Supplementary Information

Substituents Dependent Capability of Bis(ruthenium-dioxolene-terpyridine) Complexes Toward Water Oxidation

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Electronic Supplementary Information for Dalton Transactions

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Figure S1. CVs of complexes $[1]^0$ (a), $[2]^0$ (b), $[3]^0$ (c), and $[4]^0$ (d) in CH₂Cl₂.

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Figure S2. UV-vis-NIR spectra of $[1]^0$ (a), $[2]^0$ (b), and $[3]^0$ (c) in CH₂Cl₂ before and after addition 0.25, 0.50, 0.75, 1.00, 1.25, 1.50, 1.75, and 2.00 equiv. of *t*-BuOLi.

Details of CASSCF results

CASSCF calculations involving 12 electrons and 8 valence orbitals (i.e., CAS(12,8) calculations) in all possible configurations were carried out on the 2+ singlet states of the dihydroxo complexes with 3,6-Me₂q, 4-NO₂q and 3,5-Cl₂q ligands at their B3LYP optimized geometries. The methyl groups were used in place of the *tert*-butyl groups because of a limitation of the CASSCF procedure in Gaussian 03 of 1000 molecular orbitals. There are 336 possible singlet configurations, but in all three cases there turned out to be only 4 important ones. DFT (and other single-configuration methods) assume that there is only one important configuration. Figures S3-S5 show the final active space orbitals in order of increasing orbital energy for each of the three complexes, respectively. These eight orbitals are numbered according to their orbital energies in the molecules. The starting orbitals in each case were obtained from (single-configuration) Hartree-Fock calculations with the anthracene π orbitals exchanged to lower positions so that they did not appear in the initial active space. The eight active space orbitals were taken to be the six highest doubly-occupied orbitals plus the two lowest unoccupied orbitals.

It is noteworthy that in the case of the 3,6-Me₂q complex, the anthracene orbitals remained out of the active space, indicating that they are lower in energy than, for example, the Ru(q) π bonding orbitals (orbitals 261 and 263 in the case of 3,6-Me₂q ligands). In the case of the NO₂q complex, contributions from the anthracene π orbitals enter the active space but only in orbitals that are lower in energy than the Ru(q) π bonding orbitals (numbers 268 and 269). Finally, in the case of the Cl₂q complex, there is still stronger involvement of the anthracene π orbitals in the active space, and while the anthracene-based orbitals remain lower than the Ru(q) π bonding orbitals (numbers 277 and 278), neither of the latter orbitals is the HOMO. These trends indicate increasing stability (and localization on q) of the Ru(q) π bonding orbitals with dimethyl, nitro and dichloro substitution on the quinine ligands.

In all three cases, there are only two active pairs of electrons responsible for the four important configurations. These active pairs of electrons are, in fact, generalized valence bond (GVB) pairs that are "shared" or "split" between a bonding molecular orbital and the corresponding anti-bonding molecular orbital. It is this kind of valence configuration interaction that allows a molecular orbital description of bond dissociation to radical products. The CAS wavefunction for the case of the $3,6-Me_2q$ complex can thus be written

and that for the other two complexes can be written in similar fashion but with different active space orbitals involved in the GVB pairs. Here the vertical lines bracketing a list of active space orbitals denotes a Slater determinant, and the bar over the active space orbital number denotes beta spin (the absence of a bar, alpha spin). Note that all the configurations have closed shells, and that the contribution of each configuration to the total CAS wavefunction is c_i^2 , for i = 1-4. Under each of the active space orbitals in the Figures S3-S5 its orbital number is displayed. Under the orbital number is a column of four other numbers indicating the occupancy of that orbital in each of the four important configurations. The importance of each of these configurations, i.e., the percentage of that configuration contributing to the total wavefunction, is shown at the left of each line. So we see, for example, that the configuration that has the first six active space orbitals doubly occupied (i.e., the "principal configuration") constitutes only 53.6% of the total CASSCF wavefunction for the 3,6-Me₂q complex. The configuration that promotes the pair of electrons in orbital 263 (left-side Ru(q) π bonding orbital) to orbital 265 (left-side Ru(q) π anti-bonding orbital) constitutes 21.0% of the total wavefunction and indicates that the pair of electrons in the HOMO is one of the two GVB pairs. The configuration that promotes (from the principal configuration) the pair of electrons in orbital 261 (right-side $Ru(q)\pi$ bonding orbital) to orbital 264 (right-side $Ru(q)\pi$ anti-bonding orbital) constitutes 18.2% of the CASSCF wavefunction and indentifies the second GVB pair of electrons. In the final configuration, which constitutes only 7.2% of the CASSCF wavefunction, both GVB pairs are promoted from their bonding orbitals to the corresponding anti-bonding orbitals. These same GVB pairs define the important configurations in the other complexes as well, indicating substantial but not dominant radical character (i.e., Ru(III) and sq) in all the complexes.

$$\begin{split} \Psi_{\text{CAS}(12,8)} &= c_1 \left| 1 \,\overline{1} \, 2\overline{2} \, 3\overline{3} \, 4\overline{4} \, 5\overline{5} \, 6\overline{6} \right| + c_2 \left| 1 \,\overline{1} \, 2\overline{2} \, 3\overline{3} \, 4\overline{4} \, 5\overline{5} \, 8\overline{8} \right| \\ &+ c_3 \left| 1 \,\overline{1} \, 2\overline{2} \, 3\overline{3} \, 5\overline{5} \, 6\overline{6} \, 7\overline{7} \right| + c_4 \left| 1 \,\overline{1} \, 2\overline{2} \, 3\overline{3} \, 5\overline{5} \, 7\overline{7} \, 8\overline{8} \right| \end{split}$$

The assignment of formal oxidation states to the Ru and q moieties in the complexes depends both on the stability of the Ru(q) π orbitals and on the importance of the excited configurations. As can be seen in the results shown in Figures (S3-S5), the contributions of excited configurations doesn't change very much (it ranges from 47.5% to 45.6% with no obvious trend) with ligand substitution, but it is substantial in all cases. The bonding in these complexes cannot be described by a single electronic configuration. Similar calculations on [Ru₂(O)₂(3,6-Me₂q)(btpyan)]² to determine the nature of the bonding in the possible isomers

 $[(Ru^{IV}=O)_{2}(3,6-Me_{2}sq)_{2}(btpyan)]^{2+} and [(3,6-Me_{2}q)Ru^{II}-(\mu-O_{2})-Ru^{II}(3,6-Me_{2}q)(btpyan))^{2+} show that, as proposed in Scheme 6, the latter isomer is energetically favoured owing to multi-configurational effects.¹$



Figure S3. Active space orbitals and important configurations of $[Ru_2(OH)_2(3,6-Me_2q)_2(btpyan)]^{2+}$ for a CAS(12,8) calculation.



Figure S4. Active space orbitals and important configurations of $[Ru_2(OH)_2(3,5-Cl_2q)_2(btpyan)]^{2+}$ for a CAS(12,8) calculation.



Figure S5. Active space orbitals and important configurations of $[Ru_2(OH)_2(4-NO_2q)_2(btpyan)]^{2+}$ for a CAS(12,8) calculation.

References 1. Muckerman, J. T.; Tsai, M.-K.; Fujita, E.; Wada, T.; Tanaka, K.; in preparation.