources of hydrated electrons $\mathrm{e}_{\mathrm{aq}}^{\bullet-}$.[23,24] The fact that $\mathrm{e}_{\mathrm{aq}}^{\bullet-}$ is thermodynamically capable (E°, $-2.9\,\mathrm{V}$)[29] of initiating all the pinacol couplings of this work necessitated control experiments that can differentiate between the two pathways of carbonyl reduction, direct by OER *vs.* relayed by $\mathrm{e}_{\mathrm{aq}}^{\bullet-}$ obtained from OER. (The relayed variant featuring reduction by excited OER is ruled out by an extremely short lifetime.)[24] A clear-cut discrimination is possible by the dependence of the initial rate of product formation on the LED power P, which is a proportionality to P for the direct reaction and to $P^{3/2}$ for the relayed one.[24] Our results of SI–2.3 are uncontrovertible evidence for the exclusive operation of the direct mechanism, both in water and in aqueous SDS. In addition to a much larger beam diameter in the syntheses herein, which strongly disfavours two-photon processes,[23] the overall efficiency of accessing the activating catalyst species provides a rationalization. Whenever the monophotonic direct reduction of a substrate is sufficiently exergonic, it has a competitive advantage over the biphotonic relayed reduction where the same OER formation must be followed by an extra step (OER photoionization) possessing an intrinsically low quantum yield (0.011 with RuBpy, and 0.023 with RuDmb).[23] This is clearly reflected by the reaction times for the same volume and substrate concentration, which are now 16 times shorter than the previous ones via the relayed mechanism.

To allow comparisons, the illumination durations in Schemes 1 and 2 have been chosen such as to reach the end points of even the slowest transformations. The most readily reduced substrates, PhCHO or furfural in water, gave the same outcome when we doubled their concentrations while keeping all other parameters constant; and from the experiments of SI–2.3 it can be concluded that for PhCHO a reaction time of less than 1 h would suffice under the conditions of Scheme 1.

As expected,[30] the couplings are not diastereoselective; hence, each pinacol yield specified in the Schemes comprises the sum of dl and *meso* products. Also unsurprising,

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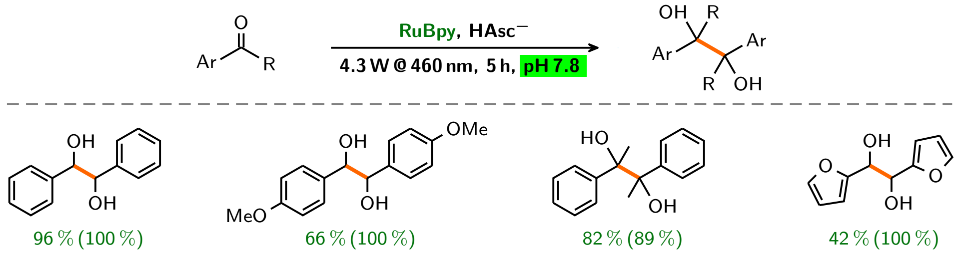
there is no influence of the catalyst on the product distribution, which is evidently determined by the chemistry following the radical anion stage. Despite the strongly basic medium in Scheme 1, some 10 % of the ascorbate weight-in concentration still exists as the monoanion $HAsc^-$ (pK_a = 11.74),[27] and the unavoidable presence of this good hydrogen donor explains why the major side products are the benzylic alcohols. Because the focus of this work lies on the earlier processes, that is, the accessibility of the radical anions through electron transfer from OER, an exhaustive characterization of the minor side products was not warranted. Where the pinacol is not the only product, we have also added the substrate consumption (parenthesized) in the Schemes to allow a breakdown to what extent the incomplete coupling is due to an insufficient reactivity of the catalyst and to additional pathways after the radical anion stage.

The very high pH of the solutions, which is dictated by the use of the dianion Asc^{2-}, is a small imperfection compromising sustainability. However, the monoanion $HAsc^-$ is also capable of quenching the MLCT state of RuBpy reductively, albeit much more slowly than does Asc^{2-} ($1.2 \times 10^7\ M^{-1}s^{-1}$ *vs.* $5.1 \times 10^9\ M^{-1}s^{-1}$),[27,31] whereas OER of RuDmb is only accessible with impractically high $HAsc^-$ concentrations. When the concentration of the sacrificial donor is doubled, pinacol couplings with RuBpy as catalyst can also be performed at the natural pH of the solutions, with slightly lengthened but still very attractive reaction durations. For the water-soluble substrates of this work, the outcome has been compiled in Scheme 2. Although benzylic alcohols are now formed with all substrates, the pinacol yields clearly show that the coupling predominates even at the high $HAsc^-$ concentrations employed.



Scheme 2: LED-induced pinacol couplings in neutral medium, with concentrations as in Scheme 1 except for 200 mM sacrificial donor $HAsc^-$, yields prior to workup and (in parentheses) substrate consumption.

3 Conclusions

As emerges from this work, the standard potential of ruthenium polypyridyl complexes lies at a tipping point for carbonyl reductions such that small shifts have a disproportionally large effect. RuBpy and RuDmb must have already reached the doorstep for successful pinacol couplings in acetonitrile such that the additional solvent-induced rise by 0.2 eV enables them to pass the threshold in water with flying colours. Striking is the fact that such a simple external change (protic *vs.* aprotic reaction medium) exerts twice as large an influence on $E^{\ominus}$(OER) as does a much more demanding internal change (dimethylation of the ligands to make the complex more electron-rich). With RuBpy in water and ascorbate as sacrificial donor, pinacol couplings can even be carried out at near-physiological pH, making these photoredox catalytic processes fully sustainable. We envisage that the approach of increasing the reductive power of ruthenium polypyridyl complexes by the solvent should be equally applicable to other reaction types — in preliminary experiments, the complexes investigated herein already proved capable of selective hydrogenations of olefinic double bonds (*e.g.*, of pyridylacrylates), dechlorinations (*e.g.*, of dichloro- and trichloroacetates), as well as cross couplings (*e.g.*, with 2-chloropyrazine as the substrate); see SI–4 for more details on all these further applications — and/or catalysts.

Conflicts of interest

There are no conflicts of interest to declare.

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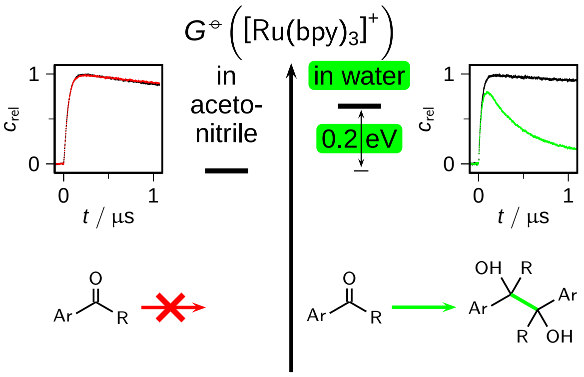

No water crisis ... but rather the opposite: this sustainable solvent increases the bandwith of ruthenium-based photoredox catalysis by allowing pinacol couplings, which are infeasible in acetonitrile or DMF.