

Photophysical Properties and Redox Potentials of Photosensitizers for Organic Photoredox Transformations

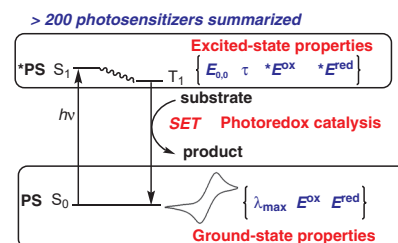
Yanyu Wu

Dooyoung Kim

Thomas S. Teets* 

Department of Chemistry, University of Houston, 3585 Cullen Blvd., Room 112, Houston, TX 77204-5003, USA
tteets@uh.edu

Published as part of the Cluster
Organic Photoredox Catalysis in Synthesis – Honoring Prof. Shunichi Fukuzumi's 70th Birthday



Received: 22.01.2021
Accepted: 15.02.2021
Published online: 15.02.2021
DOI: 10.1055/a-1390-9065; Art ID: st-2021-p0025-c



Abstract Photoredox catalysis has proven to be a powerful tool in synthetic organic chemistry. The rational design of photosensitizers with improved photocatalytic performance constitutes a major advancement in photoredox organic transformations. This review summarizes the fundamental ground-state and excited-state photophysical and electrochemical attributes of molecular photosensitizers, which are important determinants of their photocatalytic reactivity.

Key words photosensitizers, photoredox catalysis, redox potentials, excited states, photophysics, photochemistry

Introduction

Photocatalysis, in which light energy is converted into chemical bonds, was initially studied to facilitate such inorganic transformations as solar water splitting and carbon dioxide reduction.^{1–3} Since the pioneering work by the groups of MacMillan,⁴ Yoon,⁵ Stephenson,⁶ and many others,⁷ photoredox catalysis has recently garnered much recognition in the context of organic synthesis, permitting a variety of challenging organic transformations to proceed under mild conditions.^{8–11} Photochemical reactions are initiated after light harvesting by photosensitizers. Photosensitizers (PSs) are defined as chemicals that can be promoted to their electronically excited states by absorbing light; the excited molecules then permit the formation of reactive reaction intermediates by engaging in bimolecular single-electron transfer (SET) or energy-transfer processes during photocatalysis.^{12,13} PSs are also referred to as photocatalysts when used in catalytic applications. The continued interest in new reactivity and improved catalytic performance has led to the emergence of a number of different types of PSs,

including organic dyes,^{14–16} inorganic semiconductors,^{17–19} transition-metal complexes,^{7,20} and metal–organic frameworks,^{21–23} among others. Molecular PSs are particularly dominant in the field of photocatalysis on account of the maturity of the study of their photochemistry, the controllability of their structural design, and the potential to perform judicious manipulations of their electronic structure and redox properties. Most molecular PSs used in photocatalysis are inorganic or organometallic transition-metal coordination complexes, with Ir and Ru complexes being arguably the most ubiquitous.^{24–26} Metal-free organic chromophores are important alternatives to metal-based PSs, providing the potential benefits of low cost, easy purification, biocompatibility, and low toxicity.^{15,27}

The catalytic performance of molecular PSs in photoredox reactions strongly depends on their photophysical properties and their electrochemical attributes in both the ground state and excited state. Therefore, it is essential to understand and evaluate these properties to predict how a PS will interact with reaction components when designing specific photochemical transformations. Review articles on photoredox organic synthesis have mainly focused on methodology development, with some coverage of molecular-design principles, electronic structures, excited-state dynamics of the PSs, and mechanistic analyses of various types of photocatalytic reaction.^{7,14,28–31} The objective of this review is to provide a summary of the key photophysical data, excited-state energies, and ground-state and excited-state redox potentials of common molecular PSs that have been used in photoredox organic synthesis, so as to serve as a practical guide for photoredox catalysis practitioners. Partnered with Roth, Romero, and Nicewicz's catalog of ground-state redox potentials published in 2016,³² which focused primarily on small-molecule substrate molecules, this review should provide researchers with a clear

picture of the redox thermodynamics when selecting substrates and PSs for photoredox transformations. In addition, we provide an informative discussion on how to evaluate and analyze these values in relation to the photocatalytic reactivity of PSs. Because of the considerable advances made in the field of photocatalysis, it is not possible to include every single reported PS. Nevertheless, we have attempted to cover a wide variety of PSs, ranging from organic molecules to various transition-metal complexes, with a particular emphasis on those that have been applied in photochemical organic reactions.

Photophysical and Electrochemical Properties

Excited-State Energy

Upon absorption of light, usually in the UVA or visible-light region, a PS is promoted to a singlet excited state and then normally relaxes rapidly to the lowest-lying vibrational level of the lowest singlet excited state (S_1). The PS can also reach its triplet excited state (T_1) from the S_1 state through intersystem crossing (ISC). The excited-state energy ($E_{0,0}$) is the energy difference between the zeroth vibrational level of the electronic ground state (S_0) and the relevant excited state. Rigorously speaking, $E_{0,0}$ refers only to singlet states, but it is often also used in conjunction with triplet states. $E_{0,0}$ can also be abbreviated as E_{S1} or E_{T1} , corresponding to the lowest-lying singlet and triplet excited states, respectively. Complexes in their excited states are generally stronger reductants and oxidants than their ground-state counterparts. A larger value of $E_{0,0}$ represents both stronger photoreducing and photooxidizing properties. However, the value of $E_{0,0}$ should be sufficiently low that the excited state can be accessed upon UV or visible-light irradiation since it represents the minimum amount of energy that is required to access that state.

The value of $E_{0,0}$ can be estimated in a few different ways, and it is normally expressed in electron volts (eV) when used to calculate the excited-state redox potentials, as discussed in a later section. It can be determined spectroscopically from the wavelength at the intersection point of the normalized UV-vis absorption spectrum and the photoluminescence spectrum of the complex measured at room temperature.³³ For complexes that do not display room-temperature emission or do not have a crossing point between the absorption and emission spectra due to large Stokes shift (most likely to occur for triplet excited states), the maximum wavelength at the first vibronic peak of the

photoluminescence spectrum recorded at a cryogenic temperature (normally 77 K) is used to assign $E_{0,0}$.^{34,35} Alternatively, $E_{0,0}$ has been predicted by computational methods such as density functional theory (DFT) and time-dependent DFT.^{36–38}

Ground-State Redox Potentials

Formal ground-state redox potentials are normally measured by using cyclic voltammetry, a common technique for studying the redox processes of molecular species.³⁹ Complexes can feature reversible or irreversible cyclic voltammograms, as are shown in Figure 1 and Figure 2, respectively. The ground-state oxidation potential [E^{ox} or $E(\text{PS}^+/\text{PS})$] and reduction potential [E^{red} or $E(\text{PS}/\text{PS}^-)$] are related to the first one-electron oxidation and the first one-electron reduction events of the PS, respectively, as depicted in the modified Latimer diagram (Scheme 1).

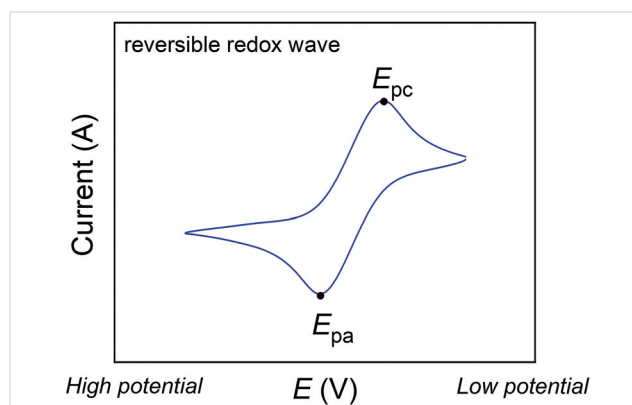


Figure 1 Example of a reversible cyclic voltammogram

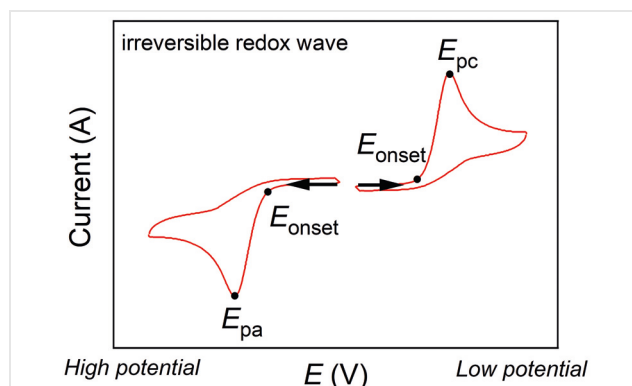
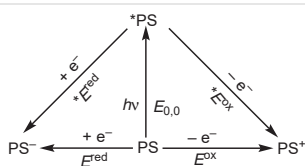


Figure 2 Example of an irreversible cyclic voltammogram; the arrows indicate the direction of the potential scan



Scheme 1 Modified Latimer diagram showing the ground-state and excited-state redox processes of a photosensitizer

For a reversible redox wave, the values of E^{ox} and E^{red} are equal to the half-wave potential ($E_{1/2}$) calculated by using Equation 1, where E_{pc} and E_{pa} are the cathodic and anodic peak potentials respectively, i.e. the potential where the maximum current of the redox wave is achieved (Figures 1 and 2).

$$E_{1/2} = \frac{1}{2} \times (E_{\text{pc}} + E_{\text{pa}})$$

Equation 1 Calculation of the half-wave potential

Irreversible oxidation and/or reduction waves imply that the redox process is followed by a chemical reaction, such as decomposition of the complex or coordination to a solvent molecule. Irreversible electrochemical behavior can be detrimental in catalytic applications, as it suggests that the one-electron reduced and/or oxidized state of the PS is chemically unstable. In this case, the cathodic and anodic peak potentials (E_{pc} and E_{pa} , respectively) are used to assign E^{red} and E^{ox} , respectively. However, it should be considered that the peak potentials do not represent thermodynamic redox potentials and that they vary on changing such experimental conditions as the solvent or the scan rate. The onset potential (E_{onset}), which represents the potential where the initial increase of current appears (Figure 2), has also been used in estimations of excited-state redox potentials.⁴⁰ An alternative method is to use the inflection-point potential (E_i) to calculate the excited-state potential for irreversible redox events, a method developed by Vullev et al.^{41,42}

Most PSs are studied under nonaqueous conditions, and the electrochemical potentials are usually either referenced against the ferrocenium/ferrocene (Fc^+/Fc) redox couple through addition of ferrocene as an internal reference during the CV experiment, or are referenced against the saturated calomel electrode (SCE). Although IUPAC recommends the use of the Fc^+/Fc reference for nonaqueous electrochemistry,³⁹ the SCE reference electrode has become popular in the field of organic (photo)redox catalysis. Therefore, to facilitate simple comparison to many other reviews and resources in this field, the ground-state and excited-state redox potentials summarized here are refer-

enced to the SCE. They are either reported with respect to the SCE reference electrode from the original work, or are corrected from the reported experimental conditions by using well-established conversions.^{43,44}

Excited-State Redox Potentials

The photoreducing and photooxidizing abilities of a PS are dictated by its excited-state redox potentials. These potential values refer to the one-electron redox reaction of the photoexcited PS ($^*\text{PS}$), as shown in Scheme 1. Typically, the excited-state reduction potential [$^*E^{\text{red}}$, or $^*E(^*\text{PS}/\text{PS}^-)$] and excited-state oxidation potential [$^*E^{\text{ox}}$, or $^*E(\text{PS}^+/^*\text{PS})$] are not directly measured and, instead, are calculated by using both the excited-state energy and the standard ground-state redox potentials, as described in Equation 2 and Equation 3, respectively. These calculations omit the change in entropy between the ground state and the excited state, as well as the Coulombic impact of charge separation due to differences in the solvent. Note that although predictions of $E_{0,0}$ and excited-state redox potentials contain some inherent uncertainty, they still provide useful thermodynamic evaluations for predicting the redox behavior of a PS in its excited state. Although it is far less common to do so, $^*E^{\text{red}}$ and $^*E^{\text{ox}}$ can also be determined by using phase-modulated voltammetry, a method in which the redox potentials of a molecular species at its excited state are measured by using an electrochemical cell equipped for light irradiation.⁴⁵ Photosensitizers with a more-positive value of $^*E^{\text{red}}$ have stronger photooxidizing power, whereas those with a more negative value of $^*E^{\text{ox}}$ demonstrate stronger photoreducing ability.

$$^*E^{\text{red}} = E^{\text{red}} + E_{0,0} \text{ (Photooxidant)}$$

Equation 2 Calculation of the excited-state reduction potential

$$^*E^{\text{ox}} = E^{\text{ox}} - E_{0,0} \text{ (Photoreductant)}$$

Equation 3 Calculation of the excited-state oxidation potential

The PS in its excited state can be a potential photoreductant and/or photooxidant, and can engage in bimolecular SET processes to produce a reactive intermediate species that initiates the targeted photochemical reaction. When used as a photoreductant, the PS will reduce an electron acceptor (EA) through an oxidative quenching mechanism. Conversely, a PS functioning as a photooxidant will oxidize an electron donor (ED), and the photocatalytic reaction will proceed through a reductive quenching cycle. The EA/ED can be an organic substrate, a sacrificial redox reagent, or a transition-metal or organic complex that acts as a synergis-

tic catalyst. Thermodynamically speaking, the value of E^{ox} should be more negative than the reduction potential of EA [$E(\text{EA}/\text{EA}^-)$] for the PS to reduce an EA, whereas E^{red} should be more positive than the oxidation potential of the ED [$E(\text{ED}^+/\text{ED})$] for the PS to be considered strong enough to oxidize an ED. Photosensitizers can be quenched by a sacrificial reductant or oxidant when there is an insufficient thermodynamic driving force to act directly on the organic substrate or catalyst, resulting in a net redox change for the catalytic cycle and the generation of byproduct(s) from the sacrificial reagent. Designing PSs with strong photoreducing and photooxidizing power is still highly desirable to ensure efficient SET processes and to improve the catalytic reactivity. As a useful reference, the ground-state electrochemical potentials of a variety of common organic substrates and sacrificial redox reagents can be found in the literature.^{32,46} In general, careful evaluation of redox properties of the PS and reaction partners is essential to the success of photochemical reactions.

Absorption Maximum Wavelength at the Lowest-Energy Absorption Peak

Analyzing the UV–vis absorption profile is important in choosing an appropriate light source for photoexcitation of the PS. A figure of merit is the peak wavelength of the lowest-energy (longest wavelength) absorption band (λ_{max}). Note that for many PSs, particularly those from the cyclometalated iridium family, it is common to have several overlapping low-energy absorption bands without a clear maximum. In these cases, the quoted λ_{max} is often in the UV region, but there is still sufficient visible absorption to permit excitation by visible light. For solar-energy harvesting, e.g. in solar fuels catalysis, it is desirable for absorption to occur over the entire solar spectrum to maximize light capture. When using an artificial light source, as is frequently done in organic photoredox catalysis, there should be some overlap between the absorption spectrum of the PS and the emission range of the light source. It is preferable to use light sources that activate the lowest-energy absorption to permit selective photoexcitation of the PS. This can avoid undesired activation of other reaction components or intermediates by high-energy light sources, potentially complicating the reaction mechanism and compromising the reaction selectivity and catalyst durability. Because most organic substrates absorb in the UV range, especially those with

aromatic functionalities, visible-light PSs are desirable and permit selective excitation of the PS in photocatalytic applications.

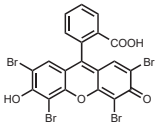
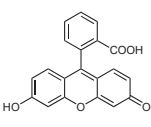
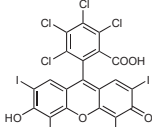
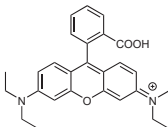
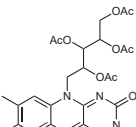
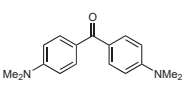
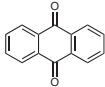
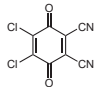
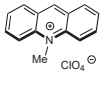
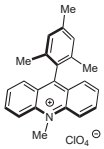
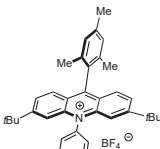
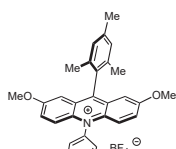
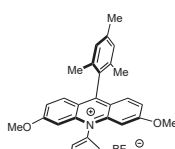
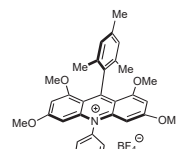
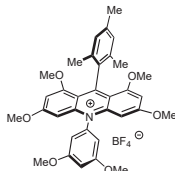
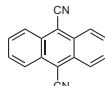
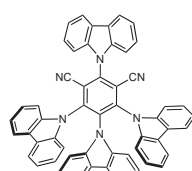
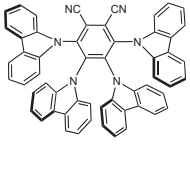
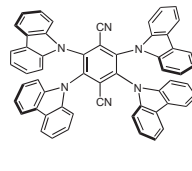
Excited-State Lifetime

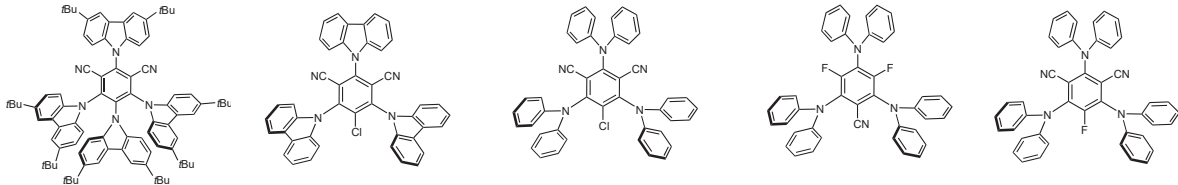
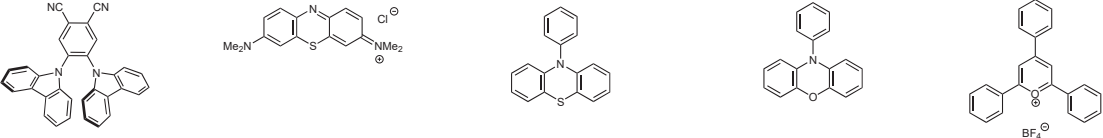
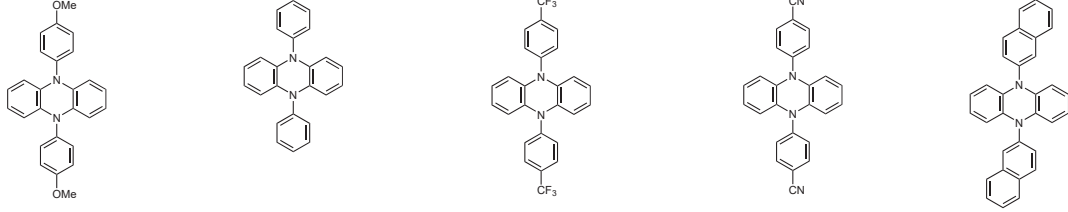
The excited-state lifetime (τ) is another relevant consideration when evaluating a PS for photoredox catalysis. An ideal PS in photocatalysis should exhibit a long-lived excited state to provide time for bimolecular SET or energy transfer to prevail over the inherent radiative or nonradiative decay pathways of the excited state. A lifetime lower than 1 ns [decay rate constant (k_r) $\geq 10^9 \text{ s}^{-1}$] indicates that the *PS will decay faster than the diffusion limit ($\sim 10^9 \text{ M}^{-1} \text{ s}^{-1}$),^{47,48} precluding any bimolecular reactivity. Triplet sensitizers typically show τ at a scale of hundreds of nanoseconds to milliseconds, several orders of magnitude longer than those of singlet PSs, due to the spin-forbidden nature of the $T_1 \rightarrow S_0$ transition. A persistent challenge in designing transition-metal-based PSs is that their ligand-field d–d states can be populated when they are lower in energy than, or thermally accessible from, the desired charge-transfer state, leading to nonradiative thermal deactivation and short-lived excited states. Overall, the design of PSs with prolonged excited-state lifetimes remains an active area of study in photoredox catalysis.

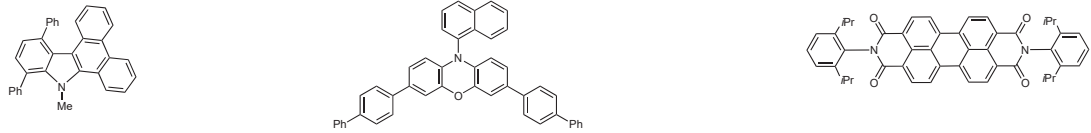
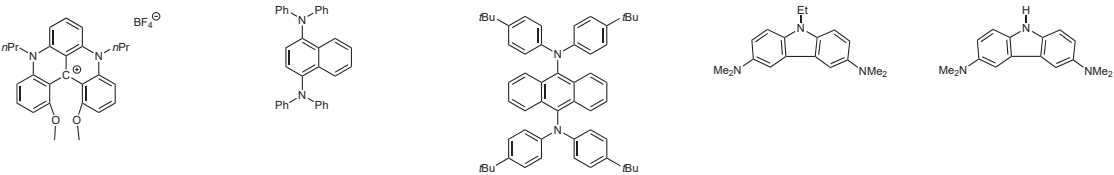
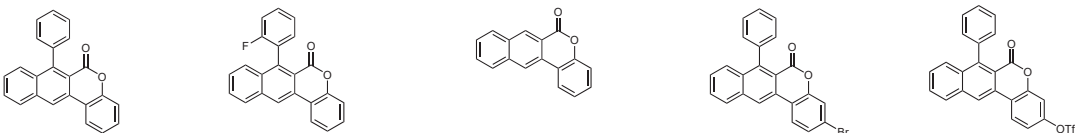
Summary of Photophysical and Electrochemical Properties of Photosensitizers

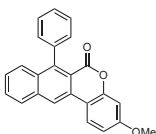
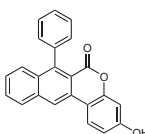
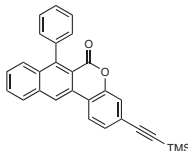
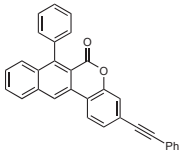
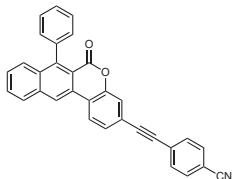
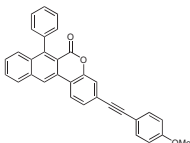
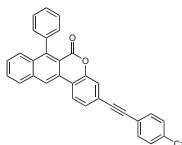
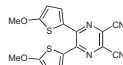
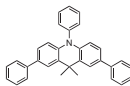
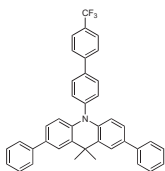
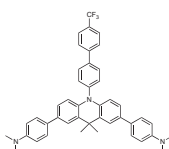
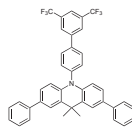
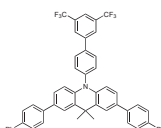
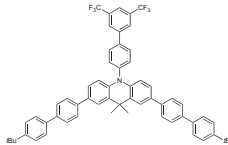
The key photophysical and electrochemical properties of PSs are listed in Tables 1–9. Organic dyes (Table 1) and polypyridyl complexes of Ru and cyclometalated Ir complexes (Table 2) make up the majority of PSs highlighted in this review, because these are the most prominent in photocatalytic organic synthesis. In the case of organic PSs, the excited-state energy, lifetime, and excited-state redox potentials for both singlet and triplet excited states are included if both items of data are available. For organic PSs, the SET process from the singlet excited state can take place before generation of the triplet excited state by ISC, due to the relatively low Φ_{ISC} (quantum yield of ISC) for organic molecules.⁴⁹ Other transition metal PSs are categorized on basis of the identity of the metal, and are summarized in Tables 3–9. In all tables, n/a indicates data not available; ^s, data for singlet excited state (S_1); and ^t, data for triplet excited state (T_1).

Table 1 Summary of Photophysical and Electrochemical Properties of Organic Photosensitizers

					
λ_{max} (nm)	539	450	549	550	443
τ (μs)	24 ^t ; 0.00266 ^s	0.0047 ^s	0.0005 ^s	0.00245 ^s	68 ^t ; 0.0057 ^s
$E_{0,0}$ (eV)	1.89 ^t ; 2.31 ^s	1.94 ^t ; 2.42 ^s	1.77 ^t ; 2.17 ^s	1.80 ^t ; 2.22 ^s	2.07 ^t ; 2.58 ^s
E^{red} (V vs. SCE)	−1.06	−1.22	−0.78	−0.96	−0.82
E^{ox} (V vs. SCE)	+0.78	+0.70	+1.09	+0.91	n/a
$^*E^{\text{red}}$ (V vs. SCE)	+0.83 ^t ; +1.25 ^s	+0.72 ^t ; +1.20 ^s	+0.99 ^t ; +1.39 ^s	+0.84 ^t ; +1.26 ^s	+1.25 ^t ; +1.76 ^s
$^*E^{\text{ox}}$ (V vs. SCE)	−1.11 ^t ; −1.53 ^s	−1.24 ^t ; 1.72 ^s	−0.68 ^t ; −1.08 ^s	−0.89 ^t ; −1.31 ^s	n/a
Refs.	50–52	51–53	51,54–56	14,51	57
					
λ_{max} (nm)	365	410	400	510	320–470
τ (μs)	3 ^t	0.0032 ^s	2.4 ^t	3.5 ^t	0.037 ^s
$E_{0,0}$ (eV)	2.70 ^t ; 2.98 ^s	2.73 ^t ; 2.88 ^s	2.67 ^t ; 3.29 ^s	2.70 ^t	2.75 ^s
E^{red} (V vs. SCE)	−2.20	−0.96	+0.51	+0.02	−0.43
E^{ox} (V vs. SCE)	+0.86	n/a	n/a	n/a	n/a
$^*E^{\text{red}}$ (V vs. SCE)	+0.50 ^t ; +0.78 ^s	+1.77 ^t ; +1.92 ^s	+3.18 ^t ; +3.8 ^s	+2.72 ^t	+2.32 ^s
$^*E^{\text{ox}}$ (V vs. SCE)	−1.84 ^t ; −2.20 ^s	n/a	n/a	n/a	n/a
Refs.	14,58–60	61–65	66,67	68	69–71
					
λ_{max} (nm)	425	420	466	407	412
τ (μs)	30 ^t ; 0.006 ^s	0.0144	0.0187	$\tau_1 = 0.003^a$ $\tau_2 = 0.0101$	$\tau_1 = 0.0013$ (92%) ^a $\tau_2 = 0.0089$ (8%)
$E_{0,0}$ (eV)	2.37 ^t ; 2.68 ^s	2.67	2.47	2.72	2.46
E^{red} (V vs. SCE)	−0.49	−0.59	−0.57	−0.71	−0.84
E^{ox} (V vs. SCE)	+1.88	n/a	n/a	n/a	n/a
$^*E^{\text{red}}$ (V vs. SCE)	+1.88 ^t ; +2.19 ^s	+2.08	+1.90	+2.01	+1.62
$^*E^{\text{ox}}$ (V vs. SCE)	−0.49 ^t ; −0.80 ^s	n/a	n/a	n/a	n/a
Refs.	72–75	76	76	76	76
					
λ_{max} (nm)	414	422	379	369	492

τ (μ s)	$\tau_1 = 0.0013^a$ $\tau_2 = 0.0123$	0.0149	5.1 ^t ; 0.4 ^s	5.03	1.46
$E_{0,0}$ (eV)	2.47	1.81 ^t ; 2.90 ^s	2.59 ^t ; 2.64 ^s	2.45 ^t	2.34 ^t
E^{red} (V vs. SCE)	−0.82	−0.91	−1.21	−1.16	−1.02
E^{ox} (V vs. SCE)	n/a	n/a	+1.52	n/a	n/a
* E^{red} (V vs. SCE)	+1.65	+0.90 ^t ; +1.99 ^s	+1.38 ^t ; +1.43 ^s	+1.29 ^t	+1.32
* E^{ox} (V vs. SCE)	n/a	n/a	−1.07 ^t ; −1.12 ^s	n/a	n/a
Refs.	76	14,77	78–81	78,80	78,80
					
λ_{max} (nm)	468	n/a	n/a	n/a	n/a
τ (μ s)	2.9	0.0069	0.0115	0.0042	0.0042
$E_{0,0}$ (eV)	2.53	2.72	2.65	2.84	2.68
E^{red} (V vs. SCE)	−1.32	−1.16	−1.41	−1.92	−1.59
E^{ox} (V vs. SCE)	+1.22	+1.79	+1.31	+1.24	+1.30
* E^{red} (V vs. SCE)	+1.21	+1.56	+1.24	+0.92	+1.09
* E^{ox} (V vs. SCE)	−1.31	−0.93	−1.34	−1.60	−1.38
Refs.	82,83	84	84	84	84
					
λ_{max} (nm)	374	665	n/a	324	417
τ (μ s)	166	77 ^t ; 0.001 ^s	$\tau_1 = 0.00081$ (54%) ^a $\tau_2 = 0.0023$ (46%)	0.0029	10 ^t ; 0.0029 ^s
$E_{0,0}$ (eV)	2.63 ^t	1.85 ^t ; 1.86 ^s	2.4 ^t ; 2.8 ^s	2.69 ^t	2.30 ^t ; 2.83 ^s
E^{red} (V vs. SCE)	−1.45	−0.30	n/a	n/a	−0.32
E^{ox} (V vs. SCE)	+1.47	+1.13	+0.68	+0.58	n/a
* E^{red} (V vs. SCE)	+1.18 ^t	+1.55 ^t ; +1.56 ^s	n/a	n/a	+1.98 ^t ; +2.51 ^s
* E^{ox} (V vs. SCE)	−1.16 ^t	−0.72 ^t ; −0.73 ^s	−1.7 ^t ; −2.1 ^s	−2.11 ^t	n/a
Refs.	78,85	14,51,86	14,87,88	89,90	77,91
					
λ_{max} (nm)	373	370	367	322	343
τ (μ s)	n/a	n/a	n/a	n/a	4.3 ^t
$E_{0,0}$ (eV)	2.31 ^t	2.34 ^t	2.37 ^t	2.21 ^t	1.9 ^t
E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a	n/a

E^{ox} (V vs. SCE)	−0.05	0.00	+0.13	+0.16	+0.21
E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a	n/a
E^{ox} (V vs. SCE)	−2.36 ^t	−2.34 ^t	−2.24 ^t	−2.06 ^t	−1.69 ^t
Refs.	92	92	92	92	93,94
					
λ_{max} (nm)	n/a	388	527		
τ (μs)	n/a	480 ^t	0.0038 ^s		
$E_{0,0}$ (eV)	3.02	2.45 ^t	2.34 ^s		
E^{red} (V vs. SCE)	n/a	n/a	−0.37		
E^{ox} (V vs. SCE)	+1.10	+0.65	+1.65		
E^{red} (V vs. SCE)	n/a	n/a	+1.97 ^s		
E^{ox} (V vs. SCE)	−1.92	−1.80 ^t	−0.69 ^s		
Refs.	95	89,93,96	97–100		
					
λ_{max} (nm)	616	375	471	388	n/a
τ (μs)	0.0055	0.009 ^s	0.031	0.017	n/a
$E_{0,0}$ (eV)	1.93	2.71 ^s	2.2	3.02	3.05
E^{red} (V vs. SCE)	−0.78	n/a	n/a	n/a	n/a
E^{ox} (V vs. SCE)	+1.32	+0.76 ^b	+0.78 ^c	+0.27	+0.29
E^{red} (V vs. SCE)	+1.15	n/a	n/a	n/a	n/a
E^{ox} (V vs. SCE)	−0.61	−1.95 ^s	−1.42	−2.75	−2.76
Refs.	101–104	105	106	107,108	109
					
λ_{max} (nm)	421	421	411	421	413
τ (μs)	0.00144	0.00207	0.00386	0.00149	0.00081
$E_{0,0}$ (eV)	3.02	3.15	3.22	3.16	3.20
E^{red} (V vs. SCE)	−1.74	−1.68	−1.67	−1.61	−1.55
E^{ox} (V vs. SCE)	+1.75	+1.81	+1.80	+1.78	+1.86
E^{red} (V vs. SCE)	+1.28	+1.47	+1.55	+1.55	+1.65
E^{ox} (V vs. SCE)	−1.27	−1.34	−1.42	−1.38	−1.34
Refs.	110	110	110	110	110

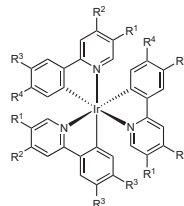
					
λ_{max} (nm)	462	461	426	434	427
τ (μs)	0.00778	0.0085	0.00253	0.00334	0.00305
$E_{0,0}$ (eV)	2.97	2.89	3.13	3.12	3.14
E^{red} (V vs. SCE)	-1.76	-1.89	-1.71	-1.70	-1.58
E^{ox} (V vs. SCE)	+1.47	+1.44	+1.73	+1.64	+1.69
* E^{red} (V vs. SCE)	+1.21	+1.00	+1.42	+1.42	+1.56
* E^{ox} (V vs. SCE)	-1.50	-1.45	-1.40	-1.48	-1.45
Refs.	110	110	110	110	110
					
λ_{max} (nm)	449	459	448	341	338
τ (μs)	0.00421	0.00249	n/a	0.0017	0.017
$E_{0,0}$ (eV)	3.08	3.12	2.01 ^t	3.23	2.73
E^{red} (V vs. SCE)	-1.65	-1.59	-1.45	n/a	n/a
E^{ox} (V vs. SCE)	+1.44	+1.35	+1.37	+0.96	+0.97
* E^{red} (V vs. SCE)	+1.43	+1.53	+0.91 ^t	n/a	n/a
* E^{ox} (V vs. SCE)	-1.64	-1.77	-1.17 ^t	-2.27	-1.76
Refs.	110	110	111–113	114	114
					
λ_{max} (nm)	348	338	358	360	
τ (μs)	0.0027, 0.0161	0.0179	0.0172	0.0168	
$E_{0,0}$ (eV)	2.50	2.62	2.63	2.63	
E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a	
E^{ox} (V vs. SCE)	+0.69	+1.02	+0.94	+0.98	
* E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a	
* E^{ox} (V vs. SCE)	-1.81	-1.60	-1.69	-1.65	
Refs.	114	114	114	114	

R		H	Et	Ph		
λ_{max} (nm)	378	414	412	408	410	408
τ (μs)	n/a	n/a	n/a	n/a	n/a	n/a
$E_{0,0}$ (eV)	2.84	2.09 ^t ; 2.57 ^s	2.11 ^t ; 2.58 ^s	2.14 ^t ; 2.57 ^s	2.13 ^t ; 2.56 ^s	2.15 ^t ; 2.55 ^s
E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a	n/a	n/a
E^{ox} (V vs. SCE)	+1.55	+0.26	+0.57	+0.68	+0.65	+0.76
* E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a	n/a	n/a
* E^{ox} (V vs. SCE)	-1.29	-1.60 ^t ; -2.31 ^s	-1.71 ^t ; -2.01 ^s	-1.61 ^t ; -1.89 ^s	-1.65 ^t ; -1.91 ^s	-1.56 ^t ; -1.79 ^s
Refs.	115–117	118,119	118,119	118,119	118,119	118,119

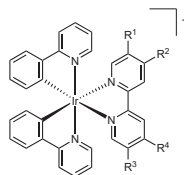
^a Biexponential.^b Redox potentials were originally referenced vs. Fc^+/Fc in MeCN and are corrected by adding 0.40 V for referencing against the SCE.^c Redox potentials were originally referenced vs. Fc^+/Fc in CH_2Cl_2 and are corrected by adding 0.46 V for referencing against the SCE.**Table 2** Summary of Photophysical and Electrochemical Properties of Ru- and Ir-Based Photosensitizers

λ_{max} (nm)	452	447	458	459	443
τ (μs)	1.1	0.5	0.875	0.99	0.74
$E_{0,0}$ (eV)	2.10	2.18	2.06	n/a	2.12
E^{red} (V vs. SCE)	-1.33	-1.36	-1.43	n/a	-0.80
E^{ox} (V vs. SCE)	+1.29	+1.26	+1.14	n/a	+1.86
* E^{red} (V vs. SCE)	+0.77	+0.82	+0.63	n/a	+1.45
* E^{ox} (V vs. SCE)	-0.81	-0.87	-0.92	n/a	-0.26
Refs.	7,120–122	120,123	124,125	126,127	120,128,129
λ_{max} (nm)	454	376	378	380	372
τ (μs)	0.131	1.9	1.6	2.04	2.16
$E_{0,0}$ (eV)	1.9	2.58	2.22	2.86	2.76

E^{red} (V vs. SCE)	−0.91	−2.23	−1.87	−2.18	−2.17
E^{ox} (V vs. SCE)	+1.69	+0.77	+0.94	+0.96	+1.06
* E^{red} (V vs. SCE)	+0.99	+0.35	+0.36	+0.68	+0.59
* E^{ox} (V vs. SCE)	−0.21	−1.88	−1.28	−1.90	−1.7
Refs.	130	131–133	134–136	132,135	132,135

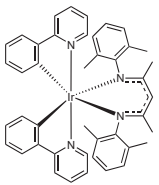
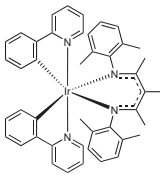
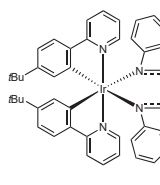
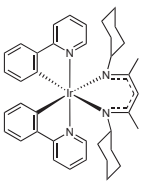
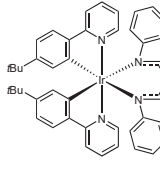
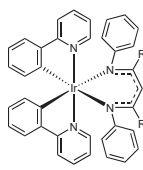
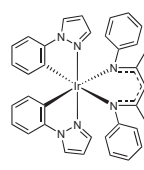
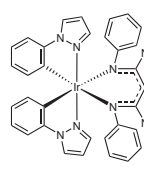
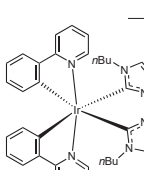


R	R ¹ = <i>t</i> -Bu; R ² = R ³ = R ⁴ = H	R ² = <i>t</i> -Bu; R ¹ = R ³ = R ⁴ = H	R ³ = <i>t</i> -Bu; R ¹ = R ² = R ⁴ = H	R ⁴ = <i>t</i> -Bu; R ¹ = R ² = R ³ = H	R ² = OMe; R ¹ = R ³ = R ⁴ = H	R ³ = OMe; R ¹ = R ² = R ⁴ = H	R ⁴ = OMe; R ¹ = R ² = R ³ = H	R ¹ = H; R ² = R ³ = R ⁴ = OMe
λ_{max} (nm)	373	382	384	382	381	397	359	396
τ (μ s)	n/a	n/a	n/a	1.97	n/a	2.86	2.24	n/a
$E_{0,0}$ (eV)	2.58	2.58	2.52	2.56	2.59	2.40	2.64	2.42
E^{red} (V vs. SCE)	−2.30	n/a	−2.26	−2.33	n/a	−2.21	−2.34	n/a
E^{ox} (V vs. SCE)	+0.68	+0.64	+0.60	+0.60	+0.59	+0.53	+0.70	+0.34
* E^{red} (V vs. SCE)	+0.28	n/a	+0.26	+0.23	n/a	+0.19	+0.26	n/a
* E^{ox} (V vs. SCE)	−1.89	−1.94	−1.92	−1.96	−2.00	−1.87	−1.95	−2.07
Refs.	131	131	131	131,132	131	131,132	131,132	131

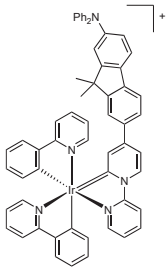
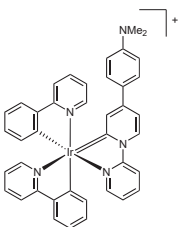
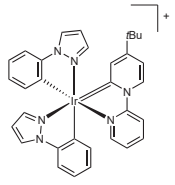
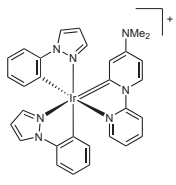
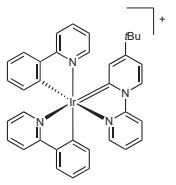
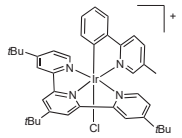
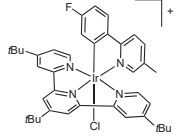
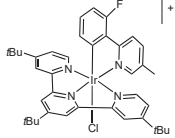
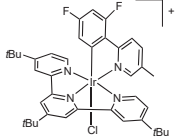
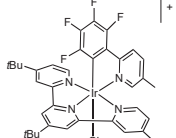


R	R ¹ = R ³ = CF ₃ ; R ² = R ⁴ = H	R ¹ = R ³ = Me; R ² = R ⁴ = H	R ¹ = R ³ = F; R ² = R ⁴ = H	R ¹ = R ² = R ³ = R ⁴ = Me	R ¹ = R ³ = H; R ² = R ⁴ = NH ₂	R ¹ = R ² = R ³ = H; R ⁴ = NH ₂	R ¹ = R ³ = Me; R ² = R ⁴ = NH ₂	R ¹ = R ³ = H; R ² = R ⁴ = <i>N</i> -pyrrolidinyl
λ_{max} (nm)	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a
τ (μ s)	0.002	0.868	0.186	1.047	1.823	0.751	1.866	1.826
$E_{0,0}$ (eV)	2.03	2.49	2.40	2.59	2.65	2.57	2.64	2.64
E^{red} (V vs. SCE)	−0.77	−1.41	−1.26	−1.52	−1.78	−1.52	−1.91	−1.74
E^{ox} (V vs. SCE)	n/a	+1.35	+1.40	+1.28	+1.15	+1.22	+1.14	+1.21
* E^{red} (V vs. SCE)	+1.26	+1.08	+1.14	+1.07	+0.87	+1.05	+0.73	+0.90
* E^{ox} (V vs. SCE)	n/a	−1.14	−1.00	−1.31	−1.50	−1.35	−1.50	−1.43
Refs.	42	42	42	42	42	42	42	42

λ_{max} (nm)	n/a	n/a	n/a	n/a	420
τ (μs)	1.56	1.62	2.16	2.11	0.31
$E_{0,0}$ (eV)	2.50	2.65	2.76	2.81	2.66
E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a	-2.05
E^{ox} (V vs. SCE)	+0.56	+0.76	+0.91	+1.05	+1.25
* E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a	+0.61
* E^{ox} (V vs. SCE)	-1.94	-1.89	-1.85	-1.76	-1.41
Refs.	137	137-139	137	137	140-142
λ_{max} (nm)	410	n/a	n/a	n/a	380
τ (μs)	0.557	0.28	n/a	n/a	2.3
$E_{0,0}$ (eV)	2.17	2.37	2.77	2.44	2.90
E^{red} (V vs. SCE)	-1.51	-0.69	-1.16	-0.79	-2.01
E^{ox} (V vs. SCE)	+1.21	+1.94	+1.87	+1.93	+1.69
* E^{red} (V vs. SCE)	+0.66	+1.68	+1.61	+1.65	+0.89
* E^{ox} (V vs. SCE)	-0.96	-0.43	-0.90	-0.51	-1.21
Refs.	25,126,143	144	144	144	145,146
λ_{max} (nm)	412	437	475	435	488
τ (μs)	2.28	3.90	0.40	0.52	n/a
$E_{0,0}$ (eV)	2.69	2.13	2.40	2.40	2.30
E^{red} (V vs. SCE)	-1.37	-1.43 ^a	n/a	n/a	n/a

E^{ox} (V vs. SCE)	+1.69	+1.03 ^a	+0.25	+0.29	+0.17
E^{red} (V vs. SCE)	+1.32	+0.70	n/a	n/a	n/a
E^{ox} (V vs. SCE)	-1.00	-1.10	-2.20	-2.10	-2.10
Refs.	147,148	149	35	35	35
					
λ_{max} (nm)	500	536	485	506	494
τ (μs)	0.53	0.63	0.15	0.35	0.51
$E_{0,0}$ (eV)	2.30	2.20	2.40	2.00	2.30
E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a	n/a
E^{ox} (V vs. SCE)	+0.30	+0.07	+0.27	+0.01	+0.13
E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a	n/a
E^{ox} (V vs. SCE)	-2.00	-2.10	-2.10	-2.00	-2.20
Refs.	35	35	35	35	35
					
R	R = Me	R = NMe ₂	R = OEt	-	-
λ_{max} (nm)	460	511	456	308	416
τ (μs)	0.20	0.76	2.0	n/a	n/a
$E_{0,0}$ (eV)	2.40	2.30	2.40	2.30	2.74
E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a	-2.03
E^{ox} (V vs. SCE)	+0.33	+0.14	+0.43	+0.30	+1.04
E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a	+0.71
E^{ox} (V vs. SCE)	-2.10	-2.20	-2.00	-2.00	-1.70
Refs.	35,150	35,150	35,150	35	40

λ_{max} (nm)	405	421	421	494	485
τ (μs)	n/a	n/a	28.7	n/a	n/a
$E_{0,0}$ (eV)	2.43	2.47	2.47	2.15	2.10
E^{red} (V vs. SCE)	-1.76	-1.97	-1.96	-1.54	-1.66
E^{ox} (V vs. SCE)	+0.84	+0.96	+0.96	+0.82	+0.88
* E^{red} (V vs. SCE)	+0.67	+0.50	+0.51	+0.61	+0.44
* E^{ox} (V vs. SCE)	-1.59	-1.51	-1.51	-1.33	-1.22
Refs.	40	40	40	40	40
λ_{max} (nm)	436	447	467	421	436
τ (μs)	6.4	3.2	n/a	n/a	96.1
$E_{0,0}$ (eV)	2.50	2.50	2.25	2.45	2.24
E^{red} (V vs. SCE)	-1.73	-1.52	-1.67	-1.97	-1.80
E^{ox} (V vs. SCE)	+1.17	+1.23	+0.89	+0.96	+0.98
* E^{red} (V vs. SCE)	+0.77	+1.03	+0.58	+0.48	+0.44
* E^{ox} (V vs. SCE)	-1.33	-1.27	-1.36	-1.49	-1.26
Refs.	40	40	40	40	40
λ_{max} (nm)	460	459	459	446	452

τ (μ s)	0.9	1.0	1.6	2.1	2.2
$E_{0,0}$ (eV)	2.61	2.63	2.65	2.69	2.72
E^{red} (V vs. SCE)	-1.65	-1.74	-1.73	-1.73	-1.76
E^{ox} (V vs. SCE)	+1.23	+1.21	+1.23	+1.22	+1.20
$*E^{\text{red}}$ (V vs. SCE)	+0.96	+0.89	+0.93	+0.97	+0.96
$*E^{\text{ox}}$ (V vs. SCE)	-1.38	-1.42	-1.42	-1.47	-1.52
Refs.	151	151	151	151	151
					
λ_{max} (nm)	494	474	485	430	494
τ (μ s)	1.8	3.0	0.2	2.4	0.1
$E_{0,0}$ (eV)	2.15	2.31	2.42	2.71	2.46
E^{red} (V vs. SCE)	-1.16	-1.27	-1.33	-1.71	-1.35
E^{ox} (V vs. SCE)	+0.91	+1.00	+1.37	+1.26	+1.37
$*E^{\text{red}}$ (V vs. SCE)	+0.99	+1.04	+1.09	+1.00	+1.11
$*E^{\text{ox}}$ (V vs. SCE)	-1.24	-1.31	-1.05	-1.45	-0.97
Refs.	151	151	151	151	151
					
λ_{max} (nm)	465	450	455	450	436
τ (μ s)	3.02	3.17	3.77	3.87	3.05
$E_{0,0}$ (eV)	2.31	2.36	2.36	2.41	2.49
E^{red} (V vs. SCE)	-1.23	-1.17	-1.21	-1.18	-1.19
E^{ox} (V vs. SCE)	+1.61	+1.70	+1.69	+1.87	+1.88
$*E^{\text{red}}$ (V vs. SCE)	+1.07	+1.19	+1.15	+1.22	+1.30
$*E^{\text{ox}}$ (V vs. SCE)	-0.70	-0.66	-0.67	-0.54	-0.61
Refs.	152	152	152	152	152

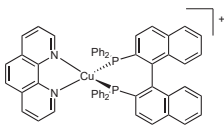
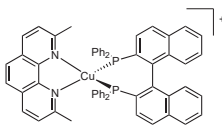
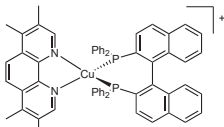
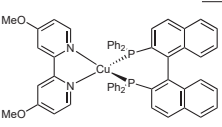
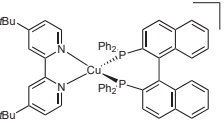
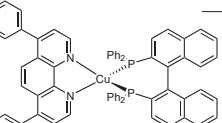
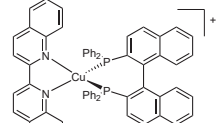
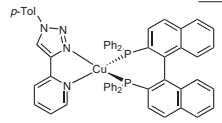
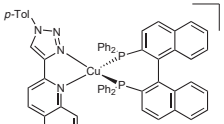
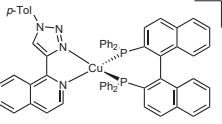
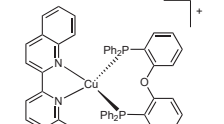
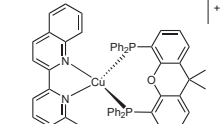
λ_{max} (nm)	435	430	337	428
τ (μs)	3.15	3.35	9.93	3.50
$E_{0,0}$ (eV)	2.49	2.54	2.64	2.58
E^{red} (V vs. SCE)	-1.14	-1.17	-1.17	-1.17
E^{ox} (V vs. SCE)	+1.83	+1.95	+2.00	+1.73, +2.01
$*E^{\text{red}}$ (V vs. SCE)	+1.35	+1.37	+1.47	+1.42
$*E^{\text{ox}}$ (V vs. SCE)	-0.66	-0.59	-0.64	-0.57
Refs.	152	152	152	152

^a Redox potentials were originally reported vs. the Ag/AgCl reference potential in MeCN, where the Fc^+/Fc redox couple appears at 0.56 V. Potentials were initially converted into the Fc^+/Fc reference and then corrected by adding 0.40 V for referencing against the SCE.

Table 3 Summary of Photophysical and Electrochemical Properties of Cu Photosensitizers

λ_{max} (nm)	n/a	387	380	385
τ (μs)	0.27	n/a	n/a	n/a
$E_{0,0}$ (eV)	2.05	2.64	2.77	2.70
E^{red} (V vs. SCE)	n/a	-1.59	-1.73	-1.66
E^{ox} (V vs. SCE)	+0.62	+1.27	+1.34	+1.35
$*E^{\text{red}}$ (V vs. SCE)	n/a	+1.05	+1.04	+1.04
$*E^{\text{ox}}$ (V vs. SCE)	-1.43	-1.37	-1.43	-1.35
Refs.	153,154	155	155	156

λ_{max} (nm)	n/a	n/a	n/a	n/a
τ (μs)	17	0.72	0.41	0.82
$E_{0,0}$ (eV)	2.57	2.19	2.23	2.27
E^{red} (V vs. SCE)	n/a	n/a	n/a	-1.64
E^{ox} (V vs. SCE)	+0.69	+1.23	+1.15	+1.25

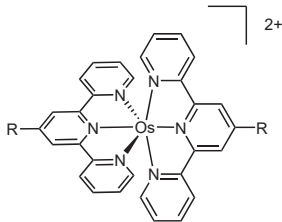
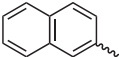
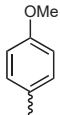
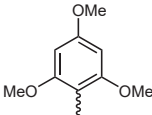
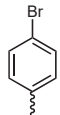
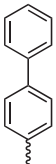
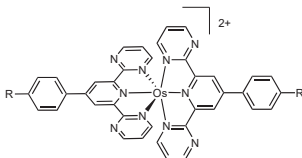
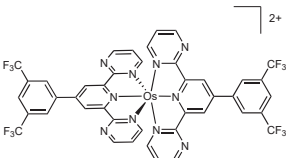
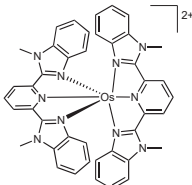
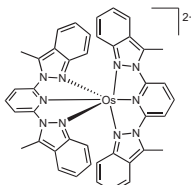
E^{red} (V vs. SCE)	n/a	n/a	n/a	+0.63
E^{ox} (V vs. SCE)	-1.88	-0.96	-1.08	-1.02
Refs.	157	158	158	159
				
λ_{max} (nm)	394	387	382	375
τ (μs)	0.0031	2.188	0.004	0.00264
$E_{0,0}$ (eV)	2.38	2.38	2.38	2.38
E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a
E^{ox} (V vs. SCE)	+0.78	+0.75	+0.87	+0.93
E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a
E^{ox} (V vs. SCE)	-1.60	-1.64	-1.52	-1.45
Refs.	160	160	160	160
				
λ_{max} (nm)	379	412	472	378
τ (μs)	0.00219	0.00278	0.004	0.00240
$E_{0,0}$ (eV)	2.38	2.38	2.38	2.38
E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a
E^{ox} (V vs. SCE)	+0.91	+0.83	+0.51	+0.71
E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a
E^{ox} (V vs. SCE)	-1.47	-1.55	-1.87	-1.67
Refs.	160	160	160	160
				
λ_{max} (nm)	410	406	443	445
τ (μs)	0.00311	0.00358	0.274	0.393
$E_{0,0}$ (eV)	2.38	2.38	1.87	1.90
E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a
E^{ox} (V vs. SCE)	+0.70	+0.66	+0.60	+1.14
E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a
E^{ox} (V vs. SCE)	-1.68	-1.72	-1.27	-0.76
Refs.	160	160	160	160

λ_{max} (nm)	373	381	374	n/a
τ (μs)	0.00742	0.00746	0.00895	n/a
$E_{0,0}$ (eV)	2.30	2.29	2.00	2.24
E^{red} (V vs. SCE)	-0.18	-0.43	-0.04	n/a
E^{ox} (V vs. SCE)	+1.07	+0.81	+1.11	+0.38
* E^{red} (V vs. SCE)	+2.12	+1.87	+1.96	n/a
* E^{ox} (V vs. SCE)	-1.23	-1.48	-0.89	-1.86
Refs.	161	161	161	162
λ_{max} (nm)	n/a	464	438	449
τ (μs)	n/a	0.0027	1.2	1.4
$E_{0,0}$ (eV)	2.73	2.15	2.45	2.40
E^{red} (V vs. SCE)	-1.96	n/a	-1.77 ^a	-1.43, -1.64 ^a
E^{ox} (V vs. SCE)	+0.8	+0.77	n/a	n/a
* E^{red} (V vs. SCE)	+0.77	n/a	+0.68	+0.97
* E^{ox} (V vs. SCE)	-1.93	-1.38	n/a	n/a
Refs.	163	160	164	164

^a Redox potentials were originally reported against the Ag/AgCl reference potential and are corrected by subtracting 0.039 V for referencing against the SCE.⁴⁴

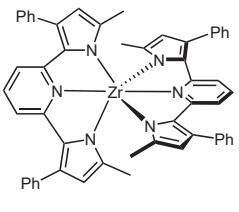
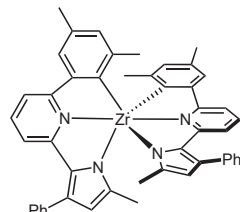
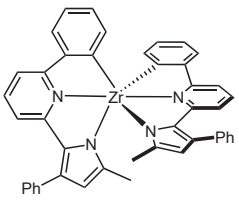
Table 4 Summary of Photophysical and Electrochemical Properties of Os Photosensitizers^a

λ_{max} (nm)	640	650	n/a
τ (μs)	0.02	0.08	n/a
$E_{0,0}$ (eV)	1.75	1.8	1.69
E^{red} (V vs. SCE)	-1.41	-1.42	-0.83
E^{ox} (V vs. SCE)	+0.79	+0.86	+1.0
* E^{red} (V vs. SCE)	+0.34	+0.38	+0.86
* E^{ox} (V vs. SCE)	-0.96	-0.94	-0.69
Refs.	165,166	165,166	166

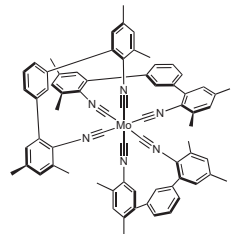
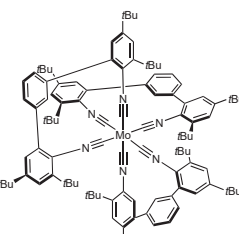
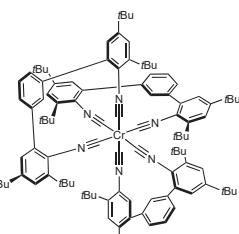
										
R	H	t-Bu								
λ_{max} (nm)	657	n/a	n/a	n/a	n/a	n/a	n/a	n/a	n/a	
τ (μs)	0.269	n/a	n/a	n/a	n/a	n/a	n/a	0.2	n/a	
$E_{0,0}$ (eV)	1.77	1.8	1.72	1.75	1.74	1.76	1.79	1.75	1.75	
E^{red} (V vs. SCE)	−1.24	−1.05	−1.00	−0.87	−0.99	−0.94	−1.01	−0.86	−0.91	
E^{ox} (V vs. SCE)	+0.94	+1.07	+1.02	+0.99	+1.01	+1.14	+1.10	+1.04	+0.99	
* E^{red} (V vs. SCE)	+0.53	+0.75	+0.72	+0.88	+0.75	+0.82	+0.78	+0.89	+0.84	
* E^{ox} (V vs. SCE)	−0.83	−0.73	−0.70	−0.76	−0.73	−0.62	−0.69	−0.71	−0.76	
Refs.	166,167	166	166	166	166	166	166	166,168	166	
	   									
R	H	OMe	–	–	–	–	–			
λ_{max} (nm)	n/a	n/a	n/a	n/a	n/a	n/a	n/a			
τ (μs)	n/a	n/a	n/a	n/a	n/a	n/a	n/a			
$E_{0,0}$ (eV)	1.77	1.79	1.78	1.71	1.96	1.71	1.96			
E^{red} (V vs. SCE)	−0.80	−0.63	−0.58	−0.98	−1.34	−0.98	−1.34			
E^{ox} (V vs. SCE)	+1.21	+1.33	+1.50	+0.77	+1.21	+0.77	+1.21			
* E^{red} (V vs. SCE)	+0.97	+1.16	+1.20	+0.73	+0.62	+0.73	+0.62			
* E^{ox} (V vs. SCE)	−0.56	−0.46	−0.28	−0.94	−0.75	−0.94	−0.75			
Refs.	166	166	166	166	166	166	166			

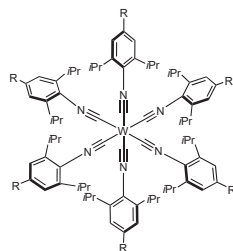
^a Redox potentials were originally reported against the Ag/AgCl reference potential and are corrected by subtracting 0.039 V for referencing against the SCE.⁴⁴

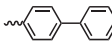
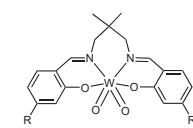
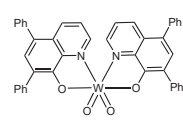
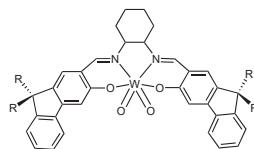
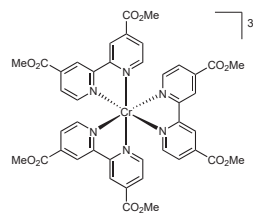
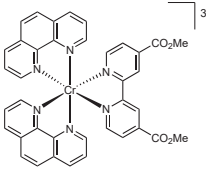
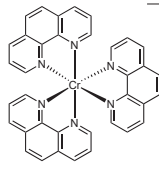
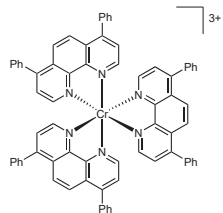
Table 5 Summary of Photophysical and Electrochemical Properties of Zr Photosensitizers

			
λ_{max} (nm)	528	471	470
τ (μs)	325	412	$\tau_1 = 77, \tau_2 = 296^c$
$E_{0,0}$ (eV)	2.09	2.19	2.21
E^{red} (V vs. SCE)	-1.60^a	-1.80^b	-1.81^b
E^{ox} (V vs. SCE)	n/a	n/a	n/a
$^*E^{\text{red}}$ (V vs. SCE)	+0.49	+0.39	+0.40
$^*E^{\text{ox}}$ (V vs. SCE)	n/a	n/a	n/a
Refs.	169,170	171	171

^a Redox potentials were originally referenced vs. Fc^+/Fc in THF and are corrected by adding 0.56 V for referencing against the SCE.^b Redox potentials were originally referenced vs. Fc^+/Fc in 1,2-difluorobenzene and are corrected by adding 0.46 V for referencing against the SCE.^c Biexponential.**Table 6** Summary of Photophysical and Electrochemical Properties of Group 6 Photosensitizers

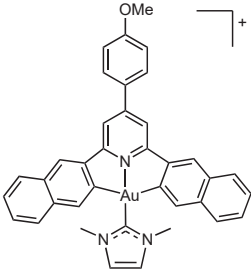
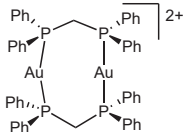
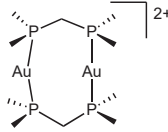
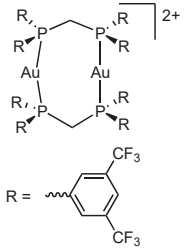
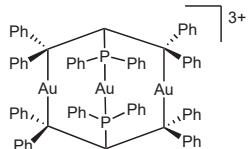
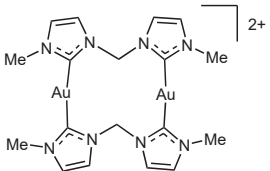
			
λ_{max} (nm)	350–550	350–550	400–600
τ (μs)	0.225	$\tau_1 = 1.04$ (76%), $\tau_2 = 2.37$ (24%) ^a	0.0022
$E_{0,0}$ (eV)	2.20	2.20	2.05
E^{red} (V vs. SCE)	n/a	n/a	n/a
E^{ox} (V vs. SCE)	-0.02	-0.08	$+0.18^b$
$^*E^{\text{red}}$ (V vs. SCE)	n/a	n/a	n/a
$^*E^{\text{ox}}$ (V vs. SCE)	-2.2	-2.3	-1.87
Refs.	172,173	172	174,175



R	H				
λ_{max} (nm)	465	n/a	n/a	n/a	n/a
τ (μs)	0.122	1.73	1.53	1.65	1.83
$E_{0,0}$ (eV)	2.28	2.12	2.08	2.14	2.15
E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a	n/a
E^{ox} (V vs. SCE)	-0.26 ^c	-0.22 ^c	-0.21 ^c	-0.19 ^c	-0.19 ^c
* E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a	n/a
* E^{ox} (V vs. SCE)	-2.54	-2.34	-2.29	-2.33	-2.34
Refs.	176–178	176	176	176	176
  					
R	H	-	(CH ₂) ₅ Me		
λ_{max} (nm)	407	420	402	396	427
τ (μs)	4.6	74.9	83.6	42	62
$E_{0,0}$ (eV)	2.39	2.70	2.59	2.22	2.36
E^{red} (V vs. SCE)	-1.29	-1.24	-1.34	-1.42 ^d	-1.37 ^d
E^{ox} (V vs. SCE)	+1.10	+1.41	+1.64	+1.55 ^d	+1.47 ^d
* E^{red} (V vs. SCE)	+1.10	+1.46	+1.25	+0.80	+0.99
* E^{ox} (V vs. SCE)	-1.29	-1.29	-0.95	-0.67	-0.89
Refs.	179,180	179	179,180	181	181
   					
λ_{max} (nm)	480	480	454	484	
τ (μs)	7.7	87	304	425	
$E_{0,0}$ (eV)	1.70	1.70	1.70	1.67	
E^{red} (V vs. SCE)	+0.14	-0.02	-0.25	-0.27	
E^{ox} (V vs. SCE)	n/a	n/a	n/a	n/a	
* E^{red} (V vs. SCE)	+1.84	+1.68	+1.45	+1.40	
* E^{ox} (V vs. SCE)	n/a	n/a	n/a	n/a	
Refs.	182,183	182,183	182,183	182,183	

^a Biexponential.^b Redox potentials were originally referenced vs. Fc⁺/Fc in THF and are corrected by adding 0.56 V for referencing against the SCE.^c Redox potentials were originally referenced vs. Fc⁺/Fc in CH₂Cl₂ and are corrected by adding 0.46 V for referencing against the SCE.^d Redox potentials were originally referenced vs. Fc⁺/Fc in MeCN and are corrected by adding 0.40 V for referencing against the SCE.

Table 7 Summary of Photophysical and Electrochemical Properties of Au Photosensitizers

				
λ_{max} (nm)	403	320	n/a	n/a
τ (μs)	506	0.85	0.40	10000
$E_{0,0}$ (eV)	2.48	2.23	2.36	2.10
E^{red} (V vs. SCE)	-1.33^a	-1.63	-1.77	-1.65
E^{ox} (V vs. SCE)	n/a	$+0.70$	$+0.49$	$+1.41$
$^*E^{\text{red}}$ (V vs. SCE)	$+1.15$	$+0.60$	$+0.59$	$+0.45$
$^*E^{\text{ox}}$ (V vs. SCE)	n/a	-1.53	-1.87	-0.69
Refs.	184	185–187	185	185
				
λ_{max} (nm)	n/a	n/a		
τ (μs)	1500	0.02		
$E_{0,0}$ (eV)	2.28	2.44		
E^{red} (V vs. SCE)	-1.54	n/a		
E^{ox} (V vs. SCE)	$+1.09$	$+0.34$		
$^*E^{\text{red}}$ (V vs. SCE)	$+0.74$	n/a		
$^*E^{\text{ox}}$ (V vs. SCE)	-1.19	-2.10		
Refs.	185	185		

^a Redox potentials were originally referenced vs. Fc^+/Fc in MeCN and are corrected by adding 0.40 V for referencing against the SCE.

Table 8 Summary of Photophysical and Electrochemical Properties of Pt Photosensitizers

λ_{max} (nm)	386	380	420	400–500	300–450
τ (μs)	2.21	0.382	11.6	0.309	0.093
$E_{0,0}$ (eV)	2.64	2.73	2.45	2.48	2.51
E^{red} (V vs. SCE)	–2.38	–2.46	–2.20	–1.18 ^a	–1.29 ^b
E^{ox} (V vs. SCE)	+0.57	+0.62	+0.52	n/a	+1.01 ^b
* E^{red} (V vs. SCE)	+0.26	+0.27	+0.25	+1.30	+1.22
* E^{ox} (V vs. SCE)	–2.07	–2.11	–1.93	n/a	–1.50
Refs.	188	188	188	189	190

^a The reference potential was not specified by the authors.^b Redox potentials were originally referenced vs. Fc^+/Fc in MeCN and are corrected by adding 0.40 V for referencing against the SCE.**Table 9** Summary of Photophysical and Electrochemical Properties of Ce Photosensitizers

λ_{max} (nm)	415	424	423	423
τ (μs)	0.024	0.0828	0.067	0.061
$E_{0,0}$ (eV)	2.24	2.70	2.39	2.37
E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a
E^{ox} (V vs. SCE)	+0.61 ^a	+0.24 ^b	+0.49 ^b	+0.59 ^b
* E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a
* E^{ox} (V vs. SCE)	–1.63	–2.46	–1.90	–1.78
Refs.	191–193	193	191–193	191, 192

R	$\text{R}^1 = \text{R}^2 = \text{SiMe}_3$	$\text{R}^1 = \text{SiMe}_3; \text{R}^2 = t\text{-Bu}$	$\text{R}^1 = \text{SiMe}_3; \text{R}^2 = i\text{-Pr}$	$\text{R}^1 = \text{Ph}; \text{R}^2 = i\text{-Pr}$	$\text{R}^1 = \text{R}^2 = \text{Ph}$	–
λ_{max} (nm)	429	438	463	461	463	329
τ (μs)	0.117	0.221	0.158	0.041	0.043	0.0221

$E_{0,0}$ (eV)	2.46	2.34	2.19	2.33	2.34	3.48
E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a	n/a	n/a
E^{ox} (V vs. SCE)	+0.32 ^b	+0.20 ^b	+0.05 ^b	−0.11 ^b	−0.10 ^b	+0.43 ^c
* E^{red} (V vs. SCE)	n/a	n/a	n/a	n/a	n/a	n/a
* E^{ox} (V vs. SCE)	−2.14	−2.14	−2.14	−2.44	−2.44	−3.05
Refs.	193,194	194	194	194	194	195,196

^a Redox potentials were originally referenced vs. Fc^+/Fc in THF and are corrected by adding 0.56 V for referencing against the SCE.

^b Redox potentials were originally referenced vs. Fc^+/Fc in CH_2Cl_2 and are corrected by adding 0.46 V for referencing against the SCE.

^c Redox potentials were originally referenced vs. Fc^+/Fc in MeCN and are corrected by adding 0.40 V for referencing against the SCE.

Conclusion

Here we have presented a comprehensive summary of the ground-state and excited-state redox properties and photophysical characteristics of PSs used in photoredox organic transformations. There are many important considerations for choosing a PS when screening photoredox reactions, and this review can serve as a guide to help researchers select a PS that has an appropriate UV-vis absorption window, redox potentials, and excited-state lifetime for their application. For reactions involving photoinduced redox transformations and when the redox potential(s) of other reaction species (the substrate, sacrificial redox reagent, and co-catalyst) are known, evaluation of the ground- and excited-state redox potentials of the PS is critical in ensuring favorable electron transfer. For reactions involving energy transfer, the most essential consideration is the relevant excited-state energy, $E_{0,0}$, which must be higher than that of the energy-transfer acceptor. We believe this article provides a useful tool for chemists who are interested in photoredox catalysis, permitting them to compare a variety of metal-free and metal-based PSs.

Conflict of Interest

The authors declare no conflict of interest.

Funding Information

We thank the National Science Foundation (grant number CHE-1846831) and the Welch Foundation (grant number E-1887) for funding our group's research on organometallic photosensitizers and photoredox catalysis.

References and Notes

- Inoue, T.; Fujishima, A.; Konishi, S.; Honda, K. *Nature* **1979**, 277, 637.
- Twilton, J.; Le, C.; Zhang, P.; Shaw, M. H.; Evans, R. W.; MacMillan, D. W. C. *Nat. Rev. Chem.* **2017**, 1, 0052.
- Lin, W.; Frei, H. *J. Am. Chem. Soc.* **2005**, 127, 1610.
- Nicewicz, D. A.; MacMillan, D. W. C. *Science* **2008**, 322, 77.
- Ischay, M. A.; Anzovino, M. E.; Du, J.; Yoon, T. P. *J. Am. Chem. Soc.* **2008**, 130, 12886.
- Narayanam, J. M. R.; Tucker, J. W.; Stephenson, C. R. J. *J. Am. Chem. Soc.* **2009**, 131, 8756.
- Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. *Chem. Rev.* **2013**, 113, 5322.
- Yoon, T. P.; Ischay, M. A.; Du, J. *Nat. Chem.* **2010**, 2, 527.
- Ravelli, D.; Protti, S.; Fagnoni, M. *Chem. Rev.* **2016**, 116, 9850.
- Ischay, M. A.; Ament, M. S.; Yoon, T. P. *Chem. Sci.* **2012**, 3, 2807.
- Nakajima, M.; Fava, E.; Loescher, S.; Jiang, Z.; Rueping, M. *Angew. Chem. Int. Ed.* **2015**, 54, 8828.
- Tucker, J. W.; Stephenson, C. R. J. *J. Org. Chem.* **2012**, 77, 1617.
- Michelin, C.; Hoffmann, N. *ACS Catal.* **2018**, 8, 12046.
- Romero, N. A.; Nicewicz, D. A. *Chem. Rev.* **2016**, 116, 10075.
- Amos, S. G. E.; Garreau, M.; Buzzetti, L.; Waser, J. *Beilstein J. Org. Chem.* **2020**, 16, 1163.
- Nicewicz, D. A.; Nguyen, T. M. *ACS Catal.* **2014**, 4, 355.
- Sato, S.; Arai, T.; Morikawa, T.; Uemura, K.; Suzuki, T. M.; Tanaka, H.; Kajino, T. *J. Am. Chem. Soc.* **2011**, 133, 15240.
- Higashida, S.; Harada, A.; Kawakatsu, R.; Fujiwara, N.; Matsumura, M. *Chem. Commun.* **2006**, 2804.
- Qi, M.-Y.; Li, Y.-H.; Anpo, M.; Tang, Z.-R.; Xu, Y.-J. *ACS Catal.* **2020**, 10, 14327.
- Hockin, B. M.; Li, C.; Robertson, N.; Zysman-Colman, E. *Catal. Sci. Technol.* **2019**, 9, 889.
- Pi, Y.; Feng, X.; Song, Y.; Xu, Z.; Li, Z.; Lin, W. *J. Am. Chem. Soc.* **2020**, 142, 10302.
- Dhakshinamoorthy, A.; Li, Z.; Garcia, H. *Chem. Soc. Rev.* **2018**, 47, 8134.
- Deng, X.; Li, Z.; García, H. *Chem. Eur. J.* **2017**, 23, 11189.
- Juris, A.; Balzani, V.; Barigelli, F.; Campagna, S.; Belser, P.; von Zelewsky, A. *Coord. Chem. Rev.* **1988**, 84, 85.
- Teegardin, K.; Day, J. I.; Chan, J.; Weaver, J. *Org. Process Res. Dev.* **2016**, 20, 1156.
- Monos, T. M.; Stephenson, C. R. J. In *Iridium(III) in Optoelectronic and Photonics Applications*; Chap. 11, Zysman-Colman, E., Ed.; Wiley: Hoboken, **2017**, 541.
- Zeitler, K. In *Visible Light Photocatalysis in Organic Chemistry*; Chap. 6, Stephenson, C. R. J.; Yoon, T. P.; MacMillan, D. W. C., Ed.; Wiley-VCH: Weinheim, **2018**, 159.
- Glaser, F.; Wenger, O. S. *Coord. Chem. Rev.* **2020**, 405, 213129.
- Shon, J.-H.; Teets, T. S. *Comments Inorg. Chem.* **2020**, 40, 53.
- Shon, J.-H.; Teets, T. S. *ACS Energy Lett.* **2019**, 4, 558.
- Marzo, L.; Pagire, S. K.; Reiser, O.; König, B. *Angew. Chem. Int. Ed.* **2018**, 57, 10034.
- Roth, H. G.; Romero, N. A.; Nicewicz, D. A. *Synlett* **2016**, 27, 714.
- Buzzetti, L.; Crisenza, G. E. M.; Melchiorre, P. *Angew. Chem. Int. Ed.* **2019**, 58, 3730.
- Radwan, Y. K.; Maity, A.; Teets, T. S. *Inorg. Chem.* **2015**, 54, 7122.

- (35) Shon, J.-H.; Sittel, S.; Teets, T. S. *ACS Catal.* **2019**, *9*, 8646.
- (36) Baik, M.-H.; Friesner, R. A. *J. Phys. Chem. A* **2002**, *106*, 7407.
- (37) Fu, Y.; Liu, L.; Yu, H.-Z.; Wang, Y.-M.; Guo, Q.-X. *J. Am. Chem. Soc.* **2005**, *127*, 7227.
- (38) Silva-Junior, M. R.; Schreiber, M.; Sauer, S. P. A.; Thiel, W. *J. Chem. Phys.* **2008**, *129*, 104103.
- (39) Elgrishi, N.; Rountree, K. J.; McCarthy, B. D.; Rountree, E. S.; Eisenhart, T. T.; Dempsey, J. L. *J. Chem. Educ.* **2018**, *95*, 197.
- (40) Yang, C.; Mehmood, F.; Lam, T. L.; Chan, S. L.-F.; Wu, Y.; Yeung, C.-S.; Guan, X.; Li, K.; Chung, C. Y.-S.; Zhou, C.-Y.; Zou, T.; Che, C.-M. *Chem. Sci.* **2016**, *7*, 3123.
- (41) Espinoza, E. M.; Clark, J. A.; Soliman, J.; Derr, J. B.; Morales, M.; Vullev, V. I. *J. Electrochem. Soc.* **2019**, *166*, H3175.
- (42) Till, N. A.; Tian, L.; Dong, Z.; Scholes, G. D.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2020**, *142*, 15830.
- (43) Connelly, N. G.; Geiger, W. E. *Chem. Rev.* **1996**, *96*, 877.
- (44) Pavlishchuk, V. V.; Addison, A. W. *Inorg. Chim. Acta* **2000**, *298*, 97.
- (45) Jones, W. E. Jr; Fox, M. A. *J. Phys. Chem.* **1994**, *98*, 5095.
- (46) Pellegrin, Y.; Odobel, F. C. R. *Chim.* **2017**, *20*, 283.
- (47) Murakami, M.; Ohkubo, K.; Fukuzumi, S. *Chem. Eur. J.* **2010**, *16*, 7820.
- (48) Kavarinos, G. J. *Top. Curr. Chem.* **1990**, *156*, 21.
- (49) Sartor, S. M.; McCarthy, B. G.; Pearson, R. M.; Miyake, G. M.; Damrauer, N. H. *J. Am. Chem. Soc.* **2018**, *140*, 4778.
- (50) Prasad Hari, D.; König, B. *Chem. Commun.* **2014**, *50*, 6688.
- (51) Shen, T.; Zhao, Z.-G.; Yu, Q.; Xu, H.-J. *J. Photochem. Photobiol. Chem.* **1989**, *47*, 203.
- (52) Lazarides, T.; McCormick, T.; Du, P.; Luo, G.; Lindley, B.; Eisenberg, R. J. *J. Am. Chem. Soc.* **2009**, *131*, 9192.
- (53) Neumann, M.; Földner, S.; König, B.; Zeitler, K. *Angew. Chem. Int. Ed.* **2011**, *50*, 951.
- (54) Lambert, C. R.; Kochevar, I. E. *Photochem. Photobiol.* **1997**, *66*, 15.
- (55) Ravello, D.; Fagnoni, M. *ChemCatChem* **2012**, *4*, 169.
- (56) Fidaly, K.; Ceballos, C.; Falguières, A.; Veitia, M. S.-I.; Guy, A.; Ferroud, C. *Green Chem.* **2012**, *14*, 1293.
- (57) März, M.; Kohout, M.; Nevesely, T.; Chudoba, J.; Prukała, D.; Niziński, S.; Sikorski, M.; Burdziński, G.; Cibulka, R. *Org. Biomol. Chem.* **2018**, *16*, 6809.
- (58) Suppan, P. J. *Chem. Soc. Faraday Trans. 1* **1975**, *71*, 539.
- (59) Loutfy, R. O.; Loutfy, R. O. *J. Phys. Chem.* **1972**, *76*, 1650.
- (60) Schweitzer, C.; Mehrdad, Z.; Noll, A.; Grabner, E.-W.; Schmidt, R. *Helv. Chim. Acta* **2001**, *84*, 2493.
- (61) Gollnick, K.; Held, S. J. *Photochem. Photobiol. A: Chem.* **1993**, *70*, 135.
- (62) Gollnick, K.; Held, S.; Mártire, D. O.; Braslavsky, S. E. *J. Photochem. Photobiol. A: Chem.* **1992**, *69*, 155.
- (63) Serpa, C.; Arnaut, L. G. *J. Phys. Chem. A* **2000**, *104*, 11075.
- (64) Cervantes-González, J.; Vosburg, D. A.; Mora-Rodriguez, S. E.; Vázquez, M. A.; Zepeda, L. G.; Villegas Gómez, C.; Lagunas-Rivera, S. *ChemCatChem* **2020**, *12*, 3811.
- (65) Yamago, S.; Miyazoe, H.; Iida, K.; Yoshida, J.-i. *Org. Lett.* **2000**, *2*, 3671.
- (66) Ohkubo, K.; Fujimoto, A.; Fukuzumi, S. *J. Am. Chem. Soc.* **2013**, *135*, 5368.
- (67) Ohkubo, K.; Hirose, K.; Fukuzumi, S. *Chem. Eur. J.* **2015**, *21*, 2855.
- (68) Giacco, T. D.; Baciocchi, E.; Lanzalunga, O.; Elisei, F. *Chem. Eur. J.* **2001**, *7*, 3005.
- (69) Fukuzumi, S.; Fujita, M.; Noura, S.; Ohkubo, K.; Suenobu, T.; Araki, Y.; Ito, O. *J. Phys. Chem. A* **2001**, *105*, 1857.
- (70) Ohkubo, K.; Suga, K.; Morikawa, K.; Fukuzumi, S. *J. Am. Chem. Soc.* **2003**, *125*, 12850.
- (71) Ravelli, D.; Fagnoni, M.; Albini, A. *Chem. Soc. Rev.* **2012**, *42*, 97.
- (72) Ohkubo, K.; Kotani, H.; Fukuzumi, S. *Chem. Commun.* **2005**, 4520.
- (73) Fukuzumi, S.; Kotani, H.; Ohkubo, K.; Ogo, S.; Tkachenko, N. V.; Lemmetyinen, H. *J. Am. Chem. Soc.* **2004**, *126*, 1600.
- (74) Benniston, A. C.; Harriman, A.; Li, P.; Rostron, J. P.; van Ramesdonk, H. J.; Groeneveld, M. M.; Zhang, H.; Verhoeven, J. W. *J. Am. Chem. Soc.* **2005**, *127*, 16054.
- (75) Romero, N. A.; Nicewicz, D. A. *J. Am. Chem. Soc.* **2014**, *136*, 17024.
- (76) Joshi-Pangu, A.; Lévesque, F.; Roth, H. G.; Oliver, S. F.; Campeau, L.-C.; Nicewicz, D.; DiRocco, D. A. *J. Org. Chem.* **2016**, *81*, 7244.
- (77) Wang, Y.; Haze, O.; Dinnocenzo, J. P.; Farid, S.; Farid, R. S.; Gould, I. R. *J. Org. Chem.* **2007**, *72*, 6970.
- (78) Ishimatsu, R.; Matsunami, S.; Kasahara, T.; Mizuno, J.; Edura, T.; Adachi, C.; Nakano, K.; Imato, T. *Angew. Chem.* **2014**, *126*, 7113.
- (79) Kretzschmar, A.; Patze, C.; Schwaebel, S. T.; Bunz, U. H. F. *J. Org. Chem.* **2015**, *80*, 9126.
- (80) Lu, J.; Pattengale, B.; Liu, Q.; Yang, S.; Shi, W.; Li, S.; Huang, J.; Zhang, J. *J. Am. Chem. Soc.* **2018**, *140*, 13719.
- (81) Saget, T.; König, B. *Chem. Eur. J.* **2020**, *26*, 7004.
- (82) Garreau, M.; Le Vaillant, F.; Waser, J. *Angew. Chem. Int. Ed.* **2019**, *58*, 8182.
- (83) Ishimatsu, R.; Edura, T.; Adachi, C.; Nakano, K.; Imato, T. *Chem. Eur. J.* **2016**, *22*, 4889.
- (84) Speckmeier, E.; Fischer, T. G.; Zeitler, K. *J. Am. Chem. Soc.* **2018**, *140*, 15353.
- (85) Rolka, A. B.; Koenig, B. *Org. Lett.* **2020**, *22*, 5035.
- (86) I. Alarcon, E.; González-Béjar, M.; Montes-Navajas, P.; Garcia, H.; Lissi, E. A.; Scaiano, J. C. *Photochem. Photobiol. Sci.* **2012**, *11*, 269.
- (87) Treat, N. J.; Sprafke, H.; Kramer, J. W.; Clark, P. G.; Barton, B. E.; Read de Alaniz, J.; Fors, B. P.; Hawker, C. J. *J. Am. Chem. Soc.* **2014**, *136*, 16096.
- (88) Discekici, E. H.; Treat, N. J.; Poelma, S. O.; Mattson, K. M.; Hudson, Z. M.; Luo, Y.; Hawker, C. J.; Read de Alaniz, J. *Chem. Commun.* **2015**, *51*, 11705.
- (89) Pearson, R. M.; Lim, C.-H.; McCarthy, B. G.; Musgrave, C. B.; Miyake, G. M. *J. Am. Chem. Soc.* **2016**, *138*, 11399.
- (90) Huber, J. R.; Mantulin, W. W. *J. Am. Chem. Soc.* **1972**, *94*, 3755.
- (91) Miranda, M. A.; Garcia, H. *Chem. Rev.* **1994**, *94*, 1063.
- (92) Theriot, J. C.; Lim, C.-H.; Yang, H.; Ryan, M. D.; Musgrave, C. B.; Miyake, G. M. *Science* **2016**, *352*, 1082.
- (93) Du, Y.; Pearson, R. M.; Lim, C.-H.; Sartor, S. M.; Ryan, M. D.; Yang, H.; Damrauer, N. H.; Miyake, G. M. *Chem. Eur. J.* **2017**, *23*, 10962.
- (94) Lim, C.-H.; Ryan, M. D.; McCarthy, B. G.; Theriot, J. C.; Sartor, S. M.; Damrauer, N. H.; Musgrave, C. B.; Miyake, G. M. *J. Am. Chem. Soc.* **2017**, *139*, 348.
- (95) Luan, Z.-H.; Qu, J.-P.; Kang, Y.-B. *J. Am. Chem. Soc.* **2020**, *142*, 20942.
- (96) Buss, B. L.; Beck, L. R.; Miyake, G. M. *Polym. Chem.* **2018**, *9*, 1658.
- (97) Marchini, M.; Gualandi, A.; Mengozzi, L.; Franchi, P.; Lucarini, M.; Cozzi, P. G.; Balzani, V.; Ceroni, P. *Phys. Chem. Chem. Phys.* **2018**, *20*, 8071.
- (98) Ramanan, C.; Smeigh, A. L.; Anthony, J. E.; Marks, T. J.; Wasielewski, M. R. *J. Am. Chem. Soc.* **2012**, *134*, 386.
- (99) Lee, S. K.; Zu, Y.; Herrmann, A.; Geerts, Y.; Müllen, K.; Bard, A. J. *J. Am. Chem. Soc.* **1999**, *121*, 3513.
- (100) Ghosh, I.; Ghosh, T.; Bardagi, J. I.; König, B. *Science* **2014**, *346*, 725.
- (101) Mei, L.; Veleta, J. M.; Gianetti, T. L. *J. Am. Chem. Soc.* **2020**, *142*, 12056.
- (102) Sørensen, T. J.; Nielsen, M. F.; Laursen, B. W. *ChemPlusChem* **2014**, *79*, 1030.

- (103) Hernández Delgado, I.; Pascal, S.; Wallabregue, A.; Duwald, R.; Besnard, C.; Guénée, L.; Nançoz, C.; Vauthey, E.; Tovar, R. C.; Lunkley, J. L.; Muller, G.; Lacour, J. *Chem. Sci.* **2016**, *7*, 4685.
- (104) Mei, L.; Gianetti, T. *Synlett* **2021**, *32*, 337.
- (105) Noto, N.; Koike, T.; Akita, M. *ACS Catal.* **2019**, *9*, 4382.
- (106) Noto, N.; Tanaka, Y.; Koike, T.; Akita, M. *ACS Catal.* **2018**, *8*, 9408.
- (107) Matsubara, R.; Yabuta, T.; Md Idros, U.; Hayashi, M.; Ema, F.; Kobori, Y.; Sakata, K. *J. Org. Chem.* **2018**, *83*, 9381.
- (108) Cybularczyk-Cecotka, M.; Szczepanik, J.; Giedyk, M. *Nat. Catal.* **2020**, *3*, 872.
- (109) Yabuta, T.; Hayashi, M.; Matsubara, R. *J. Org. Chem.* **2021**, *86*, 2545.
- (110) Mateos, J.; Rigodanza, F.; Vega-Peñaloza, A.; Sartorel, A.; Natali, M.; Bortolato, T.; Pelosi, G.; Companyó, X.; Bonchio, M.; Dell'Amico, L. *Angew. Chem. Int. Ed.* **2020**, *59*, 1302.
- (111) Hou, M.; Lin, L.; Chai, X.; Zhao, X.; Qiao, B.; Jiang, Z. *Chem. Sci.* **2019**, *10*, 6629.
- (112) Cao, K.; Tan, S. M.; Lee, R.; Yang, S.; Jia, H.; Zhao, X.; Qiao, B.; Jiang, Z. *J. Am. Chem. Soc.* **2019**, *141*, 5437.
- (113) Zhao, Y.; Zhang, C.; Chin, K. F.; Pytela, O.; Wei, G.; Liu, H.; Bureš, F.; Jiang, Z. *RSC Adv.* **2014**, *4*, 30062.
- (114) Liu, Y.; Chen, Q.; Tong, Y.; Ma, Y. *Macromolecules* **2020**, *53*, 7053.
- (115) Kim, I.; Park, B.; Kang, G.; Kim, J.; Jung, H.; Lee, H.; Baik, M.-H.; Hong, S. *Angew. Chem. Int. Ed.* **2018**, *57*, 15517.
- (116) Kim, Y.; Lee, K.; Mathi, G. R.; Kim, I.; Hong, S. *Green Chem.* **2019**, *21*, 2082.
- (117) Moon, Y.; Park, B.; Kim, I.; Kang, G.; Shin, S.; Kang, D.; Baik, M.-H.; Hong, S. *Nat. Commun.* **2019**, *10*, 4117.
- (118) Liu, D.; Jiao, M.-J.; Feng, Z.-T.; Wang, X.-Z.; Xu, G.-Q.; Xu, P.-F. *Org. Lett.* **2018**, *20*, 5700.
- (119) Lee, Y.; Kwon, M. S. *Eur. J. Org. Chem.* **2020**, 6028.
- (120) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.
- (121) Juris, A.; Balzani, V.; Belser, P.; von Zelewsky, A. *Helv. Chim. Acta* **1981**, *64*, 2175.
- (122) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815.
- (123) Young, R. C.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1976**, *98*, 286.
- (124) Damrauer, N. H.; Boussie, T. R.; Devenney, M.; McCusker, J. K. *J. Am. Chem. Soc.* **1997**, *119*, 8253.
- (125) Anderson, B. L.; Maher, A. G.; Nava, M.; Lopez, N.; Cummins, C. C.; Nocera, D. G. *J. Phys. Chem. B* **2015**, *119*, 7422.
- (126) Lowry, M. S.; Hudson, W. R.; Pascal, R. A.; Bernhard, S. *J. Am. Chem. Soc.* **2004**, *126*, 14129.
- (127) Bernhard, S.; Barron, J. A.; Houston, P. L.; Abruña, H. D.; Ruglovsky, J. L.; Gao, X.; Malliaras, G. G. *J. Am. Chem. Soc.* **2002**, *124*, 13624.
- (128) Haga, M.; Dodsworth, E. S.; Eryavec, G.; Seymour, P.; Lever, A. B. P. *Inorg. Chem.* **1985**, *24*, 1901.
- (129) Crutchley, R. J.; Lever, A. B. P. *J. Am. Chem. Soc.* **1980**, *102*, 7128.
- (130) Rillema, D. P.; Allen, G.; Meyer, T. J.; Conrad, D. *Inorg. Chem.* **1983**, *22*, 1617.
- (131) Nacsa, E. D.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2018**, *140*, 3322.
- (132) Dedeian, K.; Djurovich, P. I.; Garces, F. O.; Carlson, G.; Watts, R. J. *Inorg. Chem.* **1991**, *30*, 1685.
- (133) Nguyen, J. D.; D'Amato, E. M.; Narayanam, J. M. R.; Stephenson, C. R. J. *Nat. Chem.* **2012**, *4*, 854.
- (134) Tamayo, A. B.; Alleyne, B. D.; Djurovich, P. I.; Lamansky, S.; Tsyba, I.; Ho, N. N.; Bau, R.; Thompson, M. E. *J. Am. Chem. Soc.* **2003**, *125*, 7377.
- (135) Singh, A.; Teegardin, K.; Kelly, M.; Prasad, K. S.; Krishnan, S.; Weaver, J. D. *J. Organomet. Chem.* **2015**, 776, 51.
- (136) Kim, H.; Kim, T.; Lee, D. G.; Roh, S. W.; Lee, C. *Chem. Commun.* **2014**, *50*, 9273.
- (137) Pfund, B.; Steffen, D. M.; Schreier, M. R.; Bertrams, M.-S.; Ye, C.; Börjesson, K.; Wenger, O. S.; Kerzig, C. *J. Am. Chem. Soc.* **2020**, *142*, 10468.
- (138) Guo, X.; Okamoto, Y.; Schreier, M. R.; Ward, T. R.; Wenger, O. S. *Chem. Sci.* **2018**, *9*, 5052.
- (139) Kerzig, C.; Guo, X.; Wenger, O. S. *J. Am. Chem. Soc.* **2019**, *141*, 2122.
- (140) Kim, T.; McCarver, S. J.; Lee, C.; MacMillan, D. W. C. *Angew. Chem. Int. Ed.* **2018**, *57*, 3488.
- (141) Ochola, J. R.; Wolf, M. O. *Org. Biomol. Chem.* **2016**, *14*, 9088.
- (142) Ladouceur, S.; Zysman-Colman, E. *Eur. J. Inorg. Chem.* **2013**, 2985.
- (143) Slinker, J. D.; Gorodetsky, A. A.; Lowry, M. S.; Wang, J.; Parker, S.; Rohl, R.; Bernhard, S.; Malliaras, G. G. *J. Am. Chem. Soc.* **2004**, *126*, 2763.
- (144) Choi, G. J.; Zhu, Q.; Miller, D. C.; Gu, C. J.; Knowles, R. R. *Nature* **2016**, *539*, 268.
- (145) Lu, Z.; Yoon, T. P. *Angew. Chem. Int. Ed.* **2012**, *51*, 10329.
- (146) Lowry, M. S.; Goldsmith, J. I.; Slinker, J. D.; Rohl, R.; Pascal, R. A.; Malliaras, G. G.; Bernhard, S. *Chem. Mater.* **2005**, *17*, 5712.
- (147) Simons, R. T.; Scott, G. E.; Kanegusuku, A. G.; Roizen, J. L. *J. Org. Chem.* **2020**, *85*, 6380.
- (148) Hanss, D.; Freys, J. C.; Bernardinelli, G.; Wenger, O. S. *Eur. J. Inorg. Chem.* **2009**, 4850.
- (149) Takizawa, S.; Shimada, K.; Sato, Y.; Murata, S. *Inorg. Chem.* **2014**, *53*, 2983.
- (150) Shon, J.-H.; Teets, T. S. *Inorg. Chem.* **2017**, *56*, 15295.
- (151) Lam, T. L.; Lai, J.; Annappureddy, R. R.; Xue, M.; Yang, C.; Guan, Y.; Zhou, P.; Chan, S. L.-F. *Inorg. Chem.* **2017**, *56*, 10835.
- (152) Porras, J. A.; Mills, I. N.; Transue, W. J.; Bernhard, S. *J. Am. Chem. Soc.* **2016**, *138*, 9460.
- (153) Pirtsch, M.; Paria, S.; Matsuno, T.; Isobe, H.; Reiser, O. *Chem. Eur. J.* **2012**, *18*, 7336.
- (154) Kern, J.-M.; Sauvage, J.-P. *J. Chem. Soc., Chem. Commun.* **1987**, 546.
- (155) Zheng, L.; Jiang, Q.; Bao, H.; Zhou, B.; Luo, S.-P.; Jin, H.; Wu, H.; Liu, Y. *Org. Lett.* **2020**, *22*, 8888.
- (156) Bao, H.; Zhou, B.; Luo, S.-P.; Xu, Z.; Jin, H.; Liu, Y. *ACS Catal.* **2020**, *10*, 7563.
- (157) Knorn, M.; Rawner, T.; Czerwieniec, R.; Reiser, O. *ACS Catal.* **2015**, *5*, 5186.
- (158) Alkan-Zambada, M.; Hu, X. *Organometallics* **2018**, *37*, 3928; corrigendum: *Organometallics* **2020**, *39*, 1456.
- (159) Michelet, B.; Deldaele, C.; Kajouj, S.; Moucheron, C.; Evano, G. *Org. Lett.* **2017**, *19*, 3576.
- (160) Minozzi, C.; Caron, A.; Grenier-Petel, J.-C.; Santandrea, J.; Collins, S. K. *Angew. Chem. Int. Ed.* **2018**, *57*, 5477.
- (161) Caron, A.; Morin, É.; Collins, S. K. *ACS Catal.* **2019**, *9*, 9458.
- (162) Wang, C.; Guo, M.; Qi, R.; Shang, Q.; Liu, Q.; Wang, S.; Zhao, L.; Wang, R.; Xu, Z. *Angew. Chem. Int. Ed.* **2018**, *57*, 15841.
- (163) Nitelet, A.; Thevenet, D.; Schiavi, B.; Hardouin, C.; Fournier, J.; Tamion, R.; Pannecoucke, X.; Jubault, P.; Poisson, T. *Chem. Eur. J.* **2019**, *25*, 3262.
- (164) Wang, B.; Shelar, D. P.; Han, X.-Z.; Li, T.-T.; Guan, X.; Lu, W.; Liu, K.; Chen, Y.; Fu, W.-F.; Che, C.-M. *Chem. Eur. J.* **2015**, *21*, 1184.
- (165) Kober, E. M.; Sullivan, B. P.; Dressick, W. J.; Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1980**, *102*, 7383.

- (166) Ravetz, B. D.; Tay, N. E. S.; Joe, C. L.; Sezen-Edmonds, M.; Schmidt, M. A.; Tan, Y.; Janey, J. M.; Eastgate, M. D.; Rovis, T. *ACS Cent. Sci.* **2020**, *6*, 2053.
- (167) Sauvage, J. P.; Collin, J. P.; Chambron, J. C.; Guillerez, S.; Coudret, C.; Balzani, V.; Barigelli, F.; De Cola, L.; Flamigni, L. *Chem. Rev.* **1994**, *94*, 993.
- (168) Sasaki, Y.; Oshikawa, M.; Bharmoria, P.; Kouno, H.; Hayashi-Takagi, A.; Sato, M.; Ajioka, I.; Yanai, N.; Kimizuka, N. *Angew. Chem. Int. Ed.* **2019**, *58*, 17827.
- (169) Zhang, Y.; Petersen, J. L.; Milschmann, C. *J. Am. Chem. Soc.* **2016**, *138*, 13115.
- (170) Zhang, Y.; Lee, T. S.; Petersen, J. L.; Milschmann, C. *J. Am. Chem. Soc.* **2018**, *140*, 5934.
- (171) Zhang, Y.; Petersen, J. L.; Milschmann, C. *Organometallics* **2018**, *37*, 4488.
- (172) Herr, P.; Glaser, F.; Büldt, L. A.; Larsen, C. B.; Wenger, O. S. *J. Am. Chem. Soc.* **2019**, *141*, 14394.
- (173) Büldt, L. A.; Guo, X.; Prescimone, A.; Wenger, O. S. *Angew. Chem. Int. Ed.* **2016**, *55*, 11247.
- (174) Büldt, L. A.; Guo, X.; Vogel, R.; Prescimone, A.; Wenger, O. S. *J. Am. Chem. Soc.* **2017**, *139*, 985.
- (175) Büldt, L. A.; Wenger, O. S. *Angew. Chem. Int. Ed.* **2017**, *56*, 5676.
- (176) Sattler, W.; Henling, L. M.; Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **2015**, *137*, 1198.
- (177) Sattler, W.; Ener, M. E.; Blakemore, J. D.; Rachford, A. A.; LaBeaume, P. J.; Thackeray, J. W.; Cameron, J. F.; Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **2013**, *135*, 10614.
- (178) Mann, K. R.; Gray, H. B.; Hammond, G. S. *J. Am. Chem. Soc.* **1977**, *99*, 306.
- (179) Yu, D.; To, W.-P.; Tong, G. S. M.; Wu, L.-L.; Chan, K.-T.; Du, L.; Phillips, D. L.; Liu, Y.; Che, C.-M. *Chem. Sci.* **2020**, *11*, 6370.
- (180) Chan, K.-T.; Lam, T.-L.; Yu, D.; Du, L.; Phillips, D. L.; Kwong, C.-L.; Tong, G. S. M.; Cheng, G.; Che, C.-M. *Angew. Chem. Int. Ed.* **2019**, *58*, 14896.
- (181) Yeung, K.-T.; To, W.-P.; Sun, C.; Cheng, G.; Ma, C.; Tong, G. S. M.; Yang, C.; Che, C.-M. *Angew. Chem. Int. Ed.* **2017**, *56*, 133.
- (182) Stevenson, S. M.; Shores, M. P.; Ferreira, E. M. *Angew. Chem. Int. Ed.* **2015**, *54*, 6506.
- (183) McDaniel, A. M.; Tseng, H.-W.; Damrauer, N. H.; Shores, M. P. *Inorg. Chem.* **2010**, *49*, 7981.
- (184) To, W.-P.; Tong, G. S.-M.; Lu, W.; Ma, C.; Liu, J.; Chow, A. L.-F.; Che, C.-M. *Angew. Chem. Int. Ed.* **2012**, *51*, 2654.
- (185) McTiernan, C. D.; Morin, M.; McCallum, T.; Scaiano, J. C.; Barriault, L. *Catal. Sci. Technol.* **2015**, *6*, 201.
- (186) Nzulu, F.; Telitel, S.; Stoffelbach, F.; Graff, B.; Morlet-Savary, F.; Lalevée, J.; Fensterbank, L.; Goddard, J.-P.; Ollivier, C. *Polym. Chem.* **2015**, *6*, 4605.
- (187) McCallum, T.; Barriault, L. *Chem. Sci.* **2016**, *7*, 4754.
- (188) Choi, W. J.; Choi, S.; Ohkubo, K.; Fukuzumi, S.; Cho, E. J.; You, Y. *Chem. Sci.* **2015**, *6*, 1454.
- (189) Zhong, J.-J.; Meng, Q.-Y.; Wang, G.-X.; Liu, Q.; Chen, B.; Feng, K.; Tung, C.-H.; Wu, L.-Z. *Chem. Eur. J.* **2013**, *19*, 6443.
- (190) Zhong, J.-J.; Yang, C.; Chang, X.-Y.; Zou, C.; Lu, W.; Che, C.-M. *Chem. Commun.* **2017**, *53*, 8948.
- (191) Yin, H.; Carroll, P. J.; Anna, J. M.; Schelter, E. J. *J. Am. Chem. Soc.* **2015**, *137*, 9234.
- (192) Qiao, Y.; Schelter, E. J. *Acc. Chem. Res.* **2018**, *51*, 2926.
- (193) Yin, H.; Carroll, P. J.; Manor, B. C.; Anna, J. M.; Schelter, E. J. *J. Am. Chem. Soc.* **2016**, *138*, 5984.
- (194) Qiao, Y.; Cheisson, T.; Manor, B. C.; Carroll, P. J.; Schelter, E. J. *Chem. Commun.* **2019**, *55*, 4067.
- (195) Yin, H.; Jin, Y.; Hertzog, J. E.; Mullane, K. C.; Carroll, P. J.; Manor, B. C.; Anna, J. M.; Schelter, E. J. *J. Am. Chem. Soc.* **2016**, *138*, 16266.
- (196) Qiao, Y.; Yang, Q.; Schelter, E. J. *Angew. Chem. Int. Ed.* **2018**, *57*, 10999.