CONSPECTUS: Cyclometalated iridium(III) complexes are frequently employed in organic light emitting diodes, and they are popular photocatalysts for solar energy conversion and synthetic organic chemistry. They luminesce from redox-active excited states that can have high triplet energies and long lifetimes, making them well suited for energy transfer and photoredox catalysis. Homooleptic tris(cyclometalated) iridium(III) complexes are typically very hydrophobic and do not dissolve well in polar solvents, somewhat limiting their application scope. We developed a family of water-soluble sulfonate-decorated variants with tailored redox potentials and excited-state energies to address several key challenges in aqueous photochemistry. First, we aimed at combining enzyme with photoredox catalysis to synthesize enantioenriched products in a cyclic reaction network. Since the employed biocatalyst operates best in aqueous solution, a water-soluble photocatalyst was needed. A new tris(cyclometalated) iridium(III) complex provided enough reducing power for the photochemical reduction of imines to racemic mixtures of amines and furthermore was compatible with monoamine oxidase (MAO-N-9), which deracemized this mixture through a kinetic resolution of the racemic amine via oxidation to the corresponding imine. This process led to the accumulation of the unreactive amine enantiomer over time. In subsequent studies, we discovered that the same iridium(III) complex photoionizes under intense irradiation to give hydrated electrons as a result of consecutive two-photon excitation. With visible light as energy input, hydrated electrons become available in a catalytic fashion, thereby allowing the comparatively mild reduction of substrates that would typically only be reactive under harsher conditions. Finally, we became interested in photochemical upconversion in aqueous solution, for which it was desirable to obtain water-soluble iridium(III) compounds with very high triplet excited-state energies. This goal was achieved through improved ligand design and ultimately enabled sensitized triplet−triplet annihilation upconversion unusually far into the ultraviolet spectral range. Studies of photoredox catalysis, energy transfer catalysis, and photochemical upconversion typically rely on the use of organic solvents. Water could potentially be an attractive alternative in many cases, but photocatalyst development lags somewhat behind for aqueous solution compared to organic solvent. The purpose of this Account is to provide an overview of the breadth of new research perspectives that emerged from the development of water-soluble $\text{fac-[Ir(ppy)_3]}$ complexes ($\text{ppy} = 2$-phenylpyridine) with sulfonated ligands. We hope to inspire the use of some of these or related coordination compounds in aqueous photochemistry and to stimulate further conceptual developments at the interfaces of coordination chemistry, photophysics, biocatalysis, and sustainable chemistry.

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yield hydrated electrons. Using a sacrificial electron donor, hydrated electrons can be generated in a catalytic fashion, and photochemical reactions requiring very negative reduction potentials can be driven under continuous irradiation with a laser.

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Iridium(III) complexes with high triplet energies are developed and used to sensitize the triplet–triplet annihilation upconversion of naphthalene derivatives, resulting in blue-to-ultraviolet light conversion. The UV-emissive excited states of the naphthalenes can be exploited to drive thermodynamically demanding chemical reactions.

**INTRODUCTION**

Many current photophysical and photochemical studies rely on cyclometalated iridium(III) complexes because they exhibit particularly favorable properties. Their excited-state and redox characteristics are tunable through modification of ligands and coordination environments, making them adaptable to many different applications. For instance, both very oxidizing and strongly reducing variants of cyclometalated iridium complexes are available, whereas others have exceptionally high triplet energies. In addition to their initial role as triplet harvesters and luminophores in organic light-emitting diodes, this class of compounds, therefore, has become useful for solar energy conversion and synthetic organic photochemistry.

Homoleptic tris(cyclometalated) iridium(III) complexes represent a subgroup within the larger family of cyclometalated iridium(III) complexes, which furthermore includes many heteroleptic compounds typically containing one α-diamine coligand. The prototype of the homoleptic subgroup is fac-[Ir(ppy)₃] (ppy = 2-phenylpyridine), which luminesces from an excited state with a lifetime of 1.9 μs. Its triplet energy is relatively high (2.50 eV), and with an excited-state oxidation potential of −1.73 V vs SCE, it is a strong photoreductant.

These combined properties make fac-[Ir(ppy)₃] and its congeners (with cyclometalating ligands other than ppy) attractive luminophores and photocatalysts. However, such homoleptic tris(cyclometalated) iridium(III) complexes are typically charge-neutral and as such very lipophilic, which limits their application potential in polar solvents. In water, they are usually completely insoluble, and even the water-solubility of widely used monocationic iridium(III) complexes seems to be too low for applications in homogeneous aqueous photocatalysis. However, for some areas of photochemistry, water is an essential solvent or cosolvent, for example, light-driven water splitting, detoxification processes in environmental photochemistry, or the combination of enzymatic and photoredox catalysis. Furthermore, water is one of a rather narrow selection of fluids in which solvated electrons can exist, and hydrated electrons are super-reductants that seem yet underexplored in photocatalysis.

Our Account begins with a brief overview of water-soluble cyclometalated iridium(III) complexes, before delving into our own research on homoleptic tris(cyclometalated) variants and their applications. The core part is structured into three different sections, summarizing our efforts on (i) concurrent photoredox and enzyme catalysis, (ii) the formation and exploitation of hydrated electrons with visible light, and (iii) sensitized triplet–triplet annihilation upconversion for the generation of ultraviolet light in water. At the end, we provide some key conclusions and an outlook.

**PREVIOUSLY KNOWN WATER-SOLUBLE CYCLOMETALATED IRIDIUM(III) COMPLEXES**

Three common strategies to turn lipophilic metal complexes into water-soluble congeners include sulfonation, attachment of poly(ethylene glycol) (PEG) chains, and the introduction of quaternary alkyl ammonium groups. All three strategies have been applied to heteroleptic cyclometalated iridium(III) compounds (Figure 1) by several researchers with different

![Figure 1. Previously explored water-soluble cyclometalated iridium(III) complexes (left) and the corresponding cyclometalating ligands (right); R = H, CF₃, tBu.](https://doi.org/10.1021/acscentsci.2c00075)
backgrounds and motivations. The Castellano group used bathophenanthroline disulfonate in combination with different cyclometalating ligands (Figure 1a), and they observed strongly concentration-dependent photoluminescence quantum yields and lifetimes due to aggregation of their iridium(III) complexes in aqueous solution.18,19 This phenomenon is reminiscent of aggregation-induced emission but is uncommon for octahedral metal complexes. The group of Lo used PEGylation to obtain water-soluble cyclometalated iridium(III) complexes that can act as biological probes with low cytotoxicity and high cellular uptake efficiency (Figure 1b).20 The incorporation of an aldehyde group on one of the cyclometalating ligands furthermore permitted their covalent attachment to proteins and amine-containing polymers, to result in some of the first PEGylation reagents based on luminescent transition metal complexes. The teams of Francis and Hayne used PEG substituents to obtain water-soluble iridium(III)-based emitters for electrogenerated chemiluminescence (Figure 1c),21 and in related earlier studies furthermore employed a combination of sulfonation and PEGylation strategies for the same purpose.22 In contrast, the Roelfes group introduced quaternary ammonium groups at the 2,2′-bipyridine backbone to obtain a water-soluble iridium(III) complex that acted as photocatalyst for modification of dehydroalanine residues in peptides and proteins (Figure 1d).23 Other polycationic complexes have been developed with tumor imaging and DNA photocleavage applications in mind.24,25 Charge-neutral complexes were investigated by the teams of De Cola and Josel (Figure 1e) in the context of electrochemiluminescence in aqueous buffer solution.26 Coe and co-workers investigated water-soluble iridium(III) complexes with deprotonated N-methylbipyridinium ligands as fluorine-free blue and green emitters (Figure 1f).27,28

![Figure 2](https://example.com/figure2.png)

**Figure 2.** New sulfonated variants of the homoleptic fac-[Ir(ppy)3] complex, together with their emission spectra recorded in water at room temperature and selected key properties.

**Table 1. Photophysical and Electrochemical Properties of the Water-Soluble Complexes from Figure 2 and the Lipophilic fac-[Ir(ppy)3] Parent Complex**

| Complex                     | absorption | emission | electrochemistry |
|-----------------------------|------------|----------|------------------|
|                            | λ<sub>max</sub> (nm) | ε<sub>ext,max</sub> (nm) | λ<sub>max</sub> (nm) | τ<sub>0</sub> (ns) | φ<sub>d</sub> (nm) | E<sub>T</sub> (eV) | E<sub>ox</sub><sup>f</sup> (V vs SCE) | E<sub>ox</sub><sup>*</sup> (V vs SCE) |
| fac-[Ir(ppy)3]<sup>b</sup>  | 375        | 2800     | 510             | 1900             | 0.38              | 2.50             | 0.77              | −1.73                        |
| fac-[Ir(sCH<sub>2</sub>ppy)(ppy)₂]<sup>−</sup> | 374        | 1900     | 540             | 1560             | 0.13              | 2.50             | 0.56              | −1.94                        |
| fac-[Ir(sppy)₃]<sup>−</sup> | 360        | 900      | 522             | 1625             | 0.73              | 2.65<sup>f</sup>  | 0.76              | −1.89                        |
| fac-[Ir(sFppy)₃]<sup>−</sup> | 338        | 500      | 496             | 2165             | 0.91              | 2.76             | 0.91              | −1.85                        |
| fac-[Ir(sdFppy)₃]<sup>−</sup> | 330        | 230      | 484             | 2110             | 0.84              | 2.81             | 1.05              | −1.76                        |

<sup>a</sup>In deaerated aq. NaOH solution (50 mM) at 20 °C.<br><sup>b</sup>In CH₃CN at room temperature.<br><sup>c</sup>Maxima of the lowest energy bands.<br><sup>d</sup>Luminescence quantum yields determined relative to fac-[Ir(ppy)₃]<sup>−</sup>.<br><sup>e</sup>Energy of the emissive triplet state estimated from the short-wavelength edge (10% of maximum intensity) of the room-temperature luminescence spectrum.<br><sup>f</sup>Ground-state oxidation potential determined by cyclic voltammetry in aqueous phosphate buffer (0.1 M, pH 7).<br><sup>g</sup>Oxidation potential in the emissive excited state according to the relationship E<sub>ox</sub><sup>*</sup> = E<sub>ox</sub><sup>f</sup> − E<sub>T</sub>/e, where e is the elementary charge.<br><sup>h</sup>A triplet energy of 2.58 eV was measured in an alcohol mixture at 85 K.30
structurally analogous (charge-neutral) homoleptic tris-(cycloometalated) iridium(III) complexes. However, further chemical modifications are required to obtain sufficient water solubility as illustrated in Figure 1.15

In the course of our research on photoreductions and light-driven multielectron transfer,29 we became interested in hydrophilic variants of fac-[Ir(ppy)3] because this parent complex is known to be particularly reducing and (photo-)robust. Sulfonation was our preferred strategy to obtain water-soluble complexes (Figure 2), since long PEG chains surrounding the photoactive core seemed undesirable for allowing productive bimolecular catalyst–substrate encounters, and quaternary ammonium groups can be photochemically fragile. The sulfonation of the lipophilic fac-[Ir(ppy)3] complex and of some fluorinated variants (Figure 2b,c) was performed using trifluoroacetic anhydride in concentrated sulfuric acid.6

In addition, a cycloometalating ligand with a methanesulfonate group was prepared and reacted with the common dichlorotetrakis(2-phenylpyridine)diiridium(III) precursor to yield a tris(cycloometalated) complex with only one hydrophilic sulfonate group (Figure 2d).3 The relatively simple structural variations along the series of complexes in Figure 2 permit a remarkable modulation of oxidation potentials (E°) and triplet energies (E_T) while maintaining excited-state lifetimes (τ_0) on the order of 2 μs and good visible light absorption properties (Table 1), which is in line with similar findings made previously for lipophilic congeners.6 The widely differing emission spectra of the four anionic complexes are included in Figure 2 (panel e) to illustrate the triplet energy modulation. Furthermore, some key properties that could facilitate the selection of the proper water-soluble iridium(III) complex for a given application are listed next to the structures.

Fluorination elevates the ground state oxidation potential (E°), but with the excited-state energy (E_T) increasing simultaneously, all four complexes remain very strong photoreductants (featuring excited-state oxidation potentials, E°_ox, below −1.7 V vs SCE). Their triplet energies (E_T up to 2.81 eV) are among the highest known to date for water-soluble transition metal complexes, yet excitation in the visible region remains possible in all cases (with extinction coefficients at a common LED peak wavelength such as 455 nm (ε_{455nm}) between 230 and 1900 M⁻¹ cm⁻¹). Emission lifetimes remain long (τ_0 > 1560 ns) and luminescence quantum yields (Φ up to 0.91) are high, despite the fact that H₂O is usually an inefficient deactivator of electronically excited states due to its high-frequency O–H vibrations.

### APPLICATION OF fac-[Ir(sppy)3]³⁻ IN COMBINED ENZYME AND PHOTOREDOX CATALYSIS

In the course of our work on photoinduced multielectron transfer,29 we discovered that reductive amination of carbonyl compounds is possible by photoredox catalysis with [Ru(bpy)3]²⁺.31,32 In an ensuing collaborative effort with the Ward group, we then targeted the photochemical reduction of imines to enantioenriched amines, using 2-cyclohexyl-1-pyrroline (1a) as a model substrate (Figure 3a).3 The photochemical key step in this overall two-electron process is the reduction of the imine starting material to an α-amino alkyl radical intermediate (Figure 3b). Compared to the reduction of iminium cations achieved earlier with [Ru(bpy)3]²⁺ in the reductive amination,31,32 the reduction of charge-neutral imines was more challenging. The [Ru(bpy)3]²⁺ photocatalyst only provided trace amounts of the (racemic) amine photoproduct rac-2a even after 20 h of irradiation (Figure 3a). In a mixture of CD₃CN with 10% H₂O, the more strongly photoreducing (lipophilic) fac-[Ir(ppy)3] complex catalyzed the reaction to 99% yield after 6 h in the presence of ascorbate as sacrificial reductant. However, this solvent mixture is not at all ideal for the envisioned combination of the photochemical reduction with an enzymatic follow-up reaction. The specific plan was to rely on monoamine oxidase (MAO-N-9) to convert one of the two enantiomers of rac-2a back to the initial imine 1a, to obtain a cyclic reaction network that leads over time to enrichment of the unreactive amine enantiomer. The MAO-N-9 enzyme works best in aqueous solution, and hence a water-soluble variant of fac-[Ir(ppy)3] was needed.

Gratifyingly, with the fac-[Ir(sppy)3]³⁻ complex (Figure 2a), the reaction of 1a to rac-2a in aqueous phosphate buffer at pH 7
HYDRATED ELECTRONS FROM PHOTOIONIZATION OF fac-[Ir(sppy)_3]^3– WITH VISIBLE LIGHT

Hydrated electrons are typically formed by pulse radiolysis or ultraviolet radiation. However, Goez and co-workers demonstrated a few years ago that when [Ru(bpy)_3]^2+ in water is excited with green light, hydrated electrons are liberated. Since that [Ru(bpy)_3]^2+ species itself can be formed via green excitation of [Ru(bpy)_3]^3+, in the presence of sacrificial electron donors, the hydrated electrons become accessible via stepwise excitation with two green photons. We adapted this concept to the fac-[Ir(sppy)_3]^3– complex, but with a mechanistic twist: Instead of photoionizing its one-electron reduced form, we directly excited the long-lived 3MLCT excited state of the fac-[Ir(sppy)_3]^3– complex and achieved photoionization from an energetically high-lying triplet excited state. In pulsed laser experiments, excitation with blue light promoted fac-[Ir(sppy)_3]^3– to the 3MLCT state (Figure 4a), which has its own characteristic UV–vis absorption profile, notably with an intense band in the green spectral range (spectrum in Figure 4a), where the electronic ground state of fac-[Ir(sppy)_3]^3– does not absorb. When the sample was further excited into that specific absorption band with a green laser pulse, the fac-[Ir(sppy)_3]^3– complex was promoted from the 3MLCT state to the above-mentioned high-lying triplet state (T_a in Figure 4d), from which ionization occurs. The iridium(IV) oxidation product is readily detectable in two-pulse UV–vis transient absorption experiments, along with the spectral signature (Figure 4d) of hydrated electrons (e_{aq}^•–).

In the presence of excess triethanolamine (D_{ac} in Figure 4e), the iridium(IV) intermediate (corresponding to PC^•–) is spontaneously reduced back to the initial iridium(III) complex, and consequently, hydrated electrons can be generated in a catalytic fashion. With a redox potential of −2.9 V vs NHE, solvated electrons are strongly reducing (Figure 4d), making them attractive reductants for photoredox catalysis. Continuous (rather than pulsed) excitation is desirable for this purpose, and a laser providing an output power of 1 W at a wavelength of 447 nm, where both the electronic ground state and the 3MLCT excited state of fac-[Ir(sppy)_3]^3– absorb, represented a good choice for several photoreductions.

Figure 4. (a) Energy-level scheme relevant to monophotonic excitation of fac-[Ir(sppy)_3]^3– along with pertinent properties of its emissive 3MLCT excited state including the triplet energy (E_T), redox potential (E_{1/2} here given vs NHE for better comparison with the hydrated electron potential), and lifetime (τ). T_a denotes an energetically high-lying triplet excited state; 1A_1 is the term symbol for the electronic ground state. (b) Catalytic cycle for triplet–triplet energy transfer from the fac-[Ir(sppy)_3]^3– photocatalyst (PC) to a substrate (S). (c) Catalytic cycle for reductive photocatalysis via an oxidative excited-state quenching step and subsequent photocatalyst regeneration with a sacrificial electron donor (D_{ac}). (d) Energy-level scheme relevant to biphotonic excitation of fac-[Ir(sppy)_3]^3– along with pertinent properties of the hydrated electron (e_{aq}^•–) resulting from autoionization of the T_a excited state. (e) Catalytic cycle relevant for photoreductions with the solvated electron, following consecutive biphotonic excitation of the photocatalyst to the T_a state (1**+PC).
For instance, the photodegradation of a 10 mM solution of the benzyltrimethylammonium cation in D$_2$O (Figure 5d) was readily accomplished with 1 mol % of fac-[Ir(sppy)$_3$]$_3^{3-}$ and 5 equiv of triethanolamine. Quaternary ammonium compounds of this type are applied in many different contexts, such as antimicrobial reagents or fabric softeners, and they tend to accumulate in the environment. In wastewater treatment, they can be degraded with γ-rays or ultraviolet C light (200–280 nm). Hence, the finding that their photodegradation can also be driven with blue light seems remarkable, even though it is a two-photon process that relies on a comparatively high excitation power density provided by a focused laser beam. However, there is no need for pulsed ultrafast lasers that are typically required for the simultaneous absorption of two photons, because our consecutive absorption mechanism has a relatively long-lived intermediate (3MLCT), which can be re-excited with a simpler continuous-wave laser. Under similar conditions, the reduction of trifluoromethylbenzoate to difluoromethylbenzoate (Figure 5a) has been accomplished, albeit with a much lower yield (12%).

The mechanism of photoionization in fac-[Ir(sppy)$_3$]$_3^{3-}$ allows for reaction control through the applied excitation power density. As indicated above, photoionization results from the consecutive absorption of two photons (Figure 4d) and as such depends quadratically on the excitation power density, while the formation of the 3MLCT-excited state is linearly dependent on the excitation power density. Thus, the introduction (or the removal) of an optical lens in the beam path of a continuous-wave laser operating at constant power can determine whether hydrated electrons or only the 3MLCT-excited fac-[Ir(sppy)$_3$]$_3^{3-}$ are produced. Coincidentally, the hydrated electron and the 3MLCT excited state have very similar kinetic reactivities due to similar lifetimes (1.6 μs vs 1.4 μs), but their thermodynamic reactivities are vastly different, with relevant redox potentials of −2.9 V compared to −1.6 V vs NHE (Figure 4a,d). For substrates such as 4-bromo-2-chloro-5-fluorobenzoate (Figure 5a), in which the different halogen substituents have different thermodynamic reactivities (due to the reduction potentials needed for reductive debromination, dechlorination, and defluorination), the reaction outcome can therefore be determined by the presence or the absence of the focusing lens. In its absence, only 3MLCT-excited fac-[Ir(sppy)$_3$]$_3^{3-}$ is formed, and reductive debromination leads to the hydrodebromination product (leftward arrow in Figure 5a). When the optical lens is inserted into the beam path while keeping all other parameters constant, hydrated electrons are liberated and reductive dechlorination occurs in addition to reductive debromination (rightward arrow in Figure 5a). The reductive dehalogenations likely occur along the reaction mechanisms outlined in Figure 4e: For the debromination (Figure 4c), the photocatalyst (PC) is promoted to the 3MLCT excited state (3*PC) through the absorption of a single photon ($hν_1$), and then reduces the substrate (S) to give the oxidized photocatalyst (PC*) along with one-electron reduced substrate (S*). The sacrificial electron donor (D$_{Sac}$) triethanolamine regenerates the photocatalyst in its initial state (PC), and the oxidation product (D$_{Sac}$*) undergoes degradation. The activated substrate (S*) reductively dehalogenates to liberate a halogenide anion, and the resulting aryl radical takes up a hydrogen atom from one of the triethanolamine degradation products. For the dechlorination (Figure 4e), the triplet-excited photocatalyst (3*PC) is further excited by a second photon ($hν_2$) to yield a highly excited triplet state (3**PC in Figure 4e, named, T$_n$ in Figure 4d) from which hydrated electrons are formed and can activate the substrate.

The discrimination between reaction pathways for 4-bromo-2-chloro-5-fluorobenzoate in Figure 5a is based on the different reducing powers of the 3MLCT-excited fac-[Ir(sppy)$_3$]$_3^{3-}$ complex and the hydrated electron, as well as the fact that reductive dehalogenation requires substantially less reducing power than reductive dechlorination. An alternative mode of operation is exploited with the trans-3-fluorocinnamate substrate in Figure 5b. At low excitation power densities, the 3MLCT-excited fac-[Ir(sppy)$_3$]$_3^{3-}$ complex undergoes triplet–triplet energy transfer (TTET) to the substrate (Figure 4b) and thus sensitizes its photoisomerization from the trans- to the cis-form. At high excitation densities, hydrated electrons cause reduction of the C==C double bond.

![Figure 5](https://accounts.acs.org/acs/accounts/20200075)

**Figure 5.** Photoreactions induced with fac-[Ir(sppy)$_3$]$_3^{3-}$ under low power density (left) and high power density (right) excitation conditions. Reaction conditions: (a, b) fac-[Ir(sppy)$_3$]$^{3-}$ (2–3 mol %), triethanolamine (6 equiv) in H$_2$O; (c, d) fac-[Ir(sppy)$_3$]$_3^{3-}$ (1 mol %), triethanolamine (5 equiv) in H$_2$O and D$_2$O.

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Thus, the fac-[Ir(sppy)₃]³⁻ complex can be used for the catalytic production of hydrated electrons and furthermore allows reactivity control by the excitation power density, ε²,³⁹ complementing recent work in which the excitation wavelength dictated the reaction outcome.⁴⁰,⁴¹

ENERGY TRANSFER CATALYSIS AND PHOTOCHEMICAL UPCONVERSION TO THE ULTRAVIOLET REGION IN WATER

The cinnamate isomerization discussed in the preceding section relies on the same initial mechanistic step (general mechanism of Figure 4b) as sensitized triplet—triplet annihilation upconversion (sTTA-UC), namely, a triplet—triplet energy transfer (TTET) from the photoexcited iridium(III) complex to an energy acceptor. This isomerization has been investigated with all water-soluble photosensitizers displayed in Figure 2 with seemingly surprising results: The higher the sensitizer’s triplet energy, the lower the yield of the desired cis-isomer (Figure 6). Such counter-thermodynamic alkene isomerizations are increasingly well explored in organic solvents, and the reaction outcome strongly depends on the triplet energy of the sensitizer relative to that of the alkene, in both its cis- and trans-form.⁴¹,⁴² In our case, the TTET reactions between excited fac-[Ir(sppy)₃]³⁻, as well as fac-[Ir(s⁻CH₂ppy)(ppy)₂]³⁻, and the cis-cinnamate are endergonic (i.e., very slow), whereas all other possible TTET reactions are expected to be exergonic (Figure 6b). Consequently, only the catalyst with the lowest triplet energy efficiently accumulates the thermally less stable cis-isomer in the photostationary state,¹ highlighting the importance of tunable triplet energies.

Triplet energies are furthermore important in the context of photochemical upconversion. Sensitized triplet—triplet annihilation upconversion is a promising and widely investigated mechanism for the conversion of low-energy input light into higher energy output radiation.⁴³,⁴⁴ Many of the commonly employed annihilators are polyaromatic hydrocarbon compounds such as anthracene or pyrene derivatives, and thus sTTA-UC is typically investigated in organic solvent or in apolar gels,⁴⁵ whereas studies in neat water are extremely scarce.⁴⁶-⁴⁷ There have been numerous investigations of visible-to-visible upconversion, and while near-infrared-to-visible light conversion is gaining momentum,⁴⁸,⁴⁹ visible-to-ultraviolet upconversion seems underexplored.⁵⁰-⁵² In the course of our research focusing on the generation of highly reactive electronically excited states,⁵³-⁵⁵ we therefore became interested in blue-to-ultraviolet upconversion in water.

The triplet energy of the sensitizer is a limiting factor for the energy of the achievable upconverted light output, because the upconverted fluorescence cannot be higher than twice the energy of the two annihilated triplet excited states.⁵⁶ Consequently, for upconversion from the visible to the ultraviolet, it becomes desirable to shift the sensitizer’s triplet energy as high as possible, in contrast to what has been observed for the cinnamate photoisomerization (Figure 6). For lipophilic tris(cyclometalated) complexes of iridium(III), this had been achieved previously through partial fluorination of the ligands,⁶ and the same strategy is also applicable to our new water-soluble congeners (Figure 2).⁷ In the fac-[Ir(s⁻Fppy)₃]³⁻ parent compound (Figure 2a), the 'MLCT energy is 2.65 eV (Table 1), and this increases to 2.76 eV in fac-[Ir(s⁻CH₂ppy)₃]³⁻ where all three cyclometalated ligands are singly fluorinated (Figure 2b). Double fluorination of each ligand increases the triplet energy further to 2.81 eV in fac-[Ir(s⁻CH₂ppy)₃]³⁻ (Figure 2c), relatively close to the blue edge of the visible spectrum. Importantly, a molar extinction coefficient of 230 M⁻¹ cm⁻¹ at 455 nm (Table 1) still permits reasonably efficient excitation of this complex with a blue light source.

Our search for suitable annihilators focused largely on naphthalene and p-terphenyl derivatives with sulfonate,⁵⁶

Figure 6. Sensitized isomerization of trans-3-fluorocinnamate in water (a) with relative triplet energies of both olefin isomers and the four sulfonated iridium(III) photocatalysts (b). The sensitizer’s triplet energy (Eₜ) determines the cis/trans ratio in the photoequilibrium.

Figure 7. (a) Annihilators used for sensitized triplet—triplet annihilation upconversion (sTTA-UC) in water. (b) Energy level scheme relevant for sTTA-UC with the iridium(III) complexes from Figure 2 and the annihilators from panel a; Nap stands for the naphthalene core of the respective annihilator compounds. (c) Photoreactions induced via sTTA-UC; reaction conditions: fac-[Ir(sppy)₃]³⁻ (0.1 mM), naproxen (10 mM), isopropanol (100 mM) in H₂O (upper); fac-[Ir(sppy)₃]³⁻ (0.1 mM), naproxen (20 mM), in H₂O (lower).
The development of new photosensitizers and photocatalysts is an integral part of contemporary research in photophysics and photochemistry. With few exceptions, such research efforts typically focus on organic solvents, whereas the development of new photosensitizers and photocatalysts suitable for applications in water lags behind. In many cases of cationic transition metal complexes, counterion exchange can suffice to achieve water solubility, but other strategies have to be applied to strongly lipophilic charge-neutral coordination compounds. In the case of homeleptic tris(cyclometalated) iridium(III) complexes, ligand sulfonation leads to 3-fold negatively charged complexes that enable new photoprocesses in water. Specifically, the water solubility of this compound class with comparatively high photoreducing power permitted their combination with the MAO-N-9 enzyme to achieve the enantioselective synthesis of amines from imines. With sufficiently high excitation power densities, photoionization of fac-[Ir(sppy)3]3+ via 2-fold consecutive excitation provides hydrated electrons as super-reductants for photoredox catalysis. In combination with suitable annihilators, photochemical upconversion unusually far into the UV spectral range becomes achievable, even in a solvent (water) for which only a handful of sTTA-UC systems have been reported until now. It seems plausible that these complexes can be applied beyond photocalysis and upconversion, and fac-[Ir(sppy)3]3+ has already been shown to be an effective enhancer of [Ru(bpy)3]2+ electrochemiluminescence detection in aqueous solution.

These applications are possible owing to the high photostability, comparatively strong reducing power, and high energies of the phototactic (triplet) excited states of this family of compounds. All of these properties are maintained when going from the known lipophilic parent complexes to the new water-soluble variants. In particular, their stability under long-term irradiation with both continuous-wave lasers and high-power LEDs, as well as under pulsed excitation with relatively high peak powers, is remarkable. Thus, the inertness of octahedral low-spin d8 complexes with precious iridium(III)

after hydrogen atom abstraction from isopropanol can reduce the oxidized NPX annihilator, making the overall process catalytic. The driving-force for reductive debromination of the 4-bromo-2-chloro-5-fluorobenzoate substrate from singlet-excited NPX is substantially higher than that from the emissive excited state of fac-[Ir(sppy)3]3+. In another experiment, the photo-decomposition of benzyltrimethylammonium was possible under upconversion conditions (Figure 7c, bottom) employing a blue LED as light source, instead of a pulsed laser as for the method in Figure 5d.

The two examples in Figure 7c reveal that sensitized triplet–triplet annihilation upconversion represents a viable mechanism to access classic ultraviolet photochemistry with visible light, complementing the findings regarding the visible-light generated hydrated electrons from the previous section. The key difference is that the formation of the hydrated electrons requires very high excitation power densities (on the order of 1 kW/cm2), while the upconversion mechanism operates at substantially lower photon fluxes. Practical advantages of two-photon based mechanisms can emerge from the fact that direct UV excitation is often harmful and can suffer from selectivity and filter effect issues when compared to visible excitation.

The attraction. 1,5-Naphthalenedisulfonate (NDS) and naproxen
complex and the annihilator as a result of mutual electrostatic
interaction. 1,5-Naphthalenedisulfonate (NDS) and naproxen
excited state energy of 3.9 eV, compares very favorably
the experimental upconversion e
explainable by the moderate
theoretical limit, suggesting
at first glance that the achievable upconversion efficiency could be
high. However, direct measurements comparing the intensity of the upconverted NDS fluorescence to the
iridium(III) 3MLCT emission demonstrate that this expectation
is not fulfilled. Under high power excitation conditions
(near 400 mW), the upconversion quantum yield levels off
at roughly 0.035%, far below the theoretical limit of 50%
available for a two-photon process. In part, this is explainable by
the moderate fluorescence quantum yield of
for NDS in alkaline water, but even when considering this,
the experimental upconversion efficiency remains about 2
orders of magnitude below the theoretical limit. Evidently,
there are important energy-loss mechanisms that would require
additional studies to clarify, in addition to the excimer
formation issues observed for several water-soluble annihilators.

Gratifyingly, the upconverted NDS fluorescence occurs from
a singlet excited state with unusually high energy (3.9 eV),
even higher than what was previously the record value in
organic solvents (3.6 eV). Furthermore, the achievable pseudo
anti-Stokes shift of −1.1 eV, defined as the energy difference
between the excitation wavelength (447 nm, 2.8 eV) and the
singlet-excited state energy of 3.9 eV, compares very favorably
to most previously investigated upconversion systems in
organic solution.

While the NDS annihilator was selected with a focus on
optimizing the photophysical performance of the overall
upconversion system, the NPX annihilator (Figure 7a, bottom)
is more readily amenable to photochemical applications. The
fluorescent singlet excited state of NPX is at lower energy (3.7
eV) but, at the same time, is substantially more reducing than
the singlet excited state of NDS. In that excited singlet state,
NPX is oxidized at −2.5 V vs NHE, which is sufficient to
induce reductive debromination of 4-bromo-2-chloro-5-fluo
robenzoate under upconversion conditions. In the presence of
isopropanol as a hydrogen atom donor to the photogenerated
aryl radical, the hydrodebromination product is readily
obtained (Figure 7c, top). The dimethyl ketyl radical formed

...and ammonium groups, because these two
polyaromatic hydrocarbon frameworks have triplet energies
close to fac-[Ir(sppy)3]3−. Furthermore, their lowest singlet
excited states are at high energies with decent fluorescence
quantum yields. Despite their hydrophilic substituents,
solubility issues prevail for many of the investigated
naphthalenes and p-terphenyls under upconversion conditions,
in some cases due to an inherently low solubility in water and
in other cases because of aggregation between the iridium(III)
complex and the annihilator as a result of mutual electrostatic
attraction. 1,5-Naphthalenedisulfonate (NDS) and naproxen
(NPX) emerged as the two best suited choices (Figure 7a)
in combination with the sulfonated iridium(III) compounds in
Figure 2a–c. Following blue excitation of these sensitizers and
ultrafast intersystem crossing into their lowest 3MLCT states
(Figure 7b), triplet–triplet energy transfer to NDS is
achievable with efficiencies between 84% and 95%, producing
a very long-lived (τs = 1.1 ms) triplet state on the naphthalene
framework (termed 3Nap in Figure 7b). Upon collisional
encounter between two triplet-excited NDS molecules, triplet–
triplet annihilation (TTA) can occur to produce one NDS
molecule in its fluorescent singlet excited state (3*Nap, Figure
7b) and one in its electronic ground state (1*Nap). With NDS
in alkaline aqueous solution, triplet–triplet annihilation occurs
with a rate constant approaching the diffusion limit, suggesting
at first glance that the achievable upconversion efficiency could be
high. However, direct measurements comparing the intensity of the upconverted NDS fluorescence to the
iridium(III) 3MLCT emission demonstrate that this expectation
is not fulfilled. Under high power excitation conditions
(near 400 mW), the upconversion quantum yield levels off
at roughly 0.035%, far below the theoretical limit of 50%
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While the NDS annihilator was selected with a focus on
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isopropanol as a hydrogen atom donor to the photogenerated
aryl radical, the hydrodebromination product is readily
obtained (Figure 7c, top). The dimethyl ketyl radical formed
...
represents a significant advantage in comparison to many photoactive complexes based on abundant first-row transition metals.\textsuperscript{63} It seems plausible to expect that iridium(III) complexes will continue to play important roles in photocatalysis, now including new perspectives for different applications in water.

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\textbf{Björn Pfund} studied chemistry at the University of Applied Sciences in Zurich and the University of Basel (Switzerland). He received his M.Sc. degree under the guidance of Oliver S. Wenger in 2019, working on upconversion in water and its applications to challenging photo reductions. In 2020, he started his doctoral studies in the same group, endowed with a fellowship from the National Research Fund, Luxembourg. Currently, he is focusing on mechanistic photochemistry.

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