Proton-coupled electron transfer from a luminescent excited state†

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A luminescent cationic iridium complex with a 2,2′-biimidazole ligand forms hydrogen-bonded 1 : 1 adducts with benzoate anions; photoexcitation of the metal complex in presence of 3,5-dinitrobenzoate triggers a proton-coupled electron transfer.

Proton-coupled electron transfer (PCET) plays a pivotal role in many biologically important processes, for example in photosynthesis, respiration, and nitrogen fixation.[1] Due to the complexity of the involved biological systems, the design and synthesis of simple models for mechanistic PCET investigations is desirable. Various approaches have been explored toward this end:[2] For example, significant effort has been devoted to the investigation of functional models for the PCET reactivity of the Tyr_Z residue of photosystem II.[3,4] Others have focused on (ground-state) PCET reactions in metal biimidazoline complexes that do not aim to mimic any naturally occurring PCET interfaces but that allow unusually detailed fundamental insights.[5] Yet other researchers have investigated PCET reactions that occur from electronically excited states,[6,7,8] for instance across hydrogen-bonded amidinium-carboxylate ion pairs that resemble the aspartic acid-arginine salt bridges in proteins.[9]

In searching for new systems for phototriggered PCET investigations we reasoned that d^6 metal complexes of 2,2′-biimidazole (biimH₂) would be particularly interesting candidates. Prior spectroscopic studies on ruthenium(II) complexes with this ligand indicated that they possess the following desirable properties: (i) the MLCT excited states of these molecules are emissive and long-lived (>100 ns), (ii) in this excited state the metal complex becomes a potent electron donor, (iii) the optical absorption and emission spectra of the complex depend upon the protonation state of the 2,2′-biimidazole ligand.[10,11] This latter feature, commonly observed for various kinds of biimH₂ metal complexes, is of pivotal importance for our study as it provides a spectroscopic handle for direct observation of proton release from these molecules. Our choice fell upon the iridium(III) bis(2-(p-tolyl)pyridine) 2,2′-biimidazole complex IrbiimH₂⁺ shown in Scheme 1. This cyclometalated Ir complex has the important advantage over Ru polypyridines that its excited state is about an order of magnitude longer lived, thereby making phototriggered redox- and acid-base reactions more competitive with relaxation to the ground state. An excited state redox potential of -1.4 V vs. SCE can be estimated for this complex based on cyclic voltammetry and optical absorption/emission experiments. This is sufficiently reducing for electron transfer reactions to occur with various nitroaromatics, including the 3,5-dinitrobenzoate anion (dnb⁻). Based on prior evidence for the formation of 1 : 1 adducts between cationic 2,2′-biimidazole complexes and a variety of different anions,[11–15] the dnb⁻ was anticipated to form hydrogen-bonded donor–acceptor pairs with IrbiimH₂⁺, thereby allowing for relatively strong electronic coupling between the two redox partners. Furthermore, with the 2,2′-biimidazole nitrogen-protons already involved in hydrogen-bonds, they may be particularly prone to phototriggered transfer to the benzoate.[16]

IrbiimH₂⁺-dnb⁻ salt bridges are indeed observed in the crystal structure of our donor–acceptor couple (Fig. 1).† The two N···O distances of 2.632(4) and 2.640(4) Å are somewhat shorter than those previously observed in other ion pairs of this or similar type.[13,14] Evidence for the existence of hydrogen-bonded IrbiimH₂⁺-dnb⁻ pairs in solution comes from ¹H NMR experiments. The signals of the protons directly involved in the salt bridge cannot be observed, but benzoate addition to a solution of the iridium complex leads to shifts of the H^4 and H^5 protons of the 2,2′-biimidazole ligand as well as to shifts of some of the 2-(p-tolyl)pyridine signals. Thus, a ¹H NMR titration experiment allows determination of an association constant of $\log(K_a/M^{-1}) = 5.5$ for our ion pair in CD_2Cl_2 (see ESI†). This value is comparable to those previously reported for an amidinium-benzoate (5.7) and a Ru-biimidazole-carboxylate system (6.0) in the same solvent.[9,12]

After photoexcitation of the iridium complex at 410 nm a luminescence spectrum with two characteristic band maxima at 484 and 514 nm is observable (black trace in Fig. 2(a) and (b)). In the PF₆⁻ salt of IrbiimH₂⁺, i.e. in the absence of dnb⁻, this emission has a lifetime of 1.2 μs in deoxygenated CH_2Cl_2
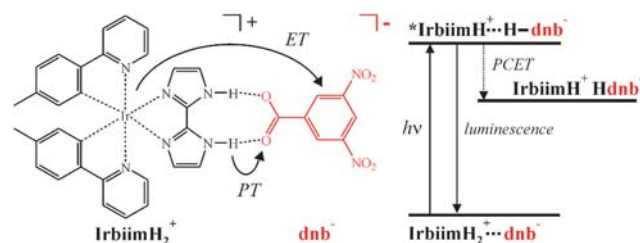
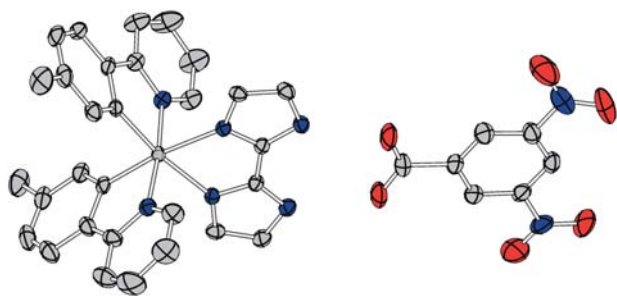[a] Department of Inorganic, Analytical and Applied Chemistry, University of Geneva, 30 quai Ernest-Ansermet, CH 1211 Geneva 4, Switzerland. E-mail: oliver.wenger@unige.ch; Fax: +41(0)22 379 60 69; Tel: +41(0)22 379 60 51
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Scheme 1

Fig. 1 X-Ray structure of the hydrogen-bonded $IrbiimH_2^+$-dnb^- ion pair. Thermal ellipsoids are drawn at the 50% probability level.
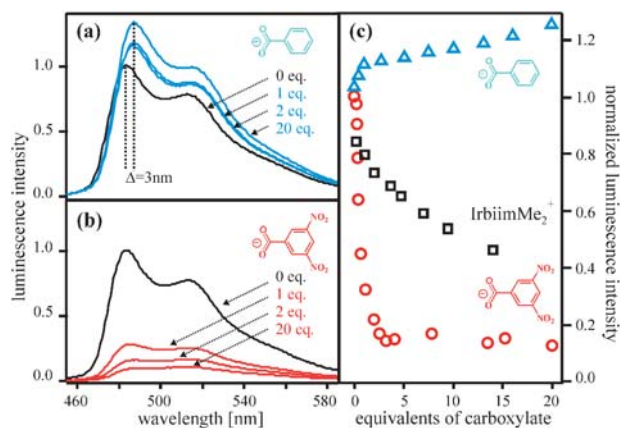

Fig. 2 (a) Luminescence of $IrbiimH_2^+$ as a function of increasing amounts of unsubstituted benzoate. (b) Luminescence of the same complex at various 3,5-dinitrobenzoate (dnb^-) concentrations. (c) Normalized iridium luminescence intensity as a function of number of equivalents of carboxylate added (blue triangles: unsubstituted benzoate, red circles: dnb^-). The black squares represent data obtained for an N,N'-dimethylated iridium complex ($IrbiimMe_2^+$) titrated with dnb^-.

solution. This long lifetime and the emission band shape are indicative of an emissive excited state that has mixed MLCT and π–π* intraligand (IL) character as frequently observed for cyclometalated Ir complexes.[17] As seen from Fig. 2(b), dnb^- addition leads to a dramatic decrease of the iridium luminescence intensity (red traces) which is interpreted as oxidative quenching of the MLCT/IL state: Electron transfer from $IrbiimH_2^+$ to the dnb^- becomes an efficient nonradiative deactivation pathway.[18] Importantly, 65% of the initial luminescence intensity is quenched upon addition of the first equivalent of dnb^- (red circles in Fig. 2(c)), whereas the 19 subsequently added equivalents only have a minor additional influence. Two effects must be responsible for this: (i) The formation of tightly bound $IrbiimH_2^+$-dnb^- ion pairs when dnb^- is added, (ii) the fact that electron transfer is very efficient within these pairs. This is supported by two independent series of control experiments: When the iridium complex is methylated at the two noncoordinating N-atoms, it results a species ($IrbiimMe_2^+$) that has essentially the same photoredox properties as the parent $IrbiimH_2^+$ complex ($E^{0*} \approx -1.4$ V; $\tau \approx 1.2$ μs), but hydrogen-bonding to dnb^- is now impossible. Consequently, oxidative quenching of the $IrbiimMe_2^+$ by dnb^- is much less efficient and follows more or less ordinary

bimolecular quenching behavior (black squares in Fig. 2(c)). To illustrate this point it may be noted that it takes more than 20 equivalents of dnb^- to quench the $IrbiimMe_2^+$ luminescence to the same extent the $IrbiimH_2^+$ luminescence is quenched with only 1 equivalent of dnb^-. In the second series of control experiments the luminescence of the $IrbiimH_2^+$ parent complex was measured in the presence of variable amounts of unsubstituted benzoate (blue traces in Fig. 2(a)). ^{1}H NMR experiments indicate that this anion also forms a salt-bridge with the iridium complex. However, the luminescence titration experiment shows that the redox inactive benzoate does not quench the iridium luminescence (blue triangles in Fig. 2(c)).

Closer inspection of the data in Fig. 2(a) and (b) reveals that not only the iridium luminescence *intensity*, but also the luminescence *spectra* are susceptible to the salt-bridge formation: Upon addition of 20 equivalents of unsubstituted benzoate to a CH_2Cl_2 solution of $IrbiimH_2^+PF_6^-$, the emission band maximum red-shifts by 3 nm (Fig. 2(a)). This indicates N–H proton delocalization away from the iridium complex. For comparison, when the PF_6^- salt of $IrbiimH_2^+$ (black trace in Fig. 3(a)) is mono-deprotonated with tetrabutylammonium hydroxide, the resulting $IrbiimH$ species emits with a maximum that is 12 nm red shifted (green trace in Fig. 3(a)). It follows that the position of the emission band maximum contains information on the protonation state of the iridium complex: small red-shifts (~ 3 nm) are indicative of the implication of N–H protons in hydrogen bonds, whereas larger red shifts (~ 12 nm) indicate full proton release. With this knowledge at hand we now discuss the spectral changes that are observed upon dnb^- addition to $IrbiimH_2^+$ in Fig. 2(b) (red traces). In these emission spectra, the intensity ratio of the two band maxima at 484 and 514 nm decreases from a value of ~ 1.3 at 0 equivalents of dnb^- to ~ 0.85 at 20 equivalents (red circles in Fig. 3(c)). The spectrum obtained at 2 equivalents of dnb^- is reproduced in Fig. 3(b) (red trace).
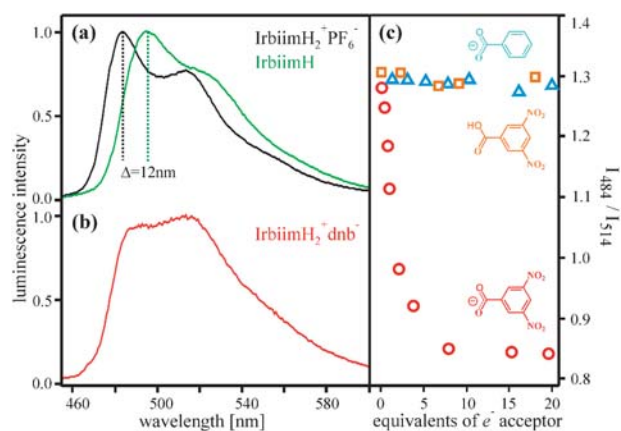
Fig. 3 (a) Luminescence of the doubly protonated $IrbiimH_2^+$ (black trace) and the singly protonated $IrbiimH$ complex (green trace, arbitrarily scaled). (b) Luminescence of the hydrogen-bonded $IrbiimH_2^+$-dnb^- ion pair. (c) Ratio of the iridium luminescence intensities at 484 nm and 514 nm as a function of benzoate concentration: Blue triangles: unsubstituted benzoate, red circles: dnb^-. Orange squares represent data obtained for the dinitrobenzoic acid (Hdnb) electron acceptor.

The bandshape of a luminescence spectrum is governed by the distortion of the ground and excited state potentials relative to one another. Generally, this distortion occurs along multiple nuclear coordinates, but as the deprotonation experiment shows, the N–H coordinate plays a particularly important role in the systems considered here. The spectral redistributions in Fig. 2(b) and Fig. 3(c) are therefore interpreted as evidence for significantly more important proton delocalization away from the biimidazole ligand than is the case for the unsubstituted benzoate. This interpretation is consistent with the observed red-shift of the emission barycenter and the increase of the emission bandwidth, i.e., an increase in the Huang–Rhys parameter. It is further consistent with the absence of these effects in control experiments where $IrbiimH_2^+$ is titrated with Hdnb (3,5-dinitrobenzoic acid) and $IrbiimMe_2^+$ with dnb^- (orange squares in Fig. 3(c)). The emissive species in Fig. 3(b) may thus be described reasonably as an $IrbiimH^+ \cdots H\text{-}dnb^-$ tautomeric form of the salt-bridge interface (Scheme 1), whereas for the unsubstituted benzoate it is rather an $IrbiimH_2^+ \cdots benzoate^-$ species. A very recent paper reports on a similar observation in amidinium-carboxylate interfaces.[19,20]

Thermodynamic arguments are useful to rationalize why the photoinduced electron transfer from $IrbiimH_2^+$ to dnb^- is indeed expected to be coupled to proton transfer: the acidity of N–H protons in metal complexed $biimH_2$ ligands typically increases by 3–4 orders of magnitude upon one-electron oxidation of the metal,[10] and the $dnb^{\bullet-}$ radical is about 3 orders of magnitude more basic than dnb^-.[21] Conversely, deprotonation of a $biimH_2$ complex typically lowers its redox potential by ~ 300 mV per proton,[22,23] and dinitrobenzoic acid (Hdnb) is easier to reduce than the dnb^- anion by about 200 mV.[21]

In conclusion, the present communication demonstrates that an iridium complex with a 2,2′-biimidazole ligand forms hydrogen-bonded 1 : 1 adducts with benzoate anions. The resulting salt-bridged ion pairs are useful model systems for PCET investigations. Two particularly favorable features of these systems are (i) the possibility to phototrigger the overall reaction, and (ii) that proton delocalization can be monitored directly by optical spectroscopy due to the close proximity of the acidic N–H protons to the metal center.

Notes and references

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