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Subtle Ligand Effects in Oxidative Photocatalysis with Iridium Complexes: Application to Photopolymerization

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Abstract: Iridium(III) complexes were designed and evaluated as efficient photoinitiators of polymerization reactions in combination with iodonium salts and silanes. Mechanistically, these reactions were shown to proceed through oxidative photoredox catalysis, generating aryl and silyl radicals under very soft irradiation conditions (blue

Introduction

Photoredox catalysis recently emerged as a powerful approach in the synthetic community for the activation of different chemical bonds, owing to the smooth generation of free radical species under soft irradiation conditions.^[1–3] As far as the mechanism is concerned, it is assumed that the excited state of the photocatalyst (PC) reacts with an oxidizing or reducing agent by an electron-transfer reaction (amine, methyl viologen, enamine, etc.), thereby generating a strong reductant or oxidant metal complex; for example, [Ru-(bpy)₃]³⁺ (bpy=bipyridine) is generated by the oxidation of *[Ru(bpy)₃]²⁺ by methyl viologen. Mainly Ru or Ir complexes have been proposed as PCs (e.g., [Ru(bpy)₃]²⁺, [Ir-(ppy)₃], [Ir(ppy)₂(dtb-bpy)]⁺, etc.; ppy=2-phenylpyridine,

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LED, xenon lamp, and even sunlight). These radicals can initiate the free radical polymerization of acrylates or can

Keywords: iridium • photochemistry • photoredox catalysis • ringopening polymerization • silyl radicals be oxidized during the catalytic cycle to promote the ring-opening polymerization of epoxy monomers. Remarkably, both the (photo)chemical reactivity and the practical efficiency are dramatically affected by the ligands. In addition, the central role played by the oxidation ability of the excited state of the photocatalyst is discussed.

dtb-bpy=4,4'-di-*tert*-butyl-2,2'-dipyridyl).^[1-3] These strong metal-centered reductants (e.g., $[Ir(ppy)_2(dtb-bpy)]$, [Ru-(bpy)₃]⁺) or oxidants (e.g., $[Ir(ppy)_3]^+$, $[Ru(bpy)_3]^{3+}$) can efficiently promote radical reactions; for example, CF₃⁻ radicals can be generated by a single-electron-transfer from [Ir-(ppy)_2(dtb-bpy)] to CF₃I. Very interestingly, the PCs are characterized by an intense visible-light absorption and can be used with practical visible light sources, such as fluorescent or LED bulbs, or even ambient sunlight.

The use of organometallic compounds as photoinitiating systems is well documented in the literature and received a revival of interest^[4] in the last years. Recently, the photoredox catalysis approach has been extended to photopolymerization applications.^[5] An efficient oxidative cycle has been proposed for the formation of silyl radicals and silylium ions (Scheme 1).^[5] 1) The PC excited state reacts with an iodonium salt to generate the strong oxidant metal complex (PC⁺) and phenyl radicals (Ph⁻). 2) Silyl radicals R₃Si⁻ are generated by a hydrogen abstraction process from Ph⁻/R₃Si–H. 3)



Scheme 1. Proposed oxidative cycle for the formation of silyl radicals and silylium ions.

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The formation of the silylium ion R_3Si^+ (R_3Si^+ can initiate the ring-opening polymerization of epoxides:^[6] $R_3Si^++M \rightarrow R_3Si-M^+$, with M=epoxy) is easily obtained by oxidation of R_3Si^- by PC⁺; moreover, a PC regeneration is observed. The oxidation of the silyl by Ph_2I^+ can also be expected.^[5]

Albeit good to excellent polymerization profiles were obtained with homoleptic complexes $[Ru(bpy)_3]^{2+}$ and $[Ir-(ppy)_3]^{[5]}$ the quest for photocatalysts with tailor-made properties represents an exciting challenge. More specifically, it would be worthwhile 1) to tune the absorption of the initiating system for a better matching with the irradiation device and 2) to enhance the chemical reactivity of the initiating systems for polymerization under very soft irradiations conditions (sunlight, household fluorescence, or blue LED bulbs). Herein, six new PCs, **Ir1–Ir6**, are presented for photopolymerization processes. The underlying chemical mechanisms are investigated by ESR and luminescence experiments.



The ligands were selected to generate different light-absorption properties, redox potentials, and excited-state reactivity. It is also worth noting that only few data are available for the selected compounds and that they have been determined in this work.

Interestingly, the selected homoleptic and heteroleptic Ir^{III} derivatives exhibit triplet emitter properties. The polymer films obtained through the new proposed approach are also characterized by original photoluminescence properties.

Results and Discussion

PCs Ir1–Ir6 in photoinitiating systems for the ring-opening polymerization: The ring-opening photopolymerization of (3,4-epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxy-late (EPOX) under air in the presence of Ir1–Ir6/Ph₂I⁺ is quite slow using blue LED bulb irradiation. Even upon xenon lamp exposure, a rather low final conversion is reached: <25% after 180 s of irradiation (Figure S1 in the Supporting Information).

In contrast, excellent polymerization profiles are obtained using the different three-component systems (PC/tris(trimethylsilyl)silane/Ph₂I+) under both blue LED bulb irradiation and xenon lamp exposure (Figure 1 and Figure S1 in the Supporting Information). The formation of the polyether network is easily characterized by its absorption band at 1080 cm⁻¹ and the epoxy conversion can be followed at 790 cm⁻¹ (Figure 1 A). A high Si-H consumption is noted (close to 50% for the different initiating systems) in full agreement with the formation of silvl radicals through the hydrogen abstraction reaction (Scheme 1, reaction 3). For Ir5/tris(trimethylsilyl)silane/Ph₂I⁺, the stability of the formulation is not good enough (<1 day) and the results obtained with Ir5 will not be discussed further. The best system (Ir1) exhibits a higher polymerization initiating ability than that found with other classical systems based on phosphine oxide or titanocene.[6]

The ligand on the Ir center strongly affects the initiating ability of these three-component systems with a reactivity following the order: $Ir1 > [Ir(ppy)_3] > Ir3 > Ir2 > Ir4 > Ir6$ (Figure 1B). This behavior is found for xenon lamp and blue LED bulb irradiation (see also the polymerization rates for xenon lamp irradiation in Table S1 in the Supporting Information). These results highlight the interest of an appropriate selection of the Ir derivatives to improve the polymerization process. For the best initiating system (Ir1/tris(trimethylsilyl)silane/Ph₂I⁺), the polymerization under sunlight is a very efficient process (Figure S2 in the Supporting Information), with a conversion >75% for 600 s of irradiation.

The formation of Ph[•] and $(TMS)_3Si[•]$ (Scheme 1) for these three-component systems can be also highly desirable to initiate radical polymerization processes. The radical addition onto the monomer will be in competition with the oxidation process 3 (Scheme 1). The polymerization profile of trimethylolpropane triacrylate is found excellent for **Ir1**/tris(trimethylsilyl)silane/Ph₂I⁺ as photoinitiating system, showing an interesting dual radical/cationic initiating character (Figure 1 C).

Role of the ligands for the PC reactivity: The visible absorption spectra of the different PCs are depicted in Figure S3 A in the Supporting Information. At 462 nm, which represents the maximal emission wavelength for the blue LED bulb, the extinction coefficients are 2100, 300, 650, 1000, 7200, and $1100 \,\mathrm{m^{-1} \, cm^{-1}}$ for Ir1, Ir2, Ir3, Ir4, Ir6, and $[\mathrm{Ir}(\mathrm{ppy})_3]$, re-



Figure 1. A) IR spectra recorded during the photopolymerization of EPOX under air in the presence of Ir1/tris(trimethylsilyl)silane/Ph₂I⁺ (0.2 %/3 %/2 % w/w); blue LED bulb irradiation at t=0, 30, 60 and 180 s. B) Polymerization profiles of EPOX (conversion vs. time) under air upon blue LED bulb irradiation in the presence of a) Ir1/tris(trimethylsilyl)silane/Ph₂I⁺ (0.2 %/3 %/2 % w/w); b) [Ir(ppy)₃]/tris(trimethylsilyl)silane/Ph₂I⁺ (0.2 %/3 %/2 % w/w); c) Ir3/tris(trimethylsilyl)silane/Ph₂I⁺ (0.2 %/3 %/2 % w/w); c) Ir3/tris(trimethylsilyl)silane/Ph₂I⁺ (0.2 %/3 %/2 % w/w); e) Ir4/tris(trimethylsilyl)silane/Ph₂I⁺ (0.2 %/3 %/2 % w/w); e) Ir4/tris(trimethylsilyl)silane/Ph₂I⁺ (0.2 %/3 %/2 % w/w); f) Ir6/tris(trimethylsilyl)silane/Ph₂I⁺ (0.2 %/3 %/2 % w/w); f) Ir6/tris(

spectively. These PCs exhibit an interesting tunable absorption and allow a recovering of the photons up to 650 nm.

Upon the blue LED bulb exposure, a bleaching of PC/ Ph₂I⁺ is found (e.g., Figure S3C in the Supporting Information for Ir1). The bleaching of Ir1 and Ir2 is accompanied by the buildup of a new absorption band ($\lambda_{max} \approx 560$ nm), as-

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cribed to the formation of **[Ir1]**⁺ and **[Ir2]**⁺ in a way similar to that reported for $[Ir(ppy)_3]$.^[5,7] This is in full agreement with the fast oxidative quenching of the different Ir derivatives by Ph₂I⁺ ($k_1 = 0.4-9 \times 10^9 \,\mathrm{m^{-1} s^{-1}}$, Table 1 and Figure 2). The luminescent excited states are strongly quenched by O₂ (Table 1), that is, their interaction rate constants with Ph₂I⁺ (k_1) were determined under argon. Upon the blue LED bulb exposure of PC/Ph₂I⁺ solutions, Ph⁻ radicals are detected by ESR spin-trapping experiments with phenyl-*N-tert*-butylnitrone (PBN, Figure 3). All these results demonstrate

Table 1. Oxidation potentials (E_{ox}) , excited state energy levels (E_T) , luminescence lifetimes under argon (τ) , rate constants for the interaction of the luminescent state with Ph₂I⁺ and O₂ in acetonitrile, and ΔG for reaction 1 for the different investigated Ir complexes. The error bar for the rate constants $(k (Ph_2I^+) \text{ and } k (O_2))$ is 10%.

| | $k (Ph_2I^+)$ | $k(O_2)$ | τ [ns] | $E_{\rm ox}$ ([V] vs. | $E_{\mathrm{T}}^{[\mathrm{c}]}$ | $\Delta G^{[d]}$ |
|-------------------------|-----------------------------|---------------------|--------------------|-----------------------|---------------------------------|------------------|
| | $\left[M^{-1}S^{-1}\right]$ | $[M^{-1}S^{-1}]$ | | SCE) | [eV] | [eV] |
| [Ir(ppy) ₃] | 5.4×10^{9} | 8.7×10^9 | 1300 | $0.77^{[a]}$ | 2.5 | -1.53 |
| Ir1 | 9.0×10^{9} | 9.1×10^{9} | 280 | 0.76 | 2.25 | -1.29 |
| Ir2 | 7.5×10^{9} | 8.9×10^{9} | 1600 | 1.10 | 2.75 | -1.45 |
| Ir3 | 8.1×10^{8} | 9.0×10^{9} | 890 | 1.30 | 2.6 | -1.1 |
| Ir4 | 8.0×10^{8} | 8.8×10^{9} | 830 | 1.27 | 2.6 | -1.13 |
| Ir6 | 4.0×10^{8} | 8.5×10^{9} | 760 ^[b] | 1.33 | 2.6 | -1.07 |
| | | | | | | |

[a] From reference [9]. [b] The long-lived transient is observed at 550 nm. [c] Evaluated from the luminescence band edge (see Figure S3 in the Supporting Information for the different luminescence spectra). [d] $\Delta G = E_{\rm ox} - E_{\rm red} - E_{\rm T}$; calculated from the classical Rehm–Weller equation, in which $E_{\rm ox}$, $E_{\rm red}$, and $E_{\rm T}$ are the oxidation potential of the donor, the reduction potential of the acceptor, and the triplet state energy; $E_{\rm red} = -0.2$ V was used for Ph₂I⁺.^[5]



Figure 2. A) Emission decay curves of **Ir4** monitored at 550 nm for different [Ph₂I⁺] (0–0.018 M); degassed (argon) acetonitrile; excitation at 355 nm. B) Emission decay curves of **Ir1** monitored at 570 nm: a) degassed (argon) and b) under air; acetonitrile; excitation at 355 nm. a.u. = arbitrary units.

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Figure 3. ESR spectra obtained after blue LED bulb irradiation of **Ir1**/ Ph₂I⁺ (in *tert*-butylbenzene/acetonitrile, phenyl-*N*-*tert*-butylnitrone (PBN) is used as spin-trap, [Ph₂I⁺] = 0.011 M): experimental 1) and simulated 2) spectra (hyperfine coupling constants for the radical adduct: $a_N = 14.4$ G and $a_H = 2.3$ G, in agreement with the known data for the Ph spin adduct).^[8]

that reaction 1 occurs for the new PCs (Scheme 1). For Ir derivatives/tris(trimethylsilyl)silane/Ph₂I⁺, the formation of the silyl radicals is also well shown by ESR spin-trapping experiments with phenyl-*N-tert*-butylnitrone (hyperfine coupling constants: $a_N \approx 15.0$ G, $a_H \approx 5.6$ G, in agreement with the known data for this structure^[8]). Photolysis experiments show that the Ir derivatives are now regenerated. All these results clearly show that the mechanism presented in Scheme 1 for [Ir(ppy)₃] still occurs for Ir1–Ir4 and Ir6.

The differences observed in PC activity $(Ir1 > [Ir(ppy)_3] >$ Ir3 > Ir2 > Ir4 > Ir6) can be ascribed to 1) the absorption properties (for 462 nm: $Ir6 > Ir1 > [Ir(ppy)_3] > Ir4 > Ir3 > Ir2$, see the absorption coefficients above) and 2) the reactivity of the luminescent state with Ph₂I⁺ to initiate the catalytic cycle (Scheme 1, reaction 1, $Ir1 > Ir2 > [Ir(ppy)_3] > Ir3 \approx$ Ir4>Ir6). The rate constants k_1 are found related to the oxidation potentials (E_{ox}) of Ir complexes (Table 1); for example, the rate constants decrease in the series Ir1 > Ir3 > Ir6 in agreement with their oxidation ability ($E_{ox} = 0.76$, 1.3, and 1.33 V for Ir1, Ir3, and Ir6, respectively). The free energy changes for reaction 1 (Scheme 1), calculated from the classical Rehm-Weller equation (Table 1), support the electron transfer process.^[10] For the iridium complexes characterized by $\Delta G < -1.29 \text{ eV}$ (Ir1, Ir2, and [Ir(ppy)₃]), the reaction is diffusion controlled $(k_1 > 5 \times 10^9 \text{ m}^{-1} \text{s}^{-1})$. For the other complexes, ΔG is less favorable and accordingly the associated rate constants decrease.

Ir1 exhibits both very good light absorption properties (> $[Ir(ppy)_3]$) and the highest k_1 , thus leading to the best performance. For **Ir6**, despite an excellent absorption, this complex is characterized by the lowest reactivity for reaction 1. For **Ir2–Ir4**, different intermediate situations occur and the PC ability is a compromise between the absorption and the excited state reactivity. The optical yields and the excited state life times can also probably affect the efficiency of the initiation.

Photoluminescence of the polymer films: Interestingly, the different iridium derivatives are involved in the photoinitiating systems as part of a catalytic cycle (see Scheme 1); these complexes acting as photocatalysts are thus regenerated after use and incorporated at their initial oxidation state into the polymers, hence providing the photoluminescence properties to the polymer film. Since such compounds are already known for their luminescence properties, for example, triplet emitters for OLED applications,^[9,11] the polymer films obtained through the new presented approach are characterized by photoluminescence properties. The emission wavelengths can be tuned by an appropriate choice of the ligand (from 480 to 620 nm, see Figure S3B in the Supporting Information). Remarkably, the luminescence of the selected compounds does not decrease during the polymerization process (Figure S4 in the Supporting Information); this is in agreement with the photocatalyst behavior of the Ir complexes, that is, these compounds are regenerated in the photoinitiating system. Interestingly, the luminescence quantum yield probably increases in the polyether network, since the photoluminescence of the film also increases during the polymerization process (Figure S4 in the Supporting Information). These unique results highlight the dual behavior of the photocatalyst: 1) The photocatalyst is necessary in the photoinitiating system for the formation of the polymer network and 2) it is incorporated in the formed polymer at its initial oxidation state by regeneration in situ of the catalyst during the catalytic process (see Scheme 1) and provides the desired photoluminescence properties to the polymer film.

Conclusion

Selected Ir complexes are presented as new photocatalysts. Interestingly, the selected ligands strongly affect the PC ability. For the oxidative cycle, the key parameters are the absorption properties and the oxidation ability of the excited states (*Ir) by Ph_2I^+ . Ir1 is proposed as a new promising PC with an enhanced reactivity. The ability of these PCs for other polymerization initiating systems based on reductive cycles will be presented in forthcoming work. The use of Ir1 for organic synthesis applications is also highly desirable and the luminescence properties of the formed polymers for OLED applications deserve to be investigated in future work.

Experimental Section

Iridium(III) complexes: The six metal complexes **Ir1–Ir6** were prepared according to the different procedures outlined in the Supporting Information. Typically, the synthetic procedure for the new complexes **Ir1, Ir4**, **Ir5**, and **Ir6** included two steps. In a first step, the chloro-bridged dimers $[Ir_2Cl_2(ppy)_4]$ (ppy=2-phenylpyridine) and $[Ir_2Cl_2(dfpyy)_4]$ (dfppy=2-(2,4-difluorophenyl)pyridine) were synthesized according to the Nonoyama route starting from ppy, dfppy, and iridium(III) chloride.^[12] Then, in a second step, all complexes were obtained by a bridged-splitting reaction

of the dimers with two equivalents of the ancillary ligand. In particular, the dimeric cleavage of $[Ir_2Cl_2(ppy)_4]$ and $[Ir_2Cl_2(dfppy)_4]$ to form the neutral complexes **Ir1** and **Ir2** was performed in the presence of Ag⁺ to remove Cl⁻. Depending on the charge of the complex, two distinct purification procedures were carried out. Purification of the neutral complexes (**Ir1** and **Ir2**) was obtained by column chromatography on silica gel, followed by the precipitation of the two complexes during evaporation of the chromatography fractions. When charged, the different complexes (**Ir3** and **Ir4**) were isolated by metathesis with a fivefold excess of an aqueous solution of sodium hexafluorophosphate from a solution of the complex in methanol. All complexes were stable under air and the structures of the complexes were established by ¹H, ¹³C, and, where applicable, ³¹P or ¹⁹F NMR spectroscopy. Complexes were also characterized by HRMS. Purities higher than 90% for the six complexes were determined from the ¹H NMR spectra.

Polymerization procedures: Tris(2-phenylpyridine)iridium $[Ir(ppy)_3]$, tris(trimethylsilyl)silane (TTMSS) and diphenyliodonium hexafluorophosphate (Ph₂I⁺) were obtained from Aldrich and used with the highest purity available. (3,4-Epoxycyclohexane)methyl 3,4-epoxycyclohexylcarboxylate (EPOX from Cytec, Uvacure 1500) and trimethylolpropane triacrylate (TMPTA from Cytec) were selected as standard epoxy and acrylic



monomers, respectively.

For the free-radical-promoted cationic polymerization (FRPCP), the twoand three-component photoinitiating systems were based (except otherwise stated) on **Ir1–Ir6**/Ph₂I⁺ (0.2 %/2 % w/w) and **Ir1–Ir6**/TTMSS/Ph₂I⁺ (0.2 %/3 %/2 % w/w). The EPOX films (25 µm thick) deposited on a BaF₂ pellet were irradiated under air inside the IR spectrometer cavity. The evolution of the epoxy group content at about 790 cm⁻¹ was continuously followed by real-time FTIR spectroscopy (Nexus 870, Nicolet), as reported in reference [5]. For free-radical polymerization (FRP), the two- and three-component photoinitiating systems were based on **Ir1–Ir6**/Ph₂I⁺ (0.2 %/2 % w/w) and **Ir1–Ir6**/TTMSS/Ph₂I⁺ (0.2 %/3 %/2 % w/w). The evolution of the double bond content was continuously followed by real time FTIR spectroscopy (see above) at about 1630 cm⁻¹. The different irradiation sources are presented in the Supporting Information.

ESR experiments: ESR spin-trapping (ESR-ST) experiments were carried out using a X-Band EMX-plus spectrometer (Bruker Biospin). The radicals were produced at room temperature under LED bulb exposure and trapped by phenyl-*N-tert*-butylnitrone (PBN), according to a procedure described in detail in reference [5].

Luminescence lifetimes: The luminescence lifetimes were determined with an Edinburgh LP900 laser flash photolysis spectrometer in emission mode. The emission wavelengths were selected from the associated luminescence spectra recorded in acetonitrile (FP-750, JASCO; spectra given in the Supporting Information).

Redox potentials: The redox potentials were measured in acetonitrile by cyclic voltammetry with tetrabutylammonium hexafluorophosphate

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(0.1 M) as a supporting electrolyte (Voltamaster 6 Radiometer; the working electrode was a platinum disk and the reference electrode a saturated calomel electrode (SCE)). Ferrocene was used as a standard and the potentials determined from the half-peak potential were referred to the reversible, formal potential of this compound (+0.44 V/SCE).

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