

Ion-Pair Effects in Photoredox Chemistry

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Summary: Reported in Nature Chemistry, Rumbles, Reid and collaborators employ time-resolved dielectric-loss spectroscopy to probe the effect of counterions on excited-state relaxation kinetics and charge transfer selectivity of a cationic photoredox catalyst. This ion-pairing phenomenon may be used to control excited-state electron transfer and affect the branching points of photoredox mechanisms.

The revival of photochemistry as a synthetic tool, especially in the area of photoredox catalysis, has enabled unprecedented reactivities derived from the manipulation of thermodynamically stable bonds to produce value-added complex targets. The superior reactivity of photocatalysts to activate stable bonds is enabled by harnessing the energy of visible and ultra-violet photons.¹ Among the versatile photoinduced electron transfer-initiated organic transformations, cationic iridium- and ruthenium-polypyridyl complexes are the most widely used photocatalysts due to their long-lived triplet metal-to-ligand charge transfer (MLCT) states.² Fine tuning the electronic properties of the primary coordination sphere of the ligands has become a routine practice to modulate excited-state energy, lifetime, and redox potential.² However, unlike redox catalysis, which has exploited secondary coordination sphere effects to great advantage,³ the effect of the secondary coordination environment of photoredox catalysts is underexplored. The influence of ion-pairing in electron transfer reactions has long been established,⁴ with accompanying theory to explain its effect on observed reaction kinetics.^{4–6} In the area of organometallic catalysis, the counterion has been shown to be essential for reaction regio- and stereo- selectivity.⁷ Notwithstanding, in photoredox catalysis, the counterion is treated merely as a spectator to balance the charge of the complex. The type of counterions is usually determined from a solubility consideration. Large non-coordinating anions, such as PF₆[−], are preferred over small and hard ones, such as Cl[−], to obtain a higher concentration of those photocatalysts in non-polar organic solvents. Additionally, different anions can adjust the excited state lifetime and the redox potential of a divalent Ru(II)-bipyridine derivative.⁸ Recently, an ion-pair intermediate comprising an iridium photocatalyst and a phosphate base has been reported to be responsible for H-atom abstraction from C(sp³)–H bonds; solid state crystallography confirms directional hydrogen bonding interaction between the bipyridine ligand on the cationic iridium complex and the phosphate anion.⁹ Despite these early examples, detailed mechanistic insights to quantify the role of counterions in photoredox reactions remain to be revealed.

Rumbles, Reid and collaborators¹⁰ have recently utilized a novel spectroscopic technique to quantify the ion-pair contribution to photoredox catalysis. Time-resolved dielectric-loss (TRDL) spectroscopy has been shown as an incisive method to measure the charge density distribution in the ground- and excited-state of an [Ir(dF(CF₃)ppy)₂(dtbpy)]⁺ (abbreviated as [Ir(^tBu)]⁺)

photocatalyst with two differing anions — hexafluorophosphate (PF_6^-) and tetrakis[3,5-bis(trifluoromethyl)phenyl] borate (BARF_4^-) (Figure 1A). The ground-state dipole moment (μ) of 10.7 D for $[\text{Ir}(\text{tBu})]\text{PF}_6$ and 4.82 D for $[\text{Ir}(\text{tBu})]\text{BARF}_4$ are revealed from the imaginary dielectric constant (ε'' , in $\varepsilon_r = \varepsilon' - i\varepsilon''$) of the two compounds in 1,4-dioxane solvent. The distinct dipole moment of the ion-pairs is consistent with the bulkier BARF_4^- resulting in a solvent-separated ion-pair, with separate cation and anion movements governed by independent Brownian motion. Accordingly, the smaller dipole moment of $[\text{Ir}(\text{tBu})]\text{BARF}_4$ originates primarily from the asymmetric charge density distribution about the $[\text{Ir}(\text{tBu})]^+$ cation owing to its non-specific interaction with the anion. Conversely, a contact ion-pair with PF_6^- can arise due to its smaller size as compared to the $[\text{Ir}(\text{tBu})]^+$ cation. This tightly bound ion-pair tumbles as a single molecular unit in solution. The measured overall dipole moment (μ_{overall}) is the vector sum of intramolecular dipole moment (μ_{intra}), resulting from $[\text{Ir}(\text{tBu})]^+$, and the intermolecular dipole moment (μ_{inter}), due to the separation between the ionic charge centers. Quantitatively, the absolute value of μ_{inter} is larger than μ_{intra} for equal-charge counterions since they must remain further from the charge center than the associated ligands. The specific interaction of the PF_6^- counterion imparts a greater intermolecular dipole that overrides, both numerically and directionally, the intramolecular one.

Beyond a static measurement, the evolution of transient dipole moments of the two compounds is ascertained by measuring the complex permittivity at different time delays after initial photoexcitation. The real and imaginary permittivity traces of both compounds fit a two-state sequential kinetic model (Figure 1B). Initially, in state A, both compounds show large increase of ε' and slight increase of ε'' , indicating a considerable change in polarizability volume with a slight increase in the dipole moment of the $[\text{Ir}(\text{tBu})]^+$ excited state. The former is due to a ligand-ligand charge transfer (LLCT) character, which leads to the dipole moment shifting among the $\text{dF}(\text{CF}_3)\text{ppy}$ and dtbpy ligands. After 50 ns, state B dominates in both compounds. The fully relaxed MLCT state of $[\text{Ir}(\text{tBu})]\text{BARF}_4$ in state B exhibits a transient dipole moment of (5.2 ± 0.1) D, which is much smaller than the expected dipole moment (16.8 D) from a fully charge-separated MLCT excited-state model with an integer charge localized on the dtbpy ligand moiety. The discrepancy indicates the partial charge transfer nature of the MLCT excited state, resulting from complex frontier orbital mixing. An intriguing observation is that in state B, $\Delta\varepsilon''$ is positive for $[\text{Ir}(\text{tBu})]\text{BARF}_4$, but negative for $[\text{Ir}(\text{tBu})]\text{PF}_6$. To rationalize this observation, a rapid contact ion-pair reorientation is proposed to occur in the MLCT excited-state of $[\text{Ir}(\text{tBu})]\text{PF}_6$ (Figure 1B). In particular, reorganization of PF_6^- mitigates the intramolecular dipole moment of $[\text{Ir}(\text{tBu})]^+$ by virtue of minimizing the electrostatic energy. Observing such excited-state dynamics related to counterion movement is intrinsically challenging with transient absorption spectroscopy, thus establishing the unique value of applying TRDL in studying secondary coordination effects on photoredox catalysis.

This $[\text{Ir}(\text{tBu})]^+ - \text{PF}_6^-$ ion-pair stabilization of the excited-state is corroborated spectroscopically. A bathochromic shift of the emission spectrum and shortened lifetime of the emitting state is observed for the PF_6^- as opposed to BARF_4 compound. The compounds also show differences in Stern–Volmer quenching experiments. In the presence of a reductant, $[\text{Ir}(\text{tBu})]\text{BARF}_4$ exhibits a greater reductive quenching rate constant; in the presence of an oxidant, $[\text{Ir}(\text{tBu})]\text{PF}_6$ exhibits the

higher reactivity. This dependence on anion character of reductive vs. oxidative excited-state charge transfer kinetics is consistent with the steric shielding and the electrostatic stabilization of charge build-up in a tightly bound ion-pair complex. In this regard, the tuning of counterions adds a handle to control the initial quenching event in photoredox catalysis.

In summary, flash photolysis TRDL spectroscopy has been applied to study the ground-state charge density distribution and excited-state reorganization dynamics of a cationic iridium photocatalyst with a tightly bound counterion versus a solvent-separated anion. Drastically distinct transient dipole moment evolution is observed due to the counterion reorganization arising from a contact ion-pair. Differences in a contact- vs solvent-separated ion-pair are manifested in the excited-state electronic structure, relaxation dynamics and photoinduced electron transfer kinetics. We anticipate this study, exhibiting the power of TRDL, will inspire further research in chemo- and stereoselective excited-state reactions controlled by judicious choice of the photocatalyst counterion.

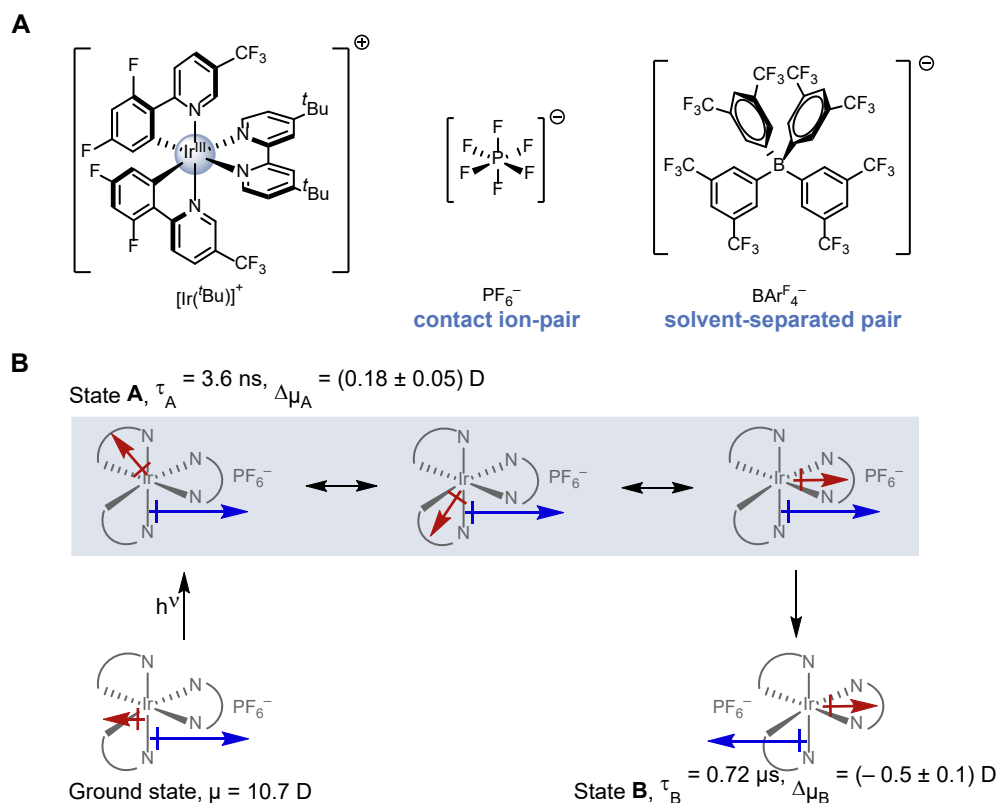


Figure 1. Elucidating counterion effects and transient dipole moments of photocatalysts. (A) Photocatalyst structure and (B) excited state dipole-moment (intramolecular, red; and intermolecular, blue) evolution as deduced from time-resolved dielectric-loss (TRDL) spectroscopy. Data from ref 10.

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