Unravelling the Super-Reductive State of Iridium Photoredox Catalysts

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ABSTRACT: Harnessing the excited state of reduced species has long posed a challenge in the field of photocatalysis. This study presents the isolation and characterization of 1-electron reduced iridium complexes commonly employed in photoredox catalysis. Stochiometric reactions unveiled an unprecedented super-reductant ability for the isolated complexes under light irradiation, reaching potentials below −3 V vs SCE. Notably, the reduced iridium complex can also be electrochemically generated *in situ* with analogous super-reductant ability, enabling electro(photo)catalysis. Experimental and computational studies reveal that photoreactivity rises from intrinsic excitation of the reduced $(bpy^{\bullet-})^*$ ligand within the iridium complex, while the metal center acts as a spectator. Corroborating this finding, the organic salt $\mathbf{Li^+bpy^{\bullet-}}$ exhibited equivalent super-reducing reactivity under photochemical conditions. Our findings shed light on the access to the super-reductant states of iridium photoredox catalysts and other metalated bipyridines, opening new opportunities for electro(photo) synthetic methodologies.

Photoredox catalysis has emerged as a powerful synthetic tool. However, attempts to provide a predictable reactivity often fail by evaluation based solely on redox potentials and lifetimes to explain reactions that proceed despite seemingly unfavorable conditions.[1,2] Certainly, recent reports suggest the involvement of non-innocent intermediates and less intuitive mechanisms, even in the long studied and prototyped iridium complexes.[3-8]

For instance, an intriguing example of such photoredox reactivity is observed with $\mathbf{[Ir(ppy)_2(^{tBu}bpy)]PF_6}$ ($\mathbf{^{tBu}PC_{Ir}^+}$; ppy = phenylpyridine, ^{tBu}bpy = 4,4′-di-tert-butyl-2,2′-dipyridyl). This complex has attracted significant interest due to its remarkable ability to activate substrates with reduction potentials up to –2.7 V, surpassing the reductive capacity of its excited state (–0.96 V) or the reduced iridium species (–1.51 V).[5] A proposed explanation for this unexpected reactivity is based on the partial hydrogenation of $^{tBu}PC_{Ir}^+$ with *in-situ* generated radical species, leading $^{H-tBu}PC_{Ir}$ (Figure 1a).[3,6] However, the calculated redox potential for $^{H-tBu}PC_{Ir}$ (E_{red} = -1.97 V) does not align with the observed reactivity with substrates displaying reduction potentials up to -2.7 V.[4]

In this line, König *et al.* reported that $^{tBu}PC_{Ir}^+$ participates in assembly-promoted single electron transfer (APSET) towards non-activated alkyl chlorides in microstructured aqueous solutions. The mechanistic hypothesis for this process involves the pre-aggregation between substrates and *in situ* reduced $^{tBu}PC_{Ir}^0$.[7] Then, a second photon absorption by $^{tBu}PC_{Ir}^0$ undergoes an outer sphere electron transfer (ET) to the substrate (Figure 1b), avoiding back ET to the electron donor. However, experimental evidence supporting a multiphoton pathway is yet to be reported.

Additionally, Wenger *et al.* reported on the use of the anionic iridium catalyst $\mathbf{Na_3[Ir(^{SO3}ppy)_3]}$ (^{SO3}ppy = -(5'-sulfonatophenyl)pyridine), which can generate solvated electrons in aqueous media ($\mathbf{e^-_{aq}}$, $E_{red} \sim$ -3.1 vs SCE) through two consecutive photon absorption steps, as supported by transient absorption spectroscopy studies (Figure 1c).[7] While solvated electrons have been detected and used in other solvents, such as ammonia,[8,9] methanol,[10,11] tetrahydrofuran (THF),[12] or acetonitrile,[13] the application of solvated electrons in non-aqueous media lacks robust evidence in the context of photocatalysis, posing a challenge for their practicality beyond aqueous systems. In the process of finalizing this manuscript, G. D. Scholes, R. R. Knowles and coworkers reported the isolation of a family of PC_{Ir}^0 metal complexes and found that the exited state has a very short lifetime but exhibits photoinduced bimolecular electron transfer reactivity with phenyl bromide (−2.4 V vs SCE) to yield quantitative formation of biphenyl upon purple or blue light (390 or 425 nm) irradiation.[9]

Motivated by the widespread use of heteroleptic iridium photoredox catalysts, such as $\mathbf{[Ir(ppy)_2(bpy)]PF_6}$, ($\mathbf{PC_{Ir}^+}$, bpy = bipyridine) in synthetic methodologies,[8,10-18] we aim a systematic investigation to uncover the mechanisms responsible for activating energetically demanding substrates. While previous studies have heavily relied on spectroscopic measurements, this study takes a direct approach by successfully isolating the elusive species generated through reductive quenching, specifically $\mathbf{[Ir(ppy)_2(bpy)]^0}$ ($\mathbf{PC_{Ir}^0}$) and $\mathbf{[Ir(^{Me}ppy)_2(bpy)]^0}$ ($\mathbf{^{Me}PC_{Ir}^0}$). The isolation of PC_{Ir}^0 and $^{Me}PC_{Ir}^0$ provides an unprecedented opportunity to explore their reactivity in detail. By addressing these knowledge gaps, this study aims to shed light on the potential of harnessing the excited state of reduced iridium complexes in photoredox catalysis and to elucidate the origin of the observed super-reductant ability in isolated complexes.
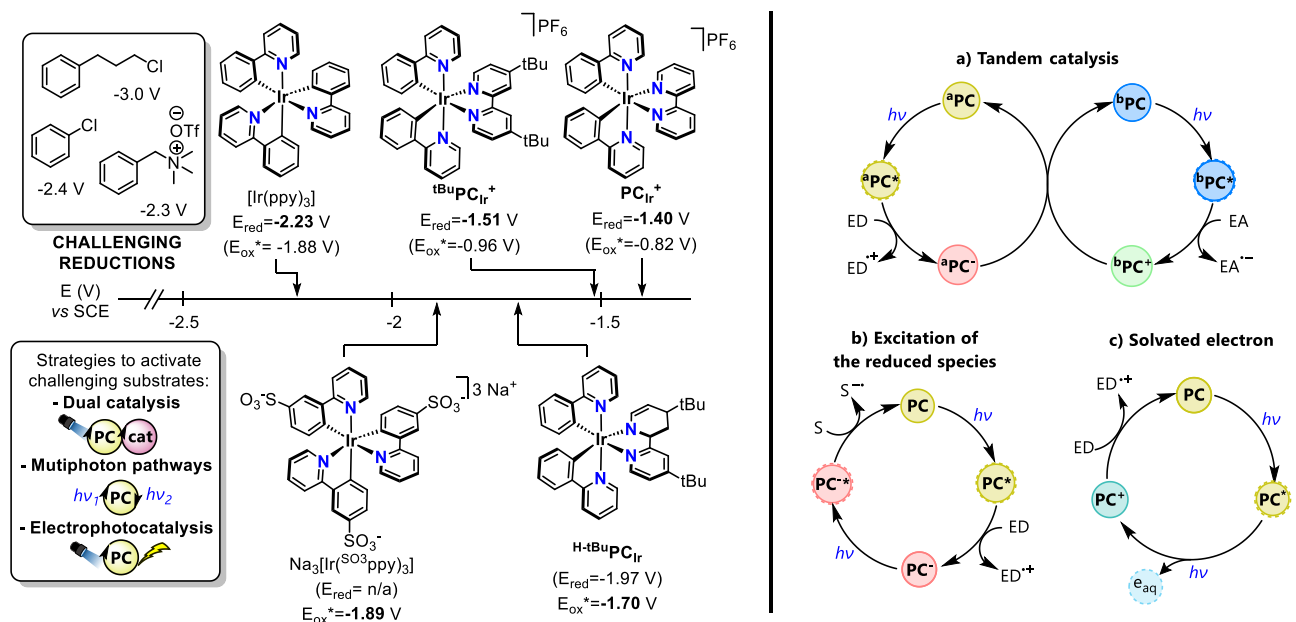
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Figure 1. Left) Selected structures and redox properties of iridium complexes[19] representative for reductive photocatalysis. Right) Recently proposed multiphoton mechanisms (**a**, **b** and **c**) for iridium-based photocatalysis. PC = photoredox catalyst, ED = electron donor, EA = electron acceptor, S = substrate.

We initiated our research focused on identifying conditions to effectively isolate species resultant from the 1-electron-reduction of heteroleptic iridium photocatalysts. Using Na/Hg alloy as an electron reduction agent, we successfully isolated the reduced species $[Ir(ppy)_2(bpy)]^0$ ($\mathbf{PC_{Ir}^0}$, $E^{0/+}$ = -1.4 V vs SCE) in 75% yield (Supporting Information, Section 4). Although crystals of $\mathbf{PC_{Ir}^0}$ were obtained, their high symmetry prevents differentiation between the C and N atoms coordinated to the iridium centre by X-ray diffraction crystallography. To overcome this, we crystallized an analogous complex with a methyl group substituted phenylpyridine ligand ($\mathbf{^{Me}PC_{Ir}^0}$, Figure 2b). Analysis of $\mathbf{^{Me}PC_{Ir}^0}$ crystal structure revealed a significant shortening of the C–C distance between the two rings in the bipyridine ligand, from 1.48 Å (±0.005 Å) to 1.35 / 1.39 Å (±0.02 and ±0.018 Å, respectively. Two molecules found in the unit cell). This geometrical change is consistent with the localization of an additional electron in the bipyridine ligand, giving rise to a radical anion character (bpy•−). Further characterization by UV-vis, EPR, and EXAFS, provides additional evidence for the electron mainly delocalized in the bipyridine ligand and the iridium centre in oxidation state III ($[Ir^{III}(^{Me}ppy)_2(bpy^{•−})]$, Supporting Information, Sections 5-7).[20, 21] The presence of the radical is also supported by density functional theory (DFT) calculations, predicting a SOMO located almost exclusively in the bpy•−fragment (Supporting Information Section 17) as proposed in previous literature.[22]

After successfully isolating and characterizing $\mathbf{PC_{Ir}^0}$ and $\mathbf{^{Me}PC_{Ir}^0}$, we could also produce them by electrochemical and photochemical methods (Figure 2 and Supporting Information Sections 4 and 8). In particular, the reductive quenching of the excited state with TBA$_2$ox is an efficient alternative protocol to isolate the reduced iridium complexes (Supporting Information, Section 4). On the other hand, we also found that the *in-situ* generation of the reduced iridium complexes chemically with Na/Hg alloy is a practical and convenient way to study its reactivity further. Although $\mathbf{PC_{Ir}^0}$ and $\mathbf{^{Me}PC_{Ir}^0}$ could also be obtained using KC$_8$, the remaining unreacted KC$_8$ was challenging to remove, complicating the subsequent photochemical studies.
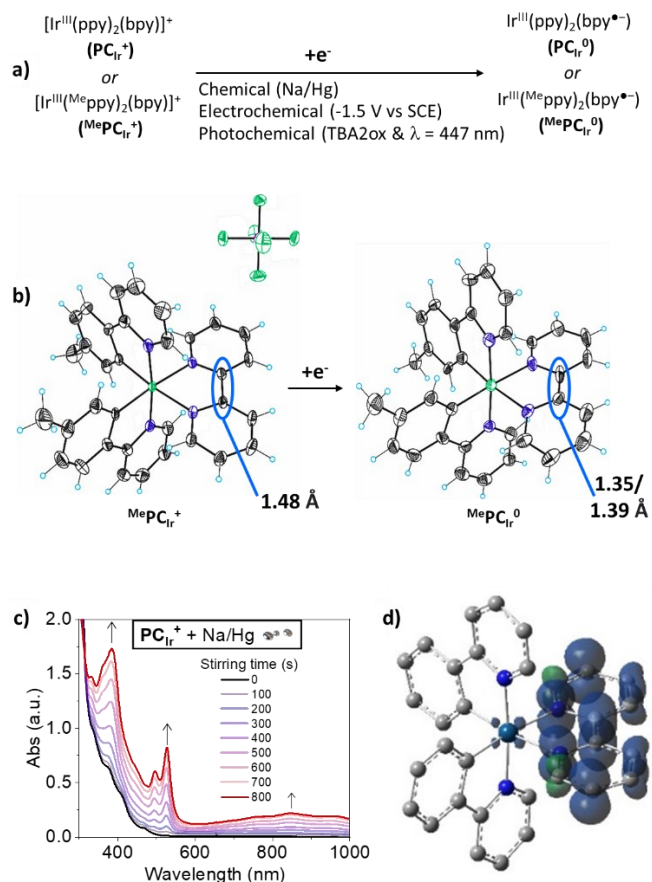

Figure 2. a) General reduction methods to form $\mathbf{PC_{Ir}^0}$ and $\mathbf{^{Me}PC_{Ir}^0}$ from $\mathbf{PC_{Ir}^+}$ and $\mathbf{^{Me}PC_{Ir}^+}$ **b)** $\mathbf{^{Me}PC_{Ir}^+}$ and $\mathbf{^{Me}PC_{Ir}^0}$ X-ray crystal structures. The C−C bond distance decrease between the **bpy** rings upon reduction is highlighted. Thermal ellipsoids are shown at 50% probability. **c)** changes in the absorption spectra observed during the chemical reduction from $\mathbf{PC_{Ir}^+}$ to $\mathbf{PC_{Ir}^0}$. **d)** calculated spin density of $\mathbf{PC_{Ir}^0}$.
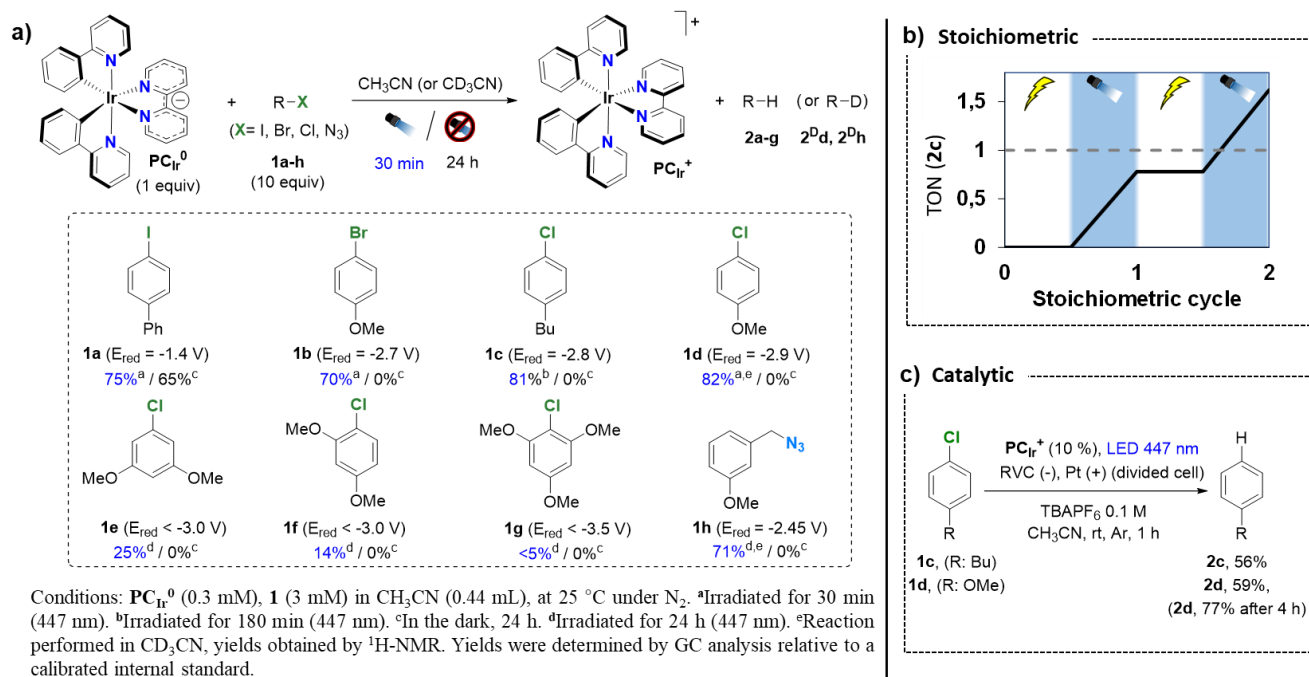
Figure 3. a) Stoichiometric experiments of **PC$_{Ir}^0$** with different aryl halides.[a,e] Reduction potentials of **1a**, **1b**, **1d**, **1h**, **1g** (vs SCE) were obtained from the literature,[23-25] and the rest were measured. **b)** Stepwise stoichiometric experiment showing the **PC$_{Ir}^0$** recyclability. Periods of -1.5 V vs SCE under the dark (white background) followed by 447 nm LED irradiation with disconnected electrodes (blue background). The yield was analyzed after each period. **c)** Electro(photo)catalytic experiments.

We next examined the reactivity of **PC$_{Ir}^0$** towards selected organic halides with a wide range of redox potentials ranging from -1.4 V to <-3.5 V vs SCE. In the dark, the reactivity of the substrates followed the expected pattern considering the redox values (Figure 3). Only iodobiphenyl (**1a**, E = −1.4 V) underwent dehalogenation in the dark (65% yield). Substrates with more negative redox potentials, such as bromoanisole (**1b**, E_{red} = –2.7 V) or chloroanisole (**1d**, E_{red} = –2.9 V), did not produce dehalogenation products after 24 h. Remarkably, **1b** - **1d** were dehalogenated under blue light irradiation after 30 min with yields equal of higher than 70% versus **PC$_{Ir}^0$**, the limiting reagent (Figure 3, yields in blue). In the case of **1d**, we analyzed the transformation of the Ir complex, where **PC$_{Ir}^+$** was recovered with 91% yield from the initial **PC$_{Ir}^+$** (See SI). Therefore, **PC$_{Ir}^0$** should reduce the aryl halide stoichiometrically. The reactivity with substrates shows that the **PC$_{Ir}^0$** reductive power is noticeably enlarged under visible light irradiation, displaying an estimated reductive potential in acetonitrile about −3.0 V vs SCE for **PC$_{Ir}^{0*}$** according to the reactivity with **1d-1f**. Only dehalogenation traces were observed for more challenging to reduce substrates (**1g**, E_{red} < –3.5 V). These experimental results provide the first direct confirmation of the ability of **PC$_{Ir}^0$** to reduce inactivated organic halides under light irradiation. When CD$_3$CN was used as a solvent, the dehalogenated products obtained from the light-driven reactions with **PC$_{Ir}^0$** yielded a deuterium atom at the dehalogenated position. This suggests a hydrogen atom abstraction from the solvent by a potential aryl radical intermediate, which could be formed by single electron reduction of the aryl halide followed by C-Hal cleavage. In agreement is observed **1h** reactivity.

These results prompted us to wonder whether conditions could be found to turnover **PC$_{Ir}^0$** to develop and identify a catalytic process via **PC$_{Ir}^{0*}$**. However, the commonly used electron donors such as amines or TBA$_2$ox can mask the **PC$_{Ir}^{0*}$** reactivity due to generating highly reactive species or even impeding it.[6,26-28] Given these considerations, we envisioned that the dehalogenation reaction could become catalytic under electro(photo)chemical conditions where sacrificial agents are absent in the cathode,[29-32] but with an electrolyte not interfering in the main reactivity. To test the hypothesis, we first verified that **1c** does not suffer C–Cl activation when applying -1.5 V vs SCE, while **PC$_{Ir}^+$** is reduced to **PC$_{Ir}^0$** (Figure 3.b and Supporting information section 13). After the accumulation of **PC$_{Ir}^0$** in the electrochemical cell, the electrodes were disconnected, and the solution was irradiated, leading to a 78% dehalogenated product **2c** (TON = 0.8, Figure 3.b). A consecutive stepwise electrochemical followed by a photochemical reaction provided an additional 84% yield (TON$_{total}$ = 1.6), surpassing the stoichiometric threshold. Furthermore, in a separate experiment, when both the electric bias and the LED source were simultaneously operated, the system was catalytic without any optimization (over 5 TONs after one hour for **2c** and **2d**, and 7.7 TONs after four hours for **2d**), showcasing the viability of engaging this reactivity in electro-photocatalytic settings.

We conducted additional mechanistic studies to gain further insight into the nature of the reactivity between **PC$_{Ir}^0$** and organic halides under irradiation. We observed that **PC$_{Ir}^0$** was non-emissive in liquid solutions or frozen acetonitrile at 77 K (Supporting Information, Section 14). This is consistent with an ultrafast non-radiative decay of the exited state within a sub-nanosecond timescale, ruling out the participation of **PC$_{Ir}^{0*}$** in diffusion-limited bimolecular SET reactions,[33] as depicted in Figure 1B. Alternatively, a reaction involving excited states of such a short lifetime could occur through the pre-aggregation of both species on an electron donor-acceptor (EDA) complex.[34-37] This could allow a photo-triggered SET that is not limited to diffusion timescale (static quenching) between ground-state **PC$_{Ir}^0$** and **1d**.[34-38] However, UV-vis absorption experiments upon adding an excess of **1d** (100 equiv.) to a solution of **PC$_{Ir}^0$** did not provide evidence for the formation of an EDA complex.

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A third possible pathway involves the ejection of a solvated electron from the excited state of the reduced iridium complex, $PC_{Ir}^{0*} \rightarrow PC_{Ir}^{+} + e^{-}_{(solv)}$ (Figure 1C). This process requires the population of an excited state in which one electron is promoted to an orbital possessing a higher energy than the one of $e^{-}_{(solv)}$. This would allow for a thermodynamically favorable electron ejection that usually occurs in the sub-nanosecond time scale.[28,38-40] We performed TD-DFT calculations to assess this possibility and better understand the electronic transitions involved in PC_{Ir}^{0} (Supporting Information section 17). TD-DFT calculations revealed that visible range electronic transitions are predominantly centered on the bpy$^{\bullet-}$ fragment of PC_{Ir}^{0}, while transitions involving Ir or ppy orbitals occur at shorter wavelengths (< 400 nm). The frontier orbitals of PC_{Ir}^{0} showed two $\pi \rightarrow \pi^*$ transitions within the visible range: 417 nm and 686 nm. These transitions correlated to experimental absorption spectra (527 nm and 850 nm, respectively) and corresponded to SOMO → LUMO+n transitions involving the promotion of the unpaired electron of bpy$^{\bullet-}$ to empty orbitals of the same ligand. The 417

nm transition could involve a thermodynamically favorable electron ejection, leading to the formation of PC_{Ir}^{+} and $e^{-}_{(solv)}$ (see SI for details), while the 686 nm transition lacks sufficient energy for favorable electron ejection.

Consistently, photochemical activation of organic halides under different irradiation wavelengths showed that not only blue (447 nm) but also green (530 nm) light excitation of PC_{Ir}^{0} resulted in productive reactivity (Figure 4a and Table S4), whereas irradiating in the yellow (590 nm) or red (660 and 850 nm) do not promote reactivity. These results correlate well with the energetic requirements for electron ejection estimated by TD-DFT and confirm that the excited states responsible for the observed photoreactivity are presumably highly energetic anti-Kasha π-π^*(bpy$^{\bullet-}$) states.[41, 42] The CH$_3$CN/CD$_3$CN scrambling could be seen as a signature of CH$_3$CN solvated electrons (Figure S13).[43-45] Collectively, these data suggest the generation of highly reducing solvated electrons as the main species responsible for dehalogenation of challenging organic halides by PC_{Ir}^{0} under light irradiation.[46]
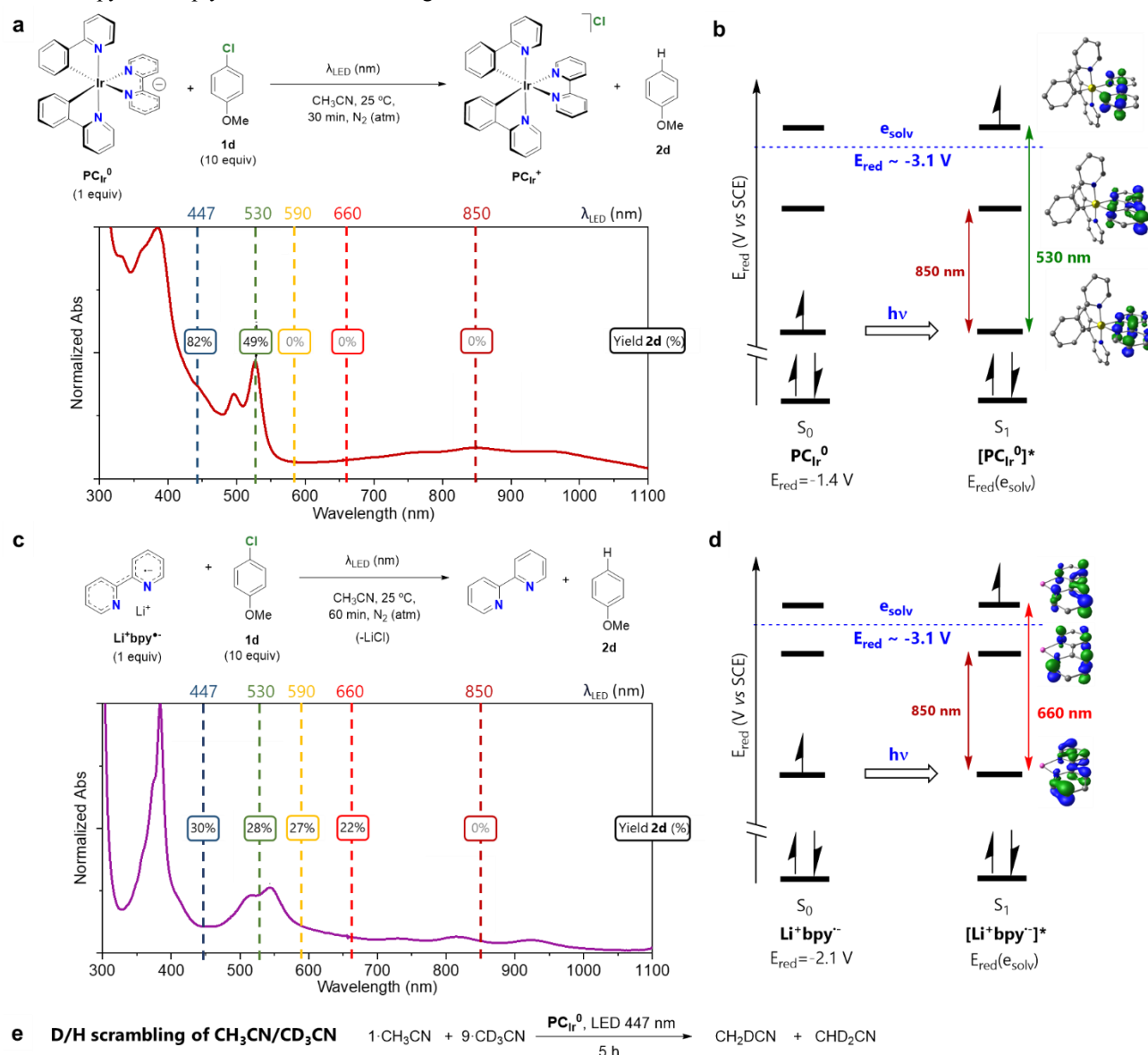

Figure 4. a) Reactivity of PC_{Ir}^{0} and **c)** Li$^+$bpy$^{\bullet-}$ with **1d** at different wavelengths (left) and in **b, d)** their corresponding summary of the representative electronic transitions according to TD-DFT calculations, and **e)** Reaction illustrating the D/H isotopic scrambling occurring under 5 h light irradiation and with PC_{Ir}^{0}, while no scrambling was observed under dark (See SI for details).

Finally, as the orbitals responsible for electron ejection at PC_{Ir}^0 are mainly centered on the bpy$^{•-}$ fragment, we wondered if a comparable photoreactivity could be found for other bpy$^{•-}$ salts. In fact, DFT analysis of $Li^+bpy^{•-}$ revealed an analogous distribution of frontier orbitals to those found in PC_{Ir}^0, which is translated into a close resemblance of both experimental UV-vis absorption spectra in the visible range (>400 nm). To our delight, we observed that dehalogenation of chloroanisole in the presence of $Li^+bpy^{•-}$ results in the desired product in a 30% yield under blue light irradiation. In contrast, the same experiment carried out in the dark or under irradiation at 850 nm resulted in no substrate conversion, again matching well with the expected suitability for electron ejection according to orbital analysis (Figure 4c, d). This constitutes proof-of-concept for the unprecedented photochemical reactivity of reduced bpy salts in which the metal cation acts as a mere Lewis acid spectator. In the context of photoredox catalysis, these results suggest that iridium complexes provide effective access to bpy$^{•-}$ fragments by absorption of a photon in the presence of a suitable electron donor, while the super-reductant ability is harnessed by absorption of a second photon by bpy$^{•-}$ to reduce challenging substrates ($E_{red} < -2.5$ V vs SCE).

In conclusion, our study has provided a novel approach for investigating the reduced intermediate of iridium photocatalysts. Our findings demonstrate that excitation of PC_{Ir}^0 enables SET reduction of highly challenging aryl chlorides ($E_{red} < -3.0$ V vs SCE), which can be catalyzed using an electro(photo)chemical cell. Our computational and experimental analyses suggest that the reactivity arises from the excitation of the bpy$^{•-}$ ligand, likely by the ejection of a solvated electron, which the isolated organic salt can replicate. We anticipate that our work will pave the way for future stoichiometric investigations of other photocatalysts and open new avenues for employing iridium complexes and even simple, transition-metal-free bipyridines in electro(photo)catalytic reductive methodologies.

ASSOCIATED CONTENT

Supporting Information. General experimental details, instrumentation, spectroscopic characterization of iridium complexes, reactivity studies under photochemical and electro(photo)chemical conditions and details of the computational studies.

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