Photocatalytic Aerobic Dehydrogenation of N-Heterocycles with Ir(III) Photosensitizers Bearing the 2(2′-Pyridyl)benzimidazole Scaffold

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ABSTRACT: Photoredox catalysis constitutes a very powerful tool in organic synthesis, due to its versatility, efficiency, and the mild conditions required by photoinduced transformations. In this paper, we present an efficient and selective photocatalytic procedure for the aerobic oxidative dehydrogenation of partially saturated N-heterocycles to afford the respective N-heteroarenes (indoles, quinolines, acridines, and quinoxalines). The protocol involves the use of new Ir(III) biscyclometalated photocatalysts of the general formula [Ir(C^N)2(N^N′)]Cl, where the C^N ligand is 2-(2,4-difluorophenyl)pyridinate, and N^N′ are different ligands based on the 2-(2′-pyridyl)benzimidazole scaffold. In-depth electrochemical and photo-physical studies as well as DFT calculations have allowed us to establish structure–activity relationships, which provide insights for the rational design of efficient metal-based dyes in photocatalytic oxidation reactions. In addition, we have formulated a dual mechanism, mediated by the radical anion superoxide, for the above-mentioned transformations.

INTRODUCTION

N-heterocycles are pivotal scaffolds in the pharmaceutical industry due to their biological activity and medicinal applications.1 In particular, indoles,2 quinolines,3,4 acridines,5,6 and quinoxalines7 display anticancer, antiinflammatory properties. Moreover, the redox couples formed by 1,2,3,4-tetrahydroquinolines (THQ) and the corresponding quinolines have been proposed as potential hydrogen-storage material systems for fuel cell applications, since the catalytic hydrogenation of quinolines takes place under mild reaction conditions and can be reverted through catalytic dehydrogenation protocols.8

Traditional procedures for preparing N-containing aromatic molecules from partially saturated N-heterocycles involve harsh reaction conditions (high temperatures), the use of stoichiometric toxic or corrosive oxidants (2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), sulfur, or metal oxides), as well as the generation of undesirable waste.9

More recently, several groups have described methodologies to prepare different aromatic N-heterocycles (N-heteroarenes) from partially saturated precursors through either catalytic dehydrogenation10 or catalytic acceptorless dehydrogenation.11,12 Nevertheless, both strategies require high temperatures and/or harsh reaction conditions and, in some cases, harmful solvents and high catalyst loadings.

The synthesis of N-heteroarenes can also be accomplished through photocatalytic approaches such as the acceptorless dehydrogenation (ADH) of THQs, indolines and similar heterocycles. Different photocatalytic systems have been successfully used to prove this methodology, namely, combinations of a Ru-photocatalyst (PC) and a Co catalyst,8,13 or an acridinium PC and a Pd metal catalyst,14 and also heterogeneous PCs, that is, hexagonal boron carbon nitride nanosheets15 or Rh-photodeposited TiO2 nanoparticles.16 This transformation produces molecular hydrogen as the only byproduct, but it must be managed through expensive procedures when operating at high scale.

Alternatively, it is possible to access N-heteroarenes through oxidative dehydrogenation (ODH) of partially saturated precursors under aerobic photocatalytic conditions, which implies the use of O2 as the hydrogen acceptor (green oxidant), visible light, and a photosensitizer. In particular, the synthesis of a variety of N-heteroarenes (quinolines, quinoxalines, quinox-
lines, acridines, and indoles) has been performed using this type of strategy in the presence of different photocatalytic systems: [Ru(bpy)_3]Cl_2,^17 Rose Bengal,^9 TiO_2 grafted with Ni(II) ions in the presence of 4-amino-TEMPO,^18 and a cobalt-phthalocyanine photosensitizer catalyst in a biphasic medium. Nevertheless, there is still scope to explore new photosensitizers with the goal of increasing product yields, reducing reaction times and employing solvents with low boiling points. What is more, additional studies should be done for a better understanding of the reaction mechanism entailed in this type of transformations.

In a previous work, we have designed a family of new Ir(III) bisscyclometalated complexes with 3-carboxines as efficient photocatalysts for the one-pot oxidative thiocyanation of indolines, which produces the respective 3-thiocyanate photoredox catalyst in a biphasic medium. We have also reported on a protocol to prepare 3-amino acridines through the Ru-photosensitized oxidative cyanation of amines. We have also presented the synthesis of new Ir(III) bisscyclometalated complexes of general formula [Ir-(C^N)_{2}(N^N')i], where C^N = 2-(2,4-difluorophenyl)-pyridinate (dpfpy) and N^N' stands for different N,N-donor ligands containing the 2-(2-pyridyl)benzimidazole scaffold. The ligand dpfpy was chosen to obtain enhanced photoabsorption and excited-state lifetimes, since this behavior is usually expected from the presence of electron-withdrawing groups, such as the –F atoms on the C^N ligands in this type of complexes. 2-(2-pyridyl)benzimidazole was selected as the scaffold for the N^N' ligands due to both its commercial availability and the presence of the imidazole N-H, which allows easy functionalization with a variety of alkyl groups. This, in turn, allows to explore the impact of different functional groups on the photophysical and photocatalytic properties of the resulting complexes (see below). In addition, we describe the evaluation of these complexes as photosensitizers in dehydrogenation processes. Furthermore, relationships between the photosensitizing abilities of these complexes and their electrochemical and photophysical properties are established. In particular, the effect of using dpfpy as the C^N ligand and the influence of the different functional groups of the N^N' ligands on the photocatalytic performance of our dyes are emphasized.

## RESULTS AND DISCUSSION

### Synthesis of Ligands and Iridium(III) Complexes

We have synthesized a family of Ir(III) bisscyclometalated compounds of general formula rac-[Ir(C^N)_{2}(N^N')]i] with the aim of developing new efficient photocatalysts. In this series of compounds, we have furnished the iridium center with two nonequivalent dfppy (dpfpy) and five different N,N' ligands based on the 2-(2-pyridyl)benzimidazole scaffold (Hyphbim = L1). The ligand 2-(2-pyridyl)benzimidazole (L1) is commercially available, and its N-functionalized derivatives (L2–L5) were prepared by reacting L1 with MeI, for L2, or the appropriate alkyl bromide (R-Br), for L3–L5, at room temperature in the presence of K_2CO_3 using DMF as solvent (see Figure 1).^24–26 The incorporation of diverse alkyl groups into the N,N' ligand aimed to reduce intermolecular interactions and to assess different effects on the photophysical and photocatalytic properties of the resulting Ir derivatives. Thus, the methyl and benzyl groups (L2, L3, and L4) were chosen to protect the respective complexes from either self-quenching or N-H reactivity. The naphthalenylmethyl group (L5) was used to evaluate the potential beneficial effect of a π-extended system on the absorption profile of its Ir derivative.

The Ir(III) compounds [Ir1]Cl--[Ir5]Cl were obtained by refluxing the iridium dimer [Ir(μ-Cl)(dpfpy)]_2 (dpfpy = 2-(2,4-difluorophenyl)pyridinate) in the presence of ligands L1-L5 (1:2 molar ratio) in a dichloromethane-methanol mixture (1:1.25; v/v) (Figure 1). The products were isolated in the form of bright yellow solids, as chloride salts of racemic mixtures corresponding to the Δ and Λ enantiomeric complexes (helical chirality).

The synthesis of the PF_6^- salts of complexes [Ir1]^+ and [Ir2]^+ has been previously described, but to the best of our knowledge, their photocatalytic activity has not been studied so far.\footnote{27,28} The iridium derivatives were unequivocally characterized by multinuclear NMR, mass spectrometry, elemental analysis, and IR spectroscopy. In addition, the crystal structures of [Ir1]Cl and the PF_6^- salts of [Ir3],[Ir4]^+, and [Ir5]^+ were determined by X-ray diffraction.

FIGURE 1. Synthesis route and molecular structures of ligands L1−L5 and complexes [Ir1]Cl--[Ir5]Cl. Complexes were obtained as racemic mixtures but only Δ enantiomers are shown.
structures of rac-[Ir5]PF6 either the monoclinic in methanol/dichloromethane. The complexes crystallize in ellipsoids are shown at the 30% probability level. The Δ enantiomers, the H atoms, the Cl− or PF6− counterions, and the solvent molecules (MeOH for rac-[Ir1]Cl) have been omitted for the sake of clarity.

The molecular structures of these complexes display a pseudo-octahedral geometry with the well-known trans-N,N and cis-C,C arrangement for the C^N ligands (Figure 2). In all the derivatives, the Ir−N bond distances for the C^N ligands (1.963(12)−2.074(12) Å) are shorter than for the N^N ligands (2.119(6)−2.181(7) Å) as a consequence of the strong trans influence exerted by the coordinated phenyl rings.30−33 Besides, the Ir−N_{bim} length is shorter than the Ir−N_{py} in the N^N ligand of every complex, likely due to the bigger π-electron density on the benzimidazole (bim) fragment relative to the pyridine (py) ring and therefore the higher π-donor ability of bim versus py. The Ir−C bond distances are standard (1.995(13)−2.020(6) Å).

Crystal Structure by X-ray Diffraction. The crystal structures of rac-[Ir1]Cl, rac-[Ir3]PF6, rac-[Ir4]PF6, and rac-[Ir5]PF6 were resolved by single-crystal X-ray diffraction. Single crystals were isolated either by slow evaporation of a methanolic solution of [Ir1]Cl or by slow diffusion of a saturated NH4PF6 aqueous solution into solutions of [Ir3]Cl, [Ir4]Cl, and [Ir5]Cl in methanol/dichloromethane. The complexes crystallize in either the monoclinic P2_{1}/c, or P2_{1}/a or triclinic P-1 space groups. The ORTEP diagrams for the corresponding Δ enantiomers are shown in Figure 2. Selected bond distances and angles along with standard deviations are collected in Table 1, and relevant crystallographic parameters are included in Table S1.

Table 1. Selected Bond Lengths (Å) for [Ir1]Cl·MeOH, [Ir3]PF6, [Ir4]PF6, and [Ir5]PF6

| [Ir1]Cl·MeOH | [Ir3]PF6 | [Ir4]PF6 | [Ir5]PF6 |
|-------------|----------|----------|----------|
| Ir(1)−N(1)  | 2.054(5) | 2.044(5) | 2.054(10)| 2.022(8) |
| Ir(1)−N(2)  | 2.054(8) | 2.054(6) | 2.043(7) | 2.032(8) |
| Ir(1)−N(3)  | 2.138(5) | 2.142(4) | 2.119(6) | 2.116(8) |
| Ir(1)−N(5)  | 2.179(5) | 2.153(5) | 2.158(6) | 2.181(7) |
| Ir(1)−C(11) | 2.020(6) | 2.019(5) | 2.013(8) | 2.000(10)|
| Ir(1)−C(22) | 2.018(6) | 2.000(5) | 2.002(7) | 2.003(9) |

L5). We also detected for all the compounds a peak corresponding to the monocationic fragment [C_{21}H_{12}F_{4}IrN_{2}]^{+}, which corresponds to the loss of the N^N ligand.

Photostability Experiments. In order to verify the photostability in solution of the new Ir(III)-complexes and the standard photocatalysts [Ir(ppy)_{2}(bpy)]Cl and [Ir(dfppy)_{2}(bpy)]Cl (denoted as [1]Cl and [2]Cl), we monitored their evolution in acetonitrile under air by 1H NMR spectroscopy (1.4 × 10^{-2} M, CD_{3}CN) over a period of 24 h under irradiation with blue light (λ_{ex} = 460 nm, 24 W) at room temperature (Figures S17−S22). All the complexes including [1]Cl and [2]Cl are remarkably stable over the 24 h irradiation period. Indeed, no degradation was observed for [Ir1]Cl−
Just 3% photodegradation was experimentally determined for [Ir4]Cl. An in-depth analysis of the spectrum, recorded for this PC upon 24 h under light exposure, allowed us to speculate that it undergoes photocleavage of the \(-\text{CH}_2-naphthyl\) group.

**Theoretical Calculations.** Density functional theory (DFT) calculations were performed on the cation complexes [Ir1]+, [Ir5]+, and also on the reference photosensitizers [Ir(ppy)\(_2\)(bpy)]\(^+\), [1]+, and [Ir(dfppy)\(_2\)(bpy)]\(^+\), [2]⁺, for a deeper comprehension of the photophysical and electrochemical properties of the synthesized compounds and to rationalize the observed trends among them and relative to [1]+ and [2]⁺. Calculations were executed at the B3LYP/(6-31GDP +LANL2DZ) level including solvent effects (CH\(_3\)CN) (see procedure in the SI and Tables S2a, S2b, and S3).

In agreement with the molecular structure determined by X-ray diffraction for [Ir1]Cl, [Ir3]PF\(_6\), [Ir4]PF\(_6\), and [Ir5]PF\(_6\), our calculations provide structures with a pseudo-octahedral geometry for [Ir1]⁺−[Ir5]⁺, [1]⁺, and [2]⁺ in their ground electronic state (S\(_0\)). Figure 3 shows the isovalue contour pictures for the molecular orbitals, from HOMO−2 (or HOMO−3) to LUMO+2, of [Ir3]⁺ and [2]⁺ at their electronic ground state (S\(_0\)). A similar sketch is shown in Figure S23b for [Ir3]⁺ and [1]⁺. The topologies of the MOs for [Ir1]⁺, [Ir2]⁺ and [Ir4]⁺ are very similar to those of [Ir3]⁺. By contrast, the MO of [Ir5]⁺ exhibit some differences that will be discussed later. The MOs of all the compounds are gathered in Tables S2a and S2b.

The HOMOs calculated for [1]⁺, [2]⁺, and the new derivatives are formed by a combination of Ir orbitals (d\(_\pi\)) and C\(^\pi\)N orbitals (\(\pi\) of ppy− or dfppy−) as described elsewhere for this type of complexes.\(^20,36,37\) Hence, the HOMOs are located on the Ir metal center and the phenyl rings of the C\(^\pi\)N ligands, although they exhibit a \(\pi\)-antibonding nature at the Ir−C\(_{\text{phenyl}}\) interfaces. On the contrary, the LUMOs are distributed mainly over the N\(^\pi\)N ligands (bpy or 2-(2′-pyridyl)benzimidazole...
Figure 5. (a) Overlaid UV–vis absorption spectra of [Ir1]Cl–[Ir5]Cl (10−5 M) in CH3CN at 25 °C along with the emission spectrum of the blue light used in the photocatalytic assays (left). (b) Overlaid emission spectra of of [Ir1]Cl–[Ir5]Cl (10−5 M) in deoxygenated CH3CN at 25 °C upon excitation with λex = 405 nm (right).

Table 2. Photophysical Properties for Complexes [Ir1]Cl–[Ir5]Cl (10−5 M) in deoxygenated CH3CN at 25 °C under λex = 405 nm

| complex | λabs (nm) | ε (M−1 cm−1) | λem (nm) | ΦPL | τ (ns) | kτ (s−1) | knr (s−1) |
|---------|-----------|--------------|----------|-----|-------|---------|---------|
| [Ir(pppy)2(bpy)]+ | 265, 310, 375, 420 | – | 602 | 0.093 | 275 | 3.38 × 105 | 33 × 104 |
| [Ir(dfppy)2(bpy)]+ | 250, 305 | – | 534 | 0.18 | 1500 | 1.20 × 105 | 5.47 × 106 |
| [Ir1]Cl | 233, 246, 348 | 0.303, 0.408, 0.206 | 522 | 0.78 | 59 | 132 × 105 | 37.3 × 105 |
| [Ir2]Cl | 238, 244, 319, 331 | 0.348, 0.428, 0.239, 0.226 | 539 | 0.36 | 2066 | 1.74 × 105 | 3.10 × 105 |
| [Ir3]Cl | 237, 244, 320, 333 | 0.328, 0.426, 0.229, 0.215 | 544 | 0.63 | 1321 | 4.77 × 105 | 2.80 × 105 |
| [Ir4]Cl | 244, 322, 334 | 0.487, 0.228, 0.213 | 544 | 0.46 | 1510 | 3.05 × 105 | 3.58 × 105 |
| [Ir5]Cl | 244, 321, 333 | 0.533, 0.268, 0.249 | 546 | 0.09 | 1012 | 0.89 × 105 | 8.99 × 105 |

aData for [1]PF6 and [2]PF6 reported by E. Zysman-Colman47,49 and De Cola,48 respectively. bRadiative deactivation rate constant: kτ = ΦPL × τ−1. cNonradiative deactivation rate constant: knr = τ−1 − kτ (assuming unitary intersystem crossing efficiency).

The nature of the emitting excited states and the emission energies for the new compounds (T1 − S0) were calculated using the time-dependent DFT (TD-DFT) method (Figure 4). The obtained values predict very similar emission λmax for [Ir1]+−[Ir5]+ and [2]+, although a blue-shift relative to the respective λmax for [1] is also predicted. All these estimations are consistent with the emission energies determined experimentally (see next section) and establish that the presence of the electron-withdrawing F atoms on the C=N ligands is the main factor affecting the emission energies.

Photophysical Properties. UV–vis Absorption Spectra. The UV–vis spectra of complexes [Ir1]Cl–[Ir5]Cl were recorded in acetonitrile solutions (10−5 M) at 25 °C (Figure 5a). The absorption spectra of complexes [Ir1]Cl–[Ir5]Cl show one intense absorption band centered at around 250 nm, which corresponds to singlet spin-allowed ligand centered transitions (1LC, n→π*) occurring in both types of ligands, the C=N (dipppy) and the N≡N. Additional bands are observed at around 313 nm for [Ir2]Cl–[Ir5]Cl and 348 nm for [Ir1]Cl. These bands are attributed to mixed spin-allowed MLCT and 1LLCT transitions. The weak absorption tails entering in the visible region come from spin-forbidden MLCT and 3LC transitions.41−43 In general, the absorption bands of [Ir5]Cl are more intense and are more extended in the range between 420 and 500 nm, and hence overlap better with the emission band of the light source used in photocatalytic assays (Figure 5a). This is likely due to the higher π-conjugation of the naphthyl group.

Emission Spectra. The emission spectra of complexes [Ir1]Cl–[Ir5]Cl were recorded in solutions of dry and deoxygenated acetonitrile (10−5 M) at 25 °C under excitation at 405 nm (see Figure 5b). All the spectra are alike, featuring a broad unstructured emission band, typical of high charge-transfer character.40 These bands have an absolute maximum between 522 and 546 nm for [Ir1]Cl–[Ir5]Cl (Table 2), which resembles the value reported for [2]PF6 (λem = 534 nm).
Nevertheless, the emission of all these complexes is blue-shifted relative to that of the archetypal photosensitizer [1]PF₆ (602 nm), as anticipated by DFT calculations.

The photoluminescence quantum yields (PLQY, Φₚₚₚₑ) were also determined in deoxygenated acetonitrile solutions (10⁻³ M). [Ir1]Cl and [Ir3]Cl display very good quantum yields of 0.78 and 0.63, respectively (Table 2). On the other hand, [Ir2]Cl and [Ir4]Cl feature moderate quantum yields of 0.36 and 0.46, respectively, while [Ir5]Cl shows a low quantum yield (0.09) similar to that for [1]PF₆ (0.093) and lower than that for [2]PF₆ (0.18). We speculate that the lower Φₚₚₑ values determined for [Ir2]Cl–[Ir5]Cl versus [Ir1]Cl are mainly due to the intramolecular rotation of the N-alkyl groups in solution, which favors the dissipation of energy by nonradiative channels for these complexes. In addition, the very low PLQY of [Ir5]Cl could be the result of an extra factor, that is, the thermal population of a ligand-centered (L₅MLCT) excited state, (T₂, 2.70 eV) close in energy to the emissive lowest excited state (T₁, 2.65 eV) (Table S3). This feature provides a nonradiative decay pathway to the ground state due to the intramolecular rotation of the N=N hydrogen-bonding interactions and thereby shortening the lifetime of the triplet excited state.

The excited-state lifetimes (τ) are excellent for the substituted derivatives [Ir2]Cl–[Ir5]Cl, between 1012 and 2066 ns and much longer than that for [1]PF₆, whereas for the nonfunctionalized compound, [Ir1]Cl, τ is much shorter, 59 ns (Table 2). However, the functionalization of the imidazoyl nitrogen has also an important effect on the lifetimes of the excited states. In particular, we speculate that the presence of the N=H group in [Ir1]Cl could accelerate the radiative deactivation of the excited state relative to its functionalized counterparts [Ir2]Cl–[Ir5]Cl. The rationale for this could be that the ground state (S₀) of [Ir1]⁺ is stabilized in acetonitrile solution through N–H–Cl⁻ or N–H–N≡C–Me hydrogen-bonding interactions. By contrast, in the excited state, which exhibits partial MLCT nature, the charge transfer from the metal center to the π* orbital of the N=N ligand decreases the polarization of the N–H bond and therefore the strength of the interaction with either the Cl⁻ counterion or the solvent molecules, shortening the lifetime of the triplet excited state (T₃). In [Ir2]Cl–[Ir5]Cl, the presence of bulky apolar alkyl groups impedes hydrogen-bonding interactions and therefore avoids the differential stabilization of S₀ relative to T₃. This would explain the longer lifetimes observed for the excited states of [Ir2]Cl–[Ir5]Cl vs [Ir1]Cl.

The radiative and nonradiative deactivation rate constants, kₚ and kₙ, were calculated from Φₚₑ and τ and are summarized in Table 2. It is worth noting that [Ir1]Cl has a kₚ < kₙ, while [Ir2]Cl–[Ir4]Cl exhibit similar values for kₚ and kₙ and [Ir5]Cl features a kₙ in 1 order of magnitude higher than kₚ.

Overall, the photophysical properties of our photosensitizers are in general superior to those reported for [1]PF₆ and [2]PF₆, and a priori the long lifetimes of [Ir2]Cl–[Ir5]Cl could favor their interaction with O₂ to generate ROS.

**Electrochemical Properties.** The redox potentials of [Ir1]Cl–[Ir5]Cl were experimentally ascertained by cyclic voltammetry (CV) in deoxygenated CH₃CN solutions (5 × 10⁻⁴ M), in order to establish the oxidative and reductive abilities of the corresponding ground and excited states, as well as the redox stability of our complexes. Potentials are referred to the ferrocenium/ferrocene (Fc+/Fc) couple.

The cyclic voltammograms (CV) of these compounds are presented in Figure 6. The anodic region of every CV shows two peaks: (a) an irreversible peak between +0.56 and +0.63 V (Table 3 and Figure 6) attributed to the oxidation of the chloride counterion (2Cl⁻ → Cl₂ + 2e⁻) and (b) a reversible one-electron oxidation peak in the range +1.19 to +1.22 V, ascribed to an oxidation process affecting the Ir(III) center along with the difluorophenyl rings of C=N ligands, as disclosed by the topography of the respective HOMO.

In the cathodic region, [Ir1]Cl exhibits two irreversible peaks (E⁻¹/₂ = +1.79 V, E⁺¹/₂ = −2.33 V). Nonetheless, complexes [Ir2]Cl–[Ir5]Cl display one pseudoreversible one-electron peak and one irreversible one-electron peak in the ranges from −1.67 to −1.76 V (E⁻¹/₂) and from −2.21 to −2.27 V (E⁺¹/₂), respectively. These waves are attributed to stepwise reductions centered in the respective N=N ligands, as suggested by the topography of the calculated LUMO for these compounds. Interestingly, the pseudoreversible nature of E⁻¹/₂ observed for [Ir2]Cl–[Ir5]Cl, compared to the irreversible character of E⁻¹/₂ obtained for [Ir1]Cl, underlines the stabilizing effect of the alkyl groups attached to the N=N ligands on the redox behavior of these dyes. Moreover, a low intensity irreversible wave is observed for complexes [Ir2]Cl–[Ir4]Cl with peaks between −1.00 and −1.11. This peak is imputed to the oxidation of a species formed in situ by chemical decomposition during the CV experiment, as it can only be seen in the return scan. The experimental electrochemical band gaps have been calculated as the difference between E⁻¹/₂ and E⁺¹/₂. They are in a very narrow range for complexes [Ir1]Cl–[Ir5]Cl and are very similar to the value reported for [2]PF₆, although are higher than the respective value for [1]PF₆ in agreement with the trends predicted theoretically for the HOMO–LUMO band gaps. Paradoxically, the excited states of this type of Ir(III) derivatives exhibit a versatile and outstanding redox behavior. Indeed, our dyes show a high excited-state redox power as oxidants, E₁/₂(1/2) ranges from +0.54 to +0.61 V, and as reductants, E₁/₂(1/2) ranges from −1.16 to −1.08 V (Figure 7 and Table S4), and they are meaningfully better excited-state oxidants than the standard photosensitizer [1]PF₆ (E₁/₂(1/2) = +0.28 V). These facts underscore their potential as photocatalysts in single electron transfer (SET) processes.

**Photocatalytic Activity in the Oxidation of Heterocycles.** The new iridium complexes were tested as photo-
catalysts in the dehydrogenation of different partially saturated heterocycles (indolines, quinolines, isoquinolines, etc.). First, we chose indoline (1a) as the model substrate and irradiated it with blue light (460 nm) in the presence of [Ir1]Cl, whereas lower yields were obtained using dichloromethane and ethanol. Thus, we could determine that acetonitrile is the best solvent choice, since it provides a quantitative yield (>99%) for indole (2a), whereas lower yields were obtained using dichloromethane and ethanol (Table 4) under analogous conditions. It is noteworthy that the transformation is selective for 2a, since no overoxidation products such as isatin were observed. Then, we performed a catalyst screening for the photooxidation of indoline (1a) using acetonitrile as solvent and a catalyst loading of 0.1 mol % for [Ir1]Cl and also for [1]Cl and [2]Cl. Consequently, we found out that [Ir3]Cl is the most efficient catalyst for the oxidative dehydrogenation of indoline (1a), whereas [Ir1]Cl provided a very low yield for 2a (entries 1 and 3, Table 5). We tentatively explain the poor yield obtained with

Table 4. Solvent Screening in the Photooxidation of Indoline 1a

| entry | solvent  | yield (%) |
|-------|----------|-----------|
| 1     | CH3CN    | 100       |
| 2     | CH2Cl2   | 65        |
| 3     | EtOH     | 48        |

*Reaction conditions: Indoline 1a (10 mM), PC ([Ir1]Cl, 1 mol %), solvent (0.5 mL), O2 (balloon, 1 atm), blue light (LED, λ = 460 nm, 24 W), room temperature, for 24 h. Yields of 2a were experimentally determined by 1H NMR integration of the corresponding reaction crudes. The yield values were calculated as the mean of three independent experiments.

Table 5. Photocatalysts Screening in the Photooxidation of Indoline 1a

| entry | complex   | yield (%) |
|-------|-----------|-----------|
| 1     | [Ir1]Cl   | 54        |
| 2     | [Ir2]Cl   | 55        |
| 3     | [Ir3]Cl   | 20        |
| 4     | [Ir1]Cl   | 42        |
| 5     | [Ir3]Cl   | 62        |
| 6     | [Ir4]Cl   | 58        |
| 7     | [Ir5]Cl   | 57        |

*Reaction conditions: Indoline 1a (10 mM), PC (0.1 mol %), acetonitrile (0.5 mL), O2 (balloon, 1 atm), blue light (LED, λ = 460 nm, 24 W), room temperature, for 24 h. Yields of 2a were experimentally determined by 1H NMR integration of the corresponding reaction crudes. The yield values were calculated as the mean of three independent experiments.
the nonalkylated luminophore [Ir1]Cl owing to the irreversible nature of its reduction [Ir4]− \rightarrow [Ir3]− and its short excited-state lifetime, as seen in Figure 6 and discussed in the Mechanism section.

By contrast, it is worth remarking that the alkylated derivatives, [Ir3]Cl−[Ir5]Cl, provide better yields than the standard PSSs, [1]Cl and [2]Cl, as a result of a balanced combination of favorable photophysical and electrochemical properties.

Next, we performed a collection of control experiments to verify the photocatalytic essence of this transformation and the role of O2. Indeed, we realized that in the absence of light, PC, or O2 (N2 atmosphere), the reaction did not proceed or was dramatically impeded, and thus we concluded that this transformation is light-driven in the presence of a PC and that oxygen is involved in the oxidation (Table 6). It is worth mentioning that the detection of a small percentage of 2a under a N2 atmosphere (entry 4, Table 6) could be due to the presence of O2 traces in the solvent (incomplete deoxygenation). Moreover, we carried out additional control experiments in the presence of DABCO (1O2 quencher),57 TEMPO (radical scavenger),58 and 1,4-benzoquinone (BQ, O2•− scavenger)56,59 to elucidate the actual oxidant. The presence of DABCO decreases the yield slightly (84%), while TEMPO and BQ cause a dramatic and significant drop of the yield, respectively. These results suggest that superoxide has a major contribution in this reaction, while singlet oxygen plays just a minor role (Table 6).

Then, we tested the substrate scope using the optimized conditions on a variety of indolines bearing different functional groups (Table 7). Most of the desired indoles were obtained in high yields and with excellent selectivities. However, the oxidation of 1-acetyl-5-bromoindoline (1f) was ineffective. This failure is likely due to the electron-withdrawing and steric effects attributed to the N-acetyl group, which inhibit the oxidation step.6,16,18 Indeed, according to our general mechanistic proposal, we presume that the reductive quenching of the triplet excited state of the PC, \([\text{Ir}4]^{3+}\)6, in the presence of 1f would give rise to an unstable radical cation intermediate due to the remarkable electron-withdrawing effect attributed to the formyl substituent on the N atom. Moreover, the oxidative dehydrogenation of 5-nitroindoline (1c) and 6-nitroindoline (1g) were also precluded (0 and 20% of respective indoles), which is likely related to the strong electron-withdrawing ability of the −NO2 group.18 Indeed, it is well-known that electron-poor nitro-aromatic substrates can undergo a photoinduced electron donation from the triplet excited state of different photosensitizers, which competes with the photoinduced reductive quenching proposed as one of the steps in the mechanism of this reaction.6,60

To validate the applicability of this protocol, we decided to scale the reaction up to 1 g of indoline (1a) in the presence of [Ir3]Cl (0.3 mol %). Thus, it was possible to obtain 2a in 95% yield by increasing the reaction time from 24 to 75 h. (See SI and 1H and 13C NMR of isolated products and characterization in Figures S19–S32).

Next, we assayed the stepwise oxidative dehydrogenation of 1,2,3,4-tetrahydroquinolines to produce the respective quinolines. First, we selected 1,2,3,4-tetrahydroquinoline (THQ, 3a) as the model substrate and applied the standard conditions using [Ir1]Cl as the photocatalyst (1 mol %) for 24 h in three different solvents, that is, acetonitrile, dichloromethane, and ethanol (Table 8).

Again, acetonitrile provided the best yield for quinoline, 4a (20%) and was chosen as the solvent for additional experiments. Partial dehydrogenation products such as 3,4-dihydroquinoline were not detected, making this protocol selective.55 A PCs screening including complexes [Ir1]Cl−[Ir5]Cl and also [1]Cl and [2]Cl was performed using a catalyst loading of 1 mol %. Unlike [Ir1]Cl, the functionalized PCs, [Ir2]Cl−[Ir5]Cl, promoted full conversions of 3a to 4a under these conditions. Hence, in order to discriminate the most active PC, we examined the photocatalytic activity of these complexes one more time, decreasing the catalyst loading down to 0.1 mol % (Table 9). In short, [Ir4]Cl turned out to be the most efficient PC (70% yield of 4a), and again, the nonalkylated complex, [Ir1]Cl, was by far the less efficient PC. Besides, complexes [Ir3]Cl−[Ir5]Cl exhibited better performances than the archetypal photosensitizer [1]Cl, and [Ir4]Cl−[Ir5]Cl are even more active than the fluorinated standard PS [2]Cl. We theorize that the good performance of [Ir5]Cl, despite its low ΦPL, could be ascribed to its better absorbivity in the visible range.

The usual control experiments were done to gain insight into the mechanism of this transformation. In particular, we observed no conversion without light or PC as well as a drastic decrease in the yield in the absence of O2 (4% of 4a, under a N2 atmosphere) (Table 10). The use of the ROS scavengers DABCO, TEMPO, and BQ revealed similar behaviors to those established for the photooxidation of indoline, that is, a slight drop in the yield of 4a in the presence of DABCO (87%), but a severe inhibition of the transformation in the presence of TEMPO (7%) and BQ (17%) relative to the standard conditions (entries 1 and 5–7 in Table 10). In conclusion, we propose that both singlet oxygen and superoxide take part in the dehydrogenation reaction of 1,2,3,4-tetrahydroquinoline, although the main role would correspond to the radical anion superoxide (O2•−). To gain additional insight into the reaction mechanism, we performed emission quenching Stern−Volmer experiments. Thus, we could determine that phosphorescence of [Ir4]Cl was strongly quenched in the presence of increasing concentrations of 3a under nitrogen, and consequently we proved that reductive quenching can be rationally proposed as the first step in the mechanism of this transformation. In other words, we concluded

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Table 6. Control Experiments for the Photooxidation of Indoline 1a

| entry | conditions | yield (%) |
|-------|------------|-----------|
| 1     | PC, O2, light | 100       |
| 2     | PC, O2, no light | 0        |
| 3     | no PC, O2, light | 0        |
| 4     | PC, N2, light | 10        |
| 5     | PC, O2, light, DABCO | 84       |
| 6     | PC, O2, light, TEMPO6 | 15       |
| 7     | PC, O2, light, BQ4 | 45       |

*Reaction conditions: Indoline 1a (10 mM), PC ([Ir3]Cl, 0.3 mol %), CH3CN (0.5 mL) at room temperature, under a saturated atmosphere of either O2 or N2 (1 atm), and under irradiation with blue light (LED, λe = 460 nm, 24 W) during 24 h in a septum-capped tube. Yields of 2a were determined by 1H NMR integration of the corresponding reaction crudes. *DABCO (3 equiv). *TEMPO (3 equiv). *BQ (3 equiv). The yield values were calculated as the mean of three independent experiments.

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that 3a can be efficiently oxidized by $[\text{Ir}_4]\text{Cl}^{\text{III}}$ with a quenching constant, $K_{sv} = 29.728 \times 10^{-1.63}$. However, we also demonstrated that the emission of $[\text{Ir}_4]\text{Cl}$ is quenched upon exposure to open air (Figure S47). Hence, oxidative quenching

Table 7. Substrate Scope for the Photooxidation of Indolines

| Entry | Substrate | Product | Yield (%) / [Photocatalyst (mol%)] |
|-------|-----------|---------|-----------------------------------|
| 1     | ![1a](image) | ![2a](image) | 100 [0.3] |
| 2     | ![1b](image) | ![2b](image) | 62 [1] |
| 3     | ![1c](image) | ![2c](image) | 0 [1.5] |
| 4     | ![1d](image) | ![2d](image) | 94 [1] |
| 5     | ![1e](image) | ![2e](image) | 100 [0.3] |
| 6     | ![1f](image) | ![2f](image) | 0 [1.5] |
| 7     | ![1g](image) | ![2g](image) | 20 [1.5] |

“Reaction conditions: Indoline (10 mM), PC ($[\text{Ir}_3]\text{Cl}$, 0.3–1.5 mol %), CH$_3$CN (0.5 mL) at room temperature, under a saturated atmosphere of O$_2$ (1 atm) and under irradiation with blue light (LED, $\lambda_{ir} = 460$ nm, 24 W) during 24 h in a septum-capped tube. Yields were determined by $^1$H NMR integration of the corresponding reaction crudes. The yield values were calculated as the mean of three independent experiments.

Table 8. Solvent Screening in the Photooxidation of 1,2,3,4-Tetrahydroquinoline 3a

| entry | solvent | yield (%) |
|-------|---------|-----------|
| 1     | CH$_3$CN | 20        |
| 2     | CH$_2$Cl$_2$ | 13    |
| 3     | EtOH     | 7         |

“Reaction conditions: 1,2,3,4-Tetrahydroquinoline 3a (10 mM), PC ($[\text{Ir}_1]\text{Cl}$, 1 mol %), solvent (0.5 mL), O$_2$ (balloon, 1 atm), blue light (LED, $\lambda_{ir} = 460$ nm, 24 W), room temperature for 24 h. Yields of 4a were experimentally determined by $^1$H NMR integration of the corresponding reaction crudes. The yield values were calculated as the mean of three independent experiments.

Table 9. Photocatalysts Screening in the Photooxidation of 1,2,3,4-Tetrahydroquinoline 3a

| entry | complex | yield (%) |
|-------|---------|-----------|
| 1     | $[\text{Ir}_1]\text{Cl}$ | 45        |
| 2     | $[\text{Ir}_2]\text{Cl}$ | 62        |
| 3     | $[\text{Ir}_3]\text{Cl}$ | 0         |
| 4     | $[\text{Ir}_4]\text{Cl}$ | 27        |
| 5     | $[\text{Ir}_5]\text{Cl}$ | 56        |
| 6     | $[\text{Ir}_6]\text{Cl}$ | 70        |
| 7     | $[\text{Ir}_7]\text{Cl}$ | 68        |

“Reaction conditions: 1,2,3,4-Tetrahydroquinoline 3a (10 mM), PC (0.1 mol %), acetonitrile (0.5 mL), O$_2$ (balloon, 1 atm), blue light (LED, $\lambda_{ir} = 460$ nm, 24 W), room temperature for 24 h. Yields of 4a were experimentally determined from $^1$H NMR integration of the corresponding reaction crudes. The yield values were calculated as the mean of three independent experiments.
of $[\text{Ir}_4]^{*6^*}$ mediated by $\text{O}_2$ can operate as the first step in the mechanism of this reaction as well. See a detailed discussion below.

To complete this study, we extended the above-mentioned protocol to a selection of tetrahydroquinolines and analogues, such as 1,2,3,4-tetrahydroisoquinoline, 9,10-dihydroacridine and several 1,2,3,4-tetrahydroquinoxalines (Table 11).

In general, we obtained high yields and excellent selectivity for most of the expected products (4b, 4c, and 4e–4h). In a previous photocatalytic protocol, Bahnemann et al. obtained a mixture between the partially dehydrogenated product 4b and the fully dehydrogenated product, when using the tetrahydroisoquinoline 3b. However, the yields for the quinoxalines, 4i–4k, and 6-methyl-quinoline, 4f, were only moderate, in the range between 52 and 62%. On the other hand, 2,3-dihydrobenzofuran-5-carboxaldehyde (3d) was not oxidized to its dehydrogenated derivative. It is noteworthy that the oxidation of 7-nitro-1,2,3,4-tetrahydroquinoline (3c) was achieved albeit with a low yield, since, as aforementioned, the nitro substituent usually behaves as a quencher for the excited state of PCs. Moreover, the yield for 3c could be improved by prolonging the reaction time and increasing the catalyst loading (>99% yield, with 5 mol % PC, 48 h).

After this, we successfully scaled our methodology up to 1 g of 3a in the presence of $[\text{Ir}_4]^{*}$(0.7 mol %) to obtain 4a with a yield of 88%, albeit it was necessary to extend the reaction time from 24 to 75 h. (see $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of isolated products in Figures S42 and S43).

**Mechanism.** Based on the experimental results summarized in Table 12 along with the bibliographic background, we propose a dual mechanism for the aerobic photooxidative dehydrogenation of 1,2,3,4-tetrahydroquinoline based on both a reductive quenching cycle (pathway A) and simultaneously on an oxidative quenching cycle (pathway B). In both cases, the reaction is mediated by the radical anion superoxide $(\text{O}_2^{* -})$, and we postulate that both mechanisms could operate concurrently (Figure 9).

**Pathway A.** First, the model Ir(III) photosensitizer, $[\text{Ir}_3]^{*}$ Cl, is promoted to the singlet excited state under irradiation with blue light and then is converted to the respective triplet excited state through intersystem crossing. This species, $[\text{Ir}^{*II}]^{*}$, exhibits a high oxidation ability and therefore is capable of generating the radical cation intermediate species A (THQ$^*$), through a SET, which entails a reductive quenching of the excited state. The redox potential of the couple THQ/THQ$^*$ determined by CV, $E(\text{THQ}/\text{THQ}^*) = +0.16$ V vs $\text{Fc}^+$/Fc (Figure S24) and compared to $E(\text{Ir}^{III}/\text{Ir}^{*IV}) = +0.59$ V to demonstrate the feasibility of this step. Concurrently, the reduced form of the PC, $[\text{Ir}^{*III}]$ is formed, and then, $[\text{Ir}^{*IV}]$ reduces $\text{O}_2$ to produce $\text{O}_2^{* -}$. Next, two protons and one additional electron are transferred from intermediate A to $\text{O}_2^{* -}$, resulting in intermediate B plus one molecule of hydrogen peroxide ($\text{H}_2\text{O}_2$). It is noteworthy that $\text{H}_2\text{O}_2$ has been detected by both $^1\text{H}$ NMR and using Quantofox peroxide sticks in the crude solutions of photocatalytic assays (see SI). Subsequently, imine-ename tautomerization facilitates the second oxidation process, yielding the aromatic heterocycle.

**Pathway B.** Alternatively, $[\text{Ir}^{*III}]^{*}$ can undergo oxidative quenching upon reaction with $\text{O}_2$ to produce $\text{O}_2^{* -}$ and concomitantly the oxidized intermediate $[\text{Ir}^*$] (Figure 9). Both the emission quenching of $[\text{Ir}_4]^{*}$ in the presence of $\text{O}_2$ and the corresponding redox potentials, $E([\text{Ir}^{III}/\text{Ir}^{*IV}] = 1.06$ V and $E(\text{O}_2/\text{O}_2^{* -}) = -0.95$ V versus $\text{Fc}^+$/Fc support this step. Subsequently, $[\text{Ir}^{*IV}]$ oxidizes THQ to generate the species A (THQ$^*$), returning to its ground state $[\text{Ir}^{*III}]$. Then, $\text{O}_2^{* -}$ and species A react to give B and C, as explained above for pathway A. A similar mechanism could operate for the photocatalytic aerobic dehydrogenation of indolines, etc.

| entry | conditions | yield (%) |
|-------|------------|-----------|
| 1     | PC, $\text{O}_2$, light | 100       |
| 2     | PC, $\text{O}_2$, no light | 0         |
| 3     | no PC, $\text{O}_2$, light | 0         |
| 4     | PC, $\text{N}_2$, light | 4         |
| 5     | PC, $\text{O}_2$, light, DABCO* | 86        |
| 6     | PC, $\text{O}_2$, light, TEMPO* | 7         |
| 7     | PC, $\text{O}_2$, light, BQ* | 17        |

*Reaction conditions: 1,2,3,4-Tetrahydroquinoline 3a (10 mM), PC ([Ir4]Cl, 0.7 mol %), CH3CN (0.5 mL) at room temperature, under a saturated atmosphere of either $\text{O}_2$ or $\text{N}_2$ (1 atm) and under irradiation with blue light (LED, $\lambda_{ex} = 460$ nm, 24 W) during 24 h in a septum-capped tube. Yields of 4a were determined by $^1\text{H}$ NMR integration of the corresponding reaction crude. DABCO (3 equiv). TEMPO (3 equiv). 1,4-Benzquinone (3 equiv). The yield values were calculated as the mean of three independent experiments.

**Table 10. Control Experiments for the Photooxidation of 1,2,3,4-Tetrahydroquinoline 3a**

**CONCLUSIONS**

In conclusion, we have designed and prepared a new family of Ir(III) photosensitizers of the general formula $[[\text{Ir}(\text{C}^\text{N})_{2}(\text{N}^\text{N})_{2})]\text{Cl}$, where $\text{C}^\text{N} = 2-(2,4-difluorophenyl)-pyridine and N$^\text{N} = 2-(2'-pyridyl)benzimidazole (L1) or its N-alkylated derivatives L2-L5. We have ascertained that these complexes are notably stable under irradiation with blue light for a period of 24 h. Moreover, we have demonstrated that they absorb weakly in the visible light region and can be excited with blue light. Indeed, all of them are emissive in the range between 522 and 546 nm ($\lambda_{em}$ = 405 nm). In particular, the N-functionalized derivatives, $[\text{Ir}_2]^{*}$Cl$^-$-$[\text{Ir}_5]^{*}$Cl$^-$ exhibit moderate or high PLQYs (9–63%) and very long excited-state lifetimes (1012–2066 ns). On the contrary, the nonalkylated compound, $[\text{Ir}_1]^{*}$Cl$^-$ exhibits a excellent PLQY (78%) but a very short excited-state lifetime (59 ns). This divergent behavior suggests that the N–H group speeds up the radiative deactivation of the excited state for $[\text{Ir}_1]^{*}$Cl$^-$ by stabilization of the ground state through hydrogen bonds with counterion/solvent molecules, whereas the replacement of the N–H with spolar N-alkyl groups prevents this effect on the ground state and lengthens the lifetime of the respective excited states in acetonitrile. Regarding their electrochemical properties, all the Ir complexes display a similar redox behavior, with electrochemical band-gaps higher than that determined for the standard photosensitizer $[\text{Ir}(ppy)_3]^{*}[(ppy)_2]^{*}$PF$_6$ [1]PF$_6$. This is due to the strong stabilization of the HOMO, associated with the presence of electron-withdrawing $-F$ atoms in the C$^\text{N}$ ligands of our PS, as revealed by theoretical calculations. Nevertheless, $[\text{Ir}_1]^{*}$Cl$^-$ features an irreversible $E_{1/2}$ in contrast to the reversible $E_{1/2}$ of its derivatives.

Upon excitation with blue light, these compounds exhibit highly efficient and selective photocatalytic activities in the preparation of a wide variety of aromatic N-heterocyclic

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products through oxidative dehydrogenation of partially saturated substrates such as different indolines, 1,2,3,4-tetrahydroquinolines, 1,2,3,4-tetrahydroisoquinoline, 9,10-dihydroacridine, and 1,2,3,4-tetrahydroquinoxalines. More specifically, the performance of the N-alkylated derivatives is better than that of [Ir1]Cl in these transformations, which seems to be linked to either the irreversible $E_{1/2}^{ir}$ of [Ir1]Cl compared to the reversible $E_{1/2}^{re}$ of [Ir2]Cl-[Ir5]Cl or the low excited-state lifetime of [Ir1]Cl. We have proved the efficiency of this methodology on a gram scale for the synthesis of 2a and 4a.

Table 11. Substrate Scope for the Photooxidation of Tetrahydroquinolines$^a$

| Entry | Substrate | Product | Yield (%) / [Photocatalyst (mol%)] |
|-------|-----------|---------|-----------------------------------|
| 1     | ![3a](image) | ![4a](image) | 100 [0.7] |
| 2     | ![3b](image) | ![4b](image) | 100 [0.7] |
| 3     | ![3c](image) | ![4c](image) | 40 / >99$^b$ [5] |
| 4     | ![3d](image) | ![4d](image) | 0 [5] |
| 5     | ![3e](image) | ![4e](image) | 100 [0.7] |
| 6     | ![3f](image) | ![4f](image) | 61 [1.5] |
| 7     | ![3g](image) | ![4g](image) | 94 [1.5] |
| 8     | ![3h](image) | ![4h](image) | 100 [0.7] |
| 9     | ![3i](image) | ![4i](image) | 52 [1.5] |
| 10    | ![3j](image) | ![4j](image) | 54 [3] |
| 11    | ![3k](image) | ![4k](image) | 62 [5] |

$^a$Reaction conditions: Substrate (10 mM), PC ([Ir4]Cl; 0.7−5 mol %), CH$_3$CN (0.5 mL) at room temperature, under a saturated atmosphere of O$_2$ (1 atm) and under irradiation with blue light (LED, $\lambda_{ir}$ = 460 nm, 24 W) during 24 h in a septum-capped tube. Yields were determined by $^1$H NMR integration of the corresponding reaction crudes. $^b$Reaction time of 48 h. The yield values were calculated as the mean of three independent experiments.
Afore-Mentioned Photocatalytic Reactions

addition of substrate \( \times \) light as the energy source, and very low PC loadings.

green oxidant, acetonitrile as a low boiling point solvent, visible quenching of \([2]\) = 0 mM; \(I = PL\) intensity of \([4]\) at \([3a] = 0 \text{ mM}; \(I = PL\) intensity of \([4]\) at different \([3a]; I_0/I = 29.728 \times [3a] + 1.0544; R^2 = 0.9996.\)

strong inhibition of photocatalytic oxidation in the presence of TEMPO and BQ (radical and \(O_2^*\) scavengers)

low photocatalytic activity obtained for \([1]\) due to irreversible reductive quenching

low dehydrogenation for \(1c\), \(1g\), and \(3c\) due to the presence of \(-\text{NO}_2\) groups which induce oxidative quenching on PS and inhibit the photocatalytic quenching steps

suitable redox potentials for sustaining both a reductive quenching cycle and an oxidative quenching cycle detection of \(\text{H}_2\text{O}_2\)

evidence of both reductive quenching of \(\text{PC}\) in the presence of \(\text{THQ}\) and oxidative quenching in the presence of \(\text{O}_2\)

control experiments performed in Tables 6 and 10 screening of photocatalysts (Tables 5 and 9) and redox potentials (Table 3) substrate scope experiments (Tables 7 and 11) see text in this section and Tables 3 and 84

\(^{1}\text{H} \text{NMR of crude and peroxide test sticks}\)

Figure 8. Stern–Volmer quenching experiments. (a) Emission quenching of \([4]\) (0.07 mM in CH3CN, 25 °C) upon incremental addition of substrate \(3a\) (0.1–2 mM) under \(N_2\) and \(\lambda_e = 405 \text{ nm.}\) (b) Stern–Volmer quenching plot, where \(I_0 = \text{PL intensity of } [4]\text{Cl} \times \infty \text{ at } [3a] = 0 \text{ mM;} I = \text{PL intensity of } [4]\text{Cl} \times \text{at different } [3a]; I_0/I = 29.728 \times [3a] + 1.0544; R^2 = 0.9996.\)

Table 12. Experimental Evidences Supporting the Reductive and Oxidative Quenching Cycles and the Participation of \(\text{O}_2^*\) in the Afore-Mentioned Photocatalytic Reactions

| evidence | experiment |
|----------|------------|

strong inhibition of photocatalytic oxidation in the presence of TEMPO and BQ (radical and \(O_2^*\) scavengers) low photocatalytic activity obtained for \([1]\) due to irreversible reductive quenching

low dehydrogenation for \(1c\), \(1g\), and \(3c\) due to the presence of \(-\text{NO}_2\) groups which induce oxidative quenching on PS and inhibit the photocatalytic quenching steps

suitable redox potentials for sustaining both a reductive quenching cycle and an oxidative quenching cycle detection of \(\text{H}_2\text{O}_2\)

evidence of both reductive quenching of \(\text{PC}\) in the presence of \(\text{THQ}\) and oxidative quenching in the presence of \(\text{O}_2\)

partially saturated substrates. The above-mentioned results provide insights and tools for the rational design of efficient photocatalysts.

**EXPERIMENTAL SECTION**

General Information and Procedures. All synthetic manipulations were carried out under an atmosphere of dry, oxygen-free nitrogen using standard Schlenk techniques. The solvents were dried and distilled under nitrogen atmosphere before use. Elemental analyses were performed with a Thermo Fisher Scientific EA Flash 2000 elemental microanalyzer. IR spectra were recorded on a Jasco FT/IR-4200 spectrophotometer (4000–400 cm⁻¹ range) with single reflection ATR measuring attachment. UV–vis absorption was measured in an Evolution 300 UV–vis double beam spectrophotometer (Thermo Scientific). Fluorescence steady-state and lifetime measurements were performed in a FLS980 (Edinburg Instruments) fluorimeter with xenon arc lamp 450W and TCSPC laser, respectively. Quantum yield was determined by using in a FLS980 (Edinburg Instruments) with xenon arc lamp 450W and Red PMT Sphere as detector. HR-ESI(+) mass spectra (position of the peaks in Da) were recorded with an Agilent LC-MS system (1200 Infinity LC/6654 Q-TOF MS spectrometer) using DCM/DMSO (4:1) as the sample solvent and (0.1%) aqueous HCOOH/McOH as the mobile phase. The experimental m/z values are expressed in Da compared with the m/z values for monoisotopic fragments. NMR samples were prepared by dissolving the suitable amount of compound in 0.5 mL of the respective deuterated solvent, and the spectra were recorded at 298 K on a Varian Unity Inova-400 (399.94 MHz for \(^1\text{H}\); 376.29 MHz for \(^19\text{F}\); 100.6 MHz for \(^13\text{C}\)).

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and the spectra were recorded at 298 K on a Varian Unity Inova-400 (399.94 MHz for \(^1\text{H}\); 376.29 MHz for \(^19\text{F}\); 100.6 MHz for \(^13\text{C}\)).
degassed and in some cases distilled prior to use. Acetanilide used in the photocatalytic experiments were acquired from a Fisher Scientific (HPLC quality). Tetraethylammonium hexafluorophosphate ([\text{Bu}_4\text{N}]\text{PF}_6) was purchased from Acros. The synthetic procedures of the ligands were previously described in the literature: L2,3 L3,4 L4,5 and L5.

X-ray Crystallography. A summary of crystal data collection and refinement parameters for rac-[Ir1]Cl, rac-[Ir3]PF6, rac-[Ir4]PF6 and rac-[Ir5]PF6 are given in Table S1. Single crystals of compounds were coated in high-vacuum grease, mounted on a glass fiber, and transferred to a Bruker SMART APEX CCD-based diffractometer equipped with a graphite monochromated CuKα radiation source (λ = 1.54178 Å) for rac-[Ir1]Cl, rac-[Ir3]PF6 and rac-[Ir4]PF6 and MoKα (λ = 0.71073 Å) for rac-[Ir5]PF6. The highly redundant data sets were integrated using SAINT and corrected for Lorentz and polarization effects. The absorption correction was based on the function fitting to the empirical transmission surface as sample by multiple equivalent measurements with the program SADABS.

The software package WINGX was used for space group determination, structure solution, and refinement by full-matrix least-squares methods based on F². A successful solution by direct methods provided most nonhydrogen atoms from the E-map. The remaining nonhydrogen atoms were placed using a riding model and included in the refinement at calculated positions. CCDC reference numbers for rac-[Ir1]Cl, rac-[Ir3]PF6, rac-[Ir4]PF6 and rac-[Ir5]PF6 are 2096987, 2096988, 2096989, and 2096990. The Supporting Information is available free of charge at

\[ \text{H}_2\text{O} \rightarrow \text{O}_2 \]

The luminescence emission spectra were recorded by exciting at 405 nm with a xenon arc lamp, and the maximum emission wavelength was measured from 420 to 800 nm. The photoluminescence quantum yields (PLQY or Φ) were calculated by detecting all sample emission through the use of an integrating sphere. For the determination of the luminescence lifetime of compounds [Ir1]Cl−[Ir5]Cl, the fluorescence decay was measured on a FLS980 spectrophotometer equipped with a TSCPC laser and a REDPMT detector. The F980 spectrometer operating software was used to collect and process luminescence lifetime data. The instrumental parameters used were as follows: λex = 405 nm, Δλexc = 0.2 nm, Δλem = 648 nm, Δλem = 4 nm, 2000 channels, integration time = 1 μs, iris setting = 100.

Electrochemical Measurements. Electrochemical measurements were performed using a portable potentiostat/galvanostat PalmSens3 (PalmSens) equipment controlled by the software PSTrace4 Version 4.4.2. All experiments were carried out using a three-electrode cell with a glassy carbon disc (diameter = 3 mm) as the working electrode, a platinum wire as the auxiliary electrode, and a Ag/AgCl (MF-2052 BASI) reference electrode separated from the bulk solution by a Vycor frit. Oxygen was removed from the solution by bubbling argon for 10 min and keeping the current of argon along the whole experiment. The measurements were recorded for acetonitrile solutions of the complexes (5 × 10⁻⁴ M) in the presence of [\text{Bu}_4\text{N}]\text{PF}_6 (0.1 M) as the supporting electrolyte by CV at a scan rate of 100 mV s⁻¹ in a clockwise direction. Ferrocene was added at the end of all the experiments as the internal reference. The potential experimentally determined for the redox couple Fc⁺/Fc was E° = 0.455 ± 0.002 V vs Ag/AgCl. Therefore, the experimental redox potentials were calculated from the corresponding voltammograms as

- E° (vs AgCl/Ag) = (Ecp + Eap)/2, for reversible peaks where Ecp and Eap stand for anodic and cathodic peak potentials, respectively. However, for irreversible peaks, the potentials were calculated as either the Eap maximum or Ecp minimum.
- E° (vs Fc⁺/Fc) = E° (vs AgCl/Ag) − 0.443, for potential values reported in reference to the (Fc⁺/Fc) redox couple.
General Information, synthesis and characterization of the Ir(III) complexes, X-ray diffraction, photo-stability, theoretical calculations and electrochemical measurements of the complexes, procedure for the photocatalytic oxidation of indolines and tetrahydroquinolines, 1H spectra and characterization of the crude and isolated products, detection of H2O2 in photocatalytic experiments, Stern–Volmer experiments, pathway B for the reaction mechanism and photophysical properties (PDF).

Accession Codes
CCDC 2096987–2096990 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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REFERENCES
(1) Vitaku, E.; Smith, D. T.; Njardarson, J. T. Analysis of the Structural Diversity, Substitution Patterns, and Frequency of Nitrogen Heterocycles among U.S. FDA Approved Pharmaceuticals. J. Med. Chem. 2014, 57 (24), 10257–10274.
(2) Kaushik, N.; Kaushik, N.; Atti, P.; Kumar, N.; Kim, C.; Verma, A.; Choi, E. Biomedical Importance of Indoles. Molecules 2013, 18 (6), 6620–6662.
(3) Desai, N. C.; Kotadiya, G. M.; Trivedi, A. R. Studies on Molecular Properties Prediction, Antitubercular and Antimicrobial Activities of Novel Quinoline Based Pyrimidine Motifs. Bioorg. Med. Chem. Lett. 2014, 24 (14), 3126–3130.
(4) Man, R.-J.; Jeelani, N.; Zhou, C.; Yang, Y.-S. Recent Progress in the Development of Quinoline Derivatives for the Exploitation of Anti-Cancer Agents. Anticancer Agents Med. Chem. 2021, 21 (7), 825–838.
(5) Fonte, M.; Tassi, N.; Gomes, P.; Teixeira, C. Acrinidine-Based Antimalarials—From the Very First Synthetic Antimalarial to Recent Developments. Molecules 2021, 26 (3), 600.
(6) Gabriel, I. ‘Acrinidines’ as New Horizons in Antifungal Treatment. Molecules 2020, 25 (7), 1480.
(7) Khatoo, H.; Abdulmalek, E. Novel Synthetic Routes to Prepare Biologically Active Quinolines and Their Derivatives: A Synthetic Review for the Last Two Decades. Molecules 2021, 26 (4), 1055.
(8) He, X.-H.; Tan, F.-F.; Zhou, C.-Z.; Zhou, G.-J.; Yang, X.-L.; Li, Y. Acceptorless Dehydrogenation of N-Heterocycles by Merging Visible-Light Photoredox Catalysis and Cobalt Catalysis. Angew. Chem. Int. Ed. 2017, 56 (11), 3080–3084.
(9) Sahoo, M. K.; Jaiswal, G.; Rana, J.; Balaraman, E. Organo-Photoredox Catalyzed Oxidative Dehydrogenation of N-Heterocycles. Chem. - A Eur. J. 2017, 23 (57), 14167–14172.
(10) Bera, S.; Bera, A.; Banerjee, D. Nickel-Catalyzed Dehydrogenation of N-Heterocycles Using Molecular Oxygen. Org. Lett. 2020, 22 (16), 6458–6463.
(11) Wu, J.; Talwar, D.; Johnston, S.; Yan, M.; Xiao, J. Acceptorless Dehydrogenation of Nitrogen Heterocycles with a Versatile Indium Catalyst. Angew. Chem. Int. Ed. 2013, 52 (27), 6983–6987.
(12) Fujita, K.; Tanaka, Y.; Kobayashi, M.; Yamaguchi, R. Homogeneous Perdehydrogenation and Perhydrogenation of Fused Bicyclic N-Heterocycles Catalyzed by Iridium Complexes Bearing a Functional Bipyridonate Ligand. J. Am. Chem. Soc. 2014, 136 (13), 4829–4832.
(13) Sahoo, M. K.; Balaraman, E. Room Temperature Catalytic Dehydrogenation of Cyclic Amines with the Liberation of H2 Using Water as a Solvent. Green Chem. 2019, 21 (8), 2119–2128.
(14) Kato, S.; Saga, Y.; Kojima, M.; Fuse, H.; Matsunaga, S.; Fukatsu, A.; Kondo, M.; Masaoka, S.; Kanai, M. Hybrid Catalysis Enabling Room-Temperature Hydrogen Gas Release from N-Heterocycles and Tetrahydronaphthalenes. J. Am. Chem. Soc. 2017, 139 (6), 2204–2207.
(15) Zheng, M.; Shi, J.; Yuan, T.; Wang, X. Metal-Free Dehydrogenation of N-Heterocycles by Ternary h-BN-CNOSheets with Visible Light. Angew. Chem. Int. Ed. 2018, 57 (19), 5487–5491.
(16) Balayeva, N. O.; Mamiyev, Z.; Dillert, R.; Zheng, N.; Bahnemann, D. W. Rh/TiO2 -Photocatalyzed Acceptorless Dehydrogenation of N-Heterocycles upon Visible-Light Illumination. ACS Catal. 2020, 10 (10), 5542–5553.
(17) Chen, S.; Wan, Q.; Badu-Tawiah, A. K. Picomole-Scale Real-Time Photoelectrocatalysis: Screening of the Visible-Light-Promoted Dehydrogenation of Tetrahydroquinolines under Ambient Conditions. Angew. Chem. Int. Ed. 2016, 55 (32), 9345–9349.
(18) Balayeva, N. O.; Zheng, N.; Dillert, R.; Bahnemann, D. W. Visible-Light-Mediated Photocatalytic Aerobic Dehydrogenation of N-Heterocycles by Surface-Grafted TiO2 and 4-Amino-TEMPO. ACS Catal. 2019, 9 (12), 10694–10704.
(19) Srinath, S.; Abinaya, R.; Prasanth, A.; Mariappan, M.; Sridhar, R.; Baskar, B. Reusable, Homogeneous Water Soluble Photoredox Catalyzed Oxidative Dehydrogenation of N-Heterocycles in a Biphasic System: Application to the Synthesis of Biologically Active Natural Products. Green Chem. 2020, 22 (8), 2575–2587.
(20) Sanz-Villafuerte, J.; Martinez-Alonso, C.; Echevarría, I.; Vaquero, M.; Carbaya, A.; Fidalgo, J.; Rodríguez, A. M.; Cuevas-Vicario, J. V.; Lima, J. C.; Moro, A. J.; et al. One-Pot Photocatalytic Transformation of Indolines into 3-Thiocyanate Indoles with New Ir(III) Photosensitizers Bearing β-Carbolines. Inorg. Chem. Front. 2021, 8 (5), 1253–1270.

(21) Echevarría, I.; Vaquero, M.; Quesada, R.; Espino, G. Synthesis of α-Amino Nitriles through one-Pot Selective Ru-Photocatalyzed Oxidative Cyanation of Amines. Inorg. Chem. Front. 2020, 7 (17), 3092–3105.

(22) Chen, Y.; Qiao, L.; Ji, L.; Chao, H. Phosphorescent Iridium(III) Complexes as Multicolor Probes for Specific Mitochondrial Imaging and Tracking. Biomaterials 2014, 35 (1), 2–13.

(23) Torres, J.; Carríon, M. C.; Leal, J.; Jalón, F. A.; Cuevas, J. V.; Rodríguez, A. M.; Castañeda, G.; Manzano, B. R. Cationic Bis-(Cycloometalated) Ir(III) Complexes with Pyridine-Carbene Ligands. Photophysical Properties and Photocatalytic Photodestruction Production from Water. Inorg. Chem. 2018, 57 (3), 970–984.

(24) Huang, W.-K.; Cheng, C.-W.; Chang, S.-M.; Lee, Y.-P.; Diao, E. W.-G. Synthesis and Electron-Transfer Properties of Benzimidazole-Functionalized Ruthenium Complexes for Highly Efficient Dye-Sensitized Solar Cells. Chem. Commun. 2010, 46 (47), 8992–8994.

(25) Vaquero, M.; Busto, N.; Fernández-Pampin, N.; Espino, G.; García, B. Appended Aromatic Moieties Determine the Cytotoxicity of Neutral Cycloometallated Platinum(II) Complexes Derived from 2-(2-Pyridyl)benzimidazole. Inorg. Chem. Front. 2020, 7 (9), 4961–4971.

(26) Shavaleev, N. M.; Bell, Z. R.; Easun, T. L.; Rutkaitė, R.; Swanson, L.; Ward, M. D. Complexes of Substituted Derivatives of 2-(2-Pyridyl)benzimidazole with Re(I), Ru(II) and Pt(II): Structures, Redox and Luminescence Properties. Dalton Trans. 2004, No. 21, 3678–3688.

(27) Sunesh, C. D.; Choe, Y. Synthesis and Characterization of Cationic Iridium Complexes for the Fabrication of Green and Yellow Light-Emitting Devices. Mater. Chem. Phys. 2015, 156, 206–213.

(28) Sunesh, C. D.; Mathai, G.; Choe, Y. Constructive Effects of Long Alkyl Chains on the Electroluminescent Properties of Cationic Iridium Complex-Based Light-Emitting Electrochemical Cells. ACS Appl. Mater. Interfaces 2014, 6 (20), 17416–17425.

(29) Sun, H.; Liu, S.; Lin, W.; Zhang, K. Y.; Lv, W.; Huang, X.; Huo, F.; Yang, H.; Jenkins, G.; Zhao, Q.; et al. Smart Responsive Phosphorescent Materials for Data Recording and Security Protection. Nat. Commun. 2014, 5 (1), 4601.

(30) Gärtner, F.; Denurra, S.; Losse, S.; Neubauer, A.; Boddien, A.; Gopffert, A.; Spanenberg, A.; Junge, H.; Lochbrunner, S.; Blug, M.; et al. Synthesis and Characterization of New Iridium Photosensitizers for Catalytic Hydrogen Generation from Water. Chem. - A Eur. J. 2012, 18 (11), 3220–3225.

(31) Lin, W.; Zhao, Q.; Sun, H.; Zhang, K. Y.; Yang, H.; Yu, Q.; Zhou, X.; Guo, S.; Liu, S.; Huang, W. An Electrochromic Phosphorescent Iridium(III) Complex for Information Recording, Encryption, and Decryption. Adv. Opt. Mater. 2015, 3 (3), 368–375.

(32) Cao, H.; Sun, H.; Yin, Y.; Wen, X.; Shan, G.; Su, Z.; Zhong, R.; Xie, W.; Li, P.; Zhu, D. Iridium(III) Complexes Adopting 1,2-Diphenyl-1H-Benzoimidazole Ligands for Highly Efficient Organic Light-Emitting Diodes with Low Efficiency Roll-off and Non-Doped Feature. J. Mater. Chem. C 2014, 2 (12), 2150–2159.

(33) Pérez-Arnaiz, C.; Acúa, M. I.; Bustó, N.; Echevarría, L.; Martínez-Alonso, M.; Espino, G.; García, B.; Domínguez, F. Thiabendazole-Based Rh(III) and Ir(III) Biscyclometalated Complexes with Mitochondria-Targeted Anticancer Activity and Metal-Sensitive Photodynamic Activity. Eur. J. Med. Chem. 2018, 157, 279–293.

(34) Baranoff, E.; Curchod, B. F. E.; Monti, F.; Steimer, F.; Accorsi, G.; Tavernelli, I.; Rothlisberger, U.; Scopelliti, R.; Grätzel, M.; Nazeeruddin, M. K. Influence of Halogen Atoms on a Homologous Series of Bis-Cycloometalated Iridium(III) Complexes. Inorg. Chem. 2012, 51 (2), 799–811.

(35) Maity, A.; Le, L. Q.; Zhu, Z.; Bao, J.; Teets, T. S. Steric and Electronic Influence of Aryl Isocyanides on the Properties of Iridium(III) Cyclometalates. Inorg. Chem. 2016, 55 (5), 2299–2308.
(53) Arias-Rotondo, D. M.; McCusker, J. K. The Photophysics of Photoredox Catalysis: A Roadmap for Catalyst Design. Chem. Soc. Rev. 2016, 45 (21), 5803–5820.

(54) Xiao, Y.; Chun, Y.-K.; Cheng, S.-C.; Ng, C.-O.; Tse, M.-K.; Lei, N.-Y.; Liu, R.; Ko, C.-C. Photocatalytic Amidation and Esterification with Perfluoroalkyl Iodide. Catal. Sci. Technol. 2021, 11 (2), 556–562.

(55) Zhang, C.; Li, S.; Bureš, F.; Lee, R.; Ye, X.; Jiang, Z. Visible Light Photocatalytic Aerobic Oxygenation of Indoles and pH as a Chemoselective Switch. ACS Catal. 2016, 6 (10), 6853–6860.

(56) Schilling, W.; Zhang, Y.; Riemer, D.; Das, S. Visible-Light-Mediated Deamidation of Indoles and Pyrroles to Pharmaceuticals and Pesticides. Chem. - A Eur. J. 2020, 26 (2), 390–395.

(57) Bonesi, S. M.; Manet, I.; Freccero, M.; Fagnoni, M.; Albini, A. Photosensitized Oxidation of Sulfides: Discriminating between the Singlet-Oxygen Mechanism and Electron Transfer Involving Superoxide Anion or Molecular Oxygen. Chem. - A Eur. J. 2006, 12 (18), 4844–4857.

(58) Li, Z.; Han, S.; Li, C.; Shao, P.; Xia, H.; Li, H.; Chen, X.; Feng, X.; Liu, X. Screening Metal-Free Photocatalysts from Isomorphic Covalent Organic Frameworks for the C-3 Functionalization of Indoles. J. Mater. Chem. A 2020, 8 (17), 8706–8715.

(59) Yu, H.; Wang, J.; Zhai, Y.; Zhang, M.; Ru, S.; Han, S.; Wei, Y. Visible-Light-Driven Photocatalytic Oxidation of Organic Chlorides Using Air and an Inorganic-Ligand Supported Nickel-Catalyst Without Photosensitizers. ChemCatChem. 2018, 10 (19), 4274–4279.

(60) Dong, W.; Ma, Q.; Ma, Z.; Duan, Q.; Lü, X.; Qiu, N.; Fei, T.; Su, Z. Phosphorescent Iridium(III) Complex Based Photoluminescence Sensor for Sensitive and Selective Detection of Picric Acid. Dye. Pigment. 2020, 172, 107799.

(61) Sun, X.; Wang, Y.; Lei, Y. Fluorescence Based Explosive Detection: From Mechanisms to Sensory Materials. Chem. Soc. Rev. 2015, 44 (22), 8019–8061.

(62) Kamal, A.; Devaiah, V.; Reddy, K. L.; Shankaraiah, N. Conversion of Amines to Imines Employing Polymer-Supported Sulfoxide (PSS) and Polymer-Supported Perruthenate (PSP): Synthesis of Pyrrolo[2,1-c][1,4]Benzodiazepines. Adv. Synth. Catal. 2006, 348 (1–2), 249–254.

(63) Aganda, K.; Hong, B.; Lee, A. Aerobic A-Oxidation of N-Substituted Tetrahydroisoquinolines to Dihydroisoquinolones via Organo-photocatalysis. Adv. Synth. Catal. 2018, 361 (5), 1124–1129.

(64) Yuan, P.-F.; Zhang, Q.-B.; Jin, X.-L.; Lei, W.-L.; Wu, L.-Z.; Liu, Q. Visible-Light-Promoted Aerobic Metal-Free Aminothiocyanation of Activated Ketones. Green Chem. 2018, 20 (24), 5464–5468.

(65) Guerrero-Corella, A.; María Martinez-Gualda, A.; Ahmadi, F.; Ming, E.; Fraile, A.; Alémán, J. Thiol-Ene/Oxidation Tandem Reaction under Visible Light Photocatalysis: Synthesis of Alkyl Sulfoxides. Chem. Commun. 2017, 53 (75), 10463–10466.

(66) Erythropel, H. C.; Zimmerman, J. B.; de Winter, T. M.; Petitjean, L.; Melmikov, F.; Lam, C. H.; Lounsbury, A. W.; Mellor, K. E.; Janković, N. Z.; Tu, Q.; et al. The Green ChemisTREE: 20 Years after Taking Root with the 12 Principles. Green Chem. 2018, 20 (9), 1929–1961.

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