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Visible-Light-Excited Singlet-Oxygen Luminescence Probe Based on $Re(CO)_3Cl(aeip)$

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A new rhenium(I) complex, $Re(CO)_3Cl(aeip)$ [where aeip = 2-(anthracen-9-yl)-1-ethyl-imidazo[4,5-*f*][1,10]phenanthroline], was designed and synthesized as a luminescence probe under visible light excitation at 410 nm for detection of singlet oxygen ($^1O_2$) in aqueous media. The new complex can specifically react with $^1O_2$ in neutral and alkaline media, which results in remarkable luminescence enhancements, with 8- and 18.7-fold increases in the luminescence quantum yields, respectively. The visible light excitation may allow the complex to be useful for biosystems.

Introduction

Singlet oxygen ($^1O_2$), the lowest excited state of the dioxygen molecule, can be used as a highly active oxidant in chemical and environmental processes.[1] In biological systems, excessive $^1O_2$ is thought to be an important toxic species as it can oxidize various kinds of biological molecules, such as DNA, protein, and lipids.[2,3] $^1O_2$ also plays an important role in the cell signaling cascade, the induction of gene expression,[4,5] the mitochondrial membrane pore transition,[6] and the bactericidal response of certain antibodies.[7,8] Moreover, as oxygen is ubiquitous and efficiently quenches electronically excited states, it is likely to be formed following irradiation in countless situations and involved in various chemical, biological, and several disease processes.[9,10] On the other hand, the artificial photochemical generation of $^1O_2$ has been used as a cancer treatment protocol to destroy malignant cancer cells or tissues in photodynamic therapy.[10–13]

Because of the outstanding importance of $^1O_2$ in photochemical and photobiological processes, the development of stable and specific probes for $^1O_2$ has attracted much interest.[14] Several methods for detecting $^1O_2$ have been developed. $^1O_2$ could be indirectly detected by its chemical products (e.g. lipid peroxidation[15,16]) or by using specific quenchers (sodium azide).[17] However, these indirect methods frequently yield no unequivocal results and no detailed insight into the primary mechanisms of action. The direct way to monitor $^1O_2$ at 1270 nm is a specific and noninvasive method, but this method suffers from weak signals, because of the lower efficiency of $^1O_2$ emission, and quantitative detection of very small amounts of $^1O_2$ is currently not possible in any medium.[15,18–20] Chemical trapping by spectroscopic probes is also found to be specific and much more sensitive than detection of the 1270-nm luminescence. The anthryl moiety is an important functional group for designing a specific $^1O_2$ trap. 9,10-Diphenylanthracene (dpa) has been reported to act as an $^1O_2$ trap by reacting specifically with $^1O_2$ to form a thermostable endoperoxide, which results in a decrease in absorbance at 335 nm (a signal of $^1O_2$ generation).[21,22] This method is less sensitive because the detection is based on the absorbance measurement. Nagano's group has synthesized two fluorescence probes for $^1O_2$ by conjugating a fluorescein fluorophore with 9,10-diphenylanthracene or 9,10-dimethylanthracene.[23,24] These probes react with $^1O_2$ to yield the corresponding endoperoxides, which give sensitive fluorescence responses. Recently, Li et al. developed a chemiluminescence probe for $^1O_2$ by incorporating an electron-rich tetrathiafulvalene unit into a reactive anthracene luminophore.[25] This probe exhibits a highly selective chemiluminescence response for $^1O_2$. The main drawback of this probe is its low water solubility; a buffer containing 50% thf is necessary to dissolve the probe, which makes it unsuitable for use in some biosystems.

Recently, Eu^{3+} and Tb^{3+} chelate-based luminescence probes for highly sensitive detection of $^1O_2$ have been reported.[26–29] These probes have the advantages of higher water solubility and sensitivity and ready elimination of background fluorescence. However, these probes need ultraviolet light excitation, which limits their applications in biosystems. In this paper, we demonstrate that a Re^I complex acts as a highly selective and sensitive $^1O_2$ luminescence probe, excitable at 410 nm in aqueous solution. The excitation by visible light is preferable for biological application as it minimizes cell damage. This is, to the best of our knowledge, the first example of transition-metal-complex-based $^1O_2$ luminescence probe with visible light excitation.

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Results and Discussion

Synthesis and Common Spectral Characteristics

The Re^I complex was readily synthesized by heating $Re(CO)_5Cl$ and aeip in toluene at reflux (see Figure 1) and was characterized by ^1H NMR, IR, and UV/Vis absorption spectroscopy, elemental analysis, and positive-ion ESI-MS. The IR spectra for the Re^I complex and aeip in KBr pellets are compared in Figure 2. The spectrum for the Re^I complex shows three CO stretching bands at 2027, 1921, and 1871 cm^{-1}, which is consistent with a *fac* configuration at the rhenium center. This indicates the formation of a new product by reaction of $Re(CO)_5Cl$ and aeip.[30] The heterocyclic C=N stretching band is observed at 1607 cm^{-1} for the Re^I complex and at 1604 cm^{-1} for aeip. The aryl ring stretching bands observed at 1530, 1499, and 1444 cm^{-1} for the Re^I complex are comparable to those (1524, 1502, 1469, and 1444 cm^{-1}) observed for aeip.[30] CH_2 antisymmetric and symmetric stretching frequencies are seen at 2974 and 2923 cm^{-1} for the Re^I complex and at 2985 and 2924 cm^{-1} for aeip, respectively.[30] The UV/Vis absorption spectra of the Re^I complex and aeip in dmso are presented in Figure 3. The anthryl-moiety-centered π–π* absorption bands at 351, 370, and 390 nm for the Re^I complex are almost unchanged relative to those (351, 369, and 389 nm) for aeip. The higher-energy π–π* absorption band is redshifted from 284 nm for free aeip to 304 nm for the Re^I complex. Importantly, the Re^I complex exhibits a new shoulder band at 420 nm, which is attributed to a metal-to-ligand charge-transfer (MLCT) transition.

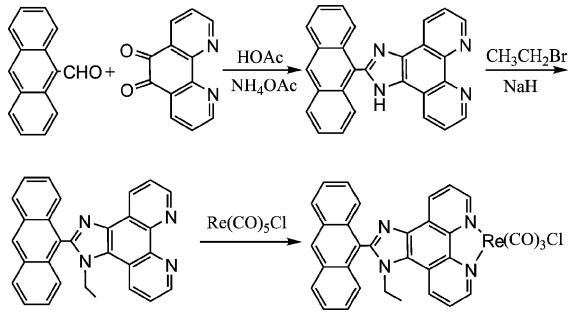

Figure 1. Synthetic route to the Re^I complex.

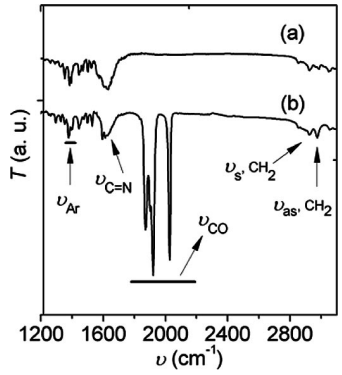

Figure 2. IR spectra of (a) $Re(CO)_3Cl(aeip)$ and (b) aeip in KBr pellets.

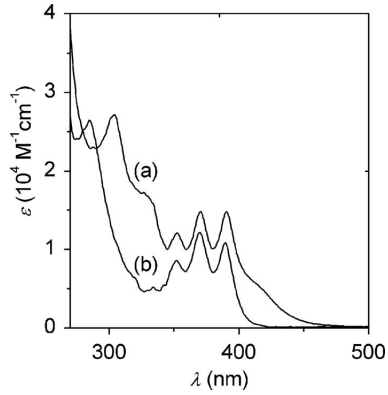

Figure 3. UV/Vis spectra of (a) $Re(CO)_3Cl(aeip)$ and (b) aeip in dmso.

Detection of $^1O_2$ With $Re(CO)_3Cl(aeip)$ as a Probe in Aqueous Media

It is well known that the anthracene skeleton can react with $^1O_2$ to form its endoperoxide, thus strongly affecting the luminescence properties of the fluorophores.[21,24,31–35] The Re^I complex is almost nonluminescent in the absence of $^1O_2$, probably because the anthryl moiety quenches the luminescent Re→aeip metal-to-ligand charge-transfer (MLCT) excited state through exchange triplet–triplet intramolecular energy transfer, as revealed in analogous Re^I complexes.[36] On the contrary, the Re^I complex become strongly luminescent in the presence of $^1O_2$ because of the termination of electronic coupling between the anthryl and the parent Re^I complex moieties caused by endoperoxide formation (see Figure 4).

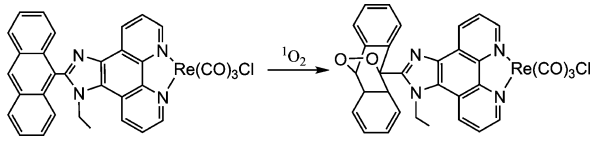

Figure 4. Reaction of the Re^I complex with $^1O_2$.

$^1O_2$ can be quantitatively generated from the H_2O_2/NaOCl system in neutral media[37] or from the H_2O_2/MoO_4^{2-} system in alkaline media[24,25] (one $^1O_2$ molecule can be formed quantitatively by the reaction of two H_2O_2 molecules).[23,38–41] After addition of H_2O_2, the Re^I complex reacted with $^1O_2$, which results in a gradual reduction in the absorption intensities of the anthryl moiety at 370 nm and 390 nm (see Figure 5). This is consistent with the obser-

vations reported for many anthryl-moiety-containing compounds.[28] The changes in the emission spectra of the Re^{I} complex upon reaction with varied concentrations of $^1O_2$ are shown in Figure 6, which reveals the effects of the formation of the endoperoxide on the luminescence intensities of the Re^{I} complex. The luminescence intensities of the complex increases with increasing concentrations of $^1O_2$, and the luminescence quantum yields increase from 8.9×10^{-5} to 7.1×10^{-4} and from 4.7×10^{-5} to 8.7×10^{-4} in the neutral and alkaline media, respectively. The luminescent intensities for the Re^{I} complex after reaction with $^1O_2$ in the neutral and the alkaline solutions decrease by less than 3.5% and 2.1% after a one-hour shelf time, respectively, which is indicative of the good stability of the endoperoxide of the Re^{I} complex. Good linear plots of log I vs. log [$^1O_2$] were obtained as shown in Figure 7. The $^1O_2$ detection limits of the Re^{I} complex in the alkaline and neutral media, calculated as the concentration corresponding to three standard deviations of the background signal, are 10.5 and 4.9 nM, respectively. The latter is about 15-times lower than that of the reported chemiluminescence probe[25] and comparable to those (2.8–10.8 nM) reported for the Eu^{3+}- and Tb^{3+}-complex-based luminescence probes,[27–29] which indicates that the Re^{I} complex is a highly sensitive luminescence probe for $^1O_2$.

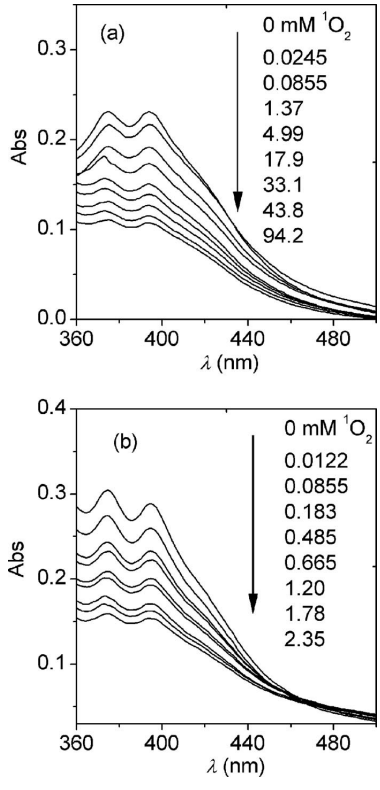

Figure 5. Changes in the UV/Vis spectra of the Re^{I} complex upon increasing concentrations of $^1O_2$ in (a) neutral ([Re] = 2.01×10^{-5} M) (b) and alkaline media ([Re] = 2.87×10^{-5} M).

To investigate the reaction specificity of the Re^{I} complex towards $^1O_2$, the reactions of the Re^{I} complex with several reactive oxygen species (ROS) were examined. As shown in

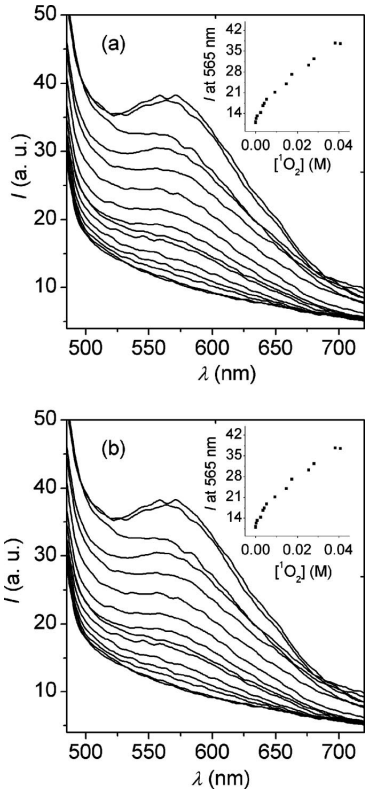

Figure 6. Changes in the emission spectra (λ_{ex} = 410 nm) of the Re^{I} complex upon increasing concentrations of $^1O_2$ (a) in neutral ([Re] = 2.01×10^{-5} M) and (b) alkaline media ([Re] = 2.87×10^{-5} M).

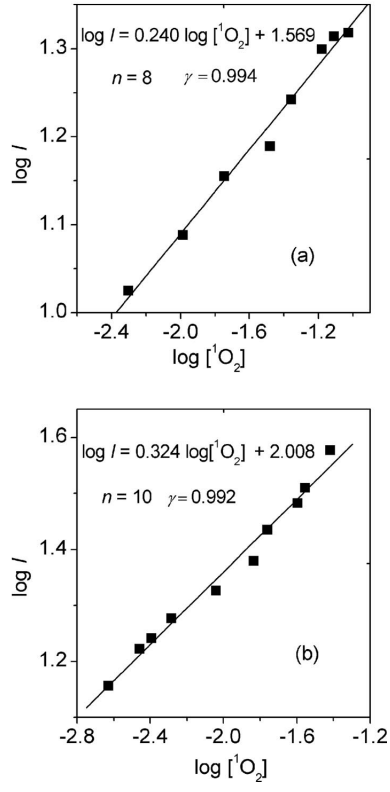

Figure 7. Calibration curves for $^1O_2$ derived from the luminescence intensities at 565 nm for the Re^{I} complex in (a) neutral ([Re] = 2.01×10^{-5} M) and (b) alkaline media ([Re] = 2.87×10^{-5} M).

Figure 8, the luminescence intensities of the Re^I complex increase remarkably upon reaction with $^1O_2$, whereas they are little affected by addition of H_2O_2, ·OH, and $ONOO^-$ in both alkaline and neutral media. This may be attributed to the specific reactivity of the anthracene unit toward $^1O_2$.[21,23,24] Thus, we can conclude that the Re^I complex is a specific luminescence probe for $^1O_2$ in aqueous media.

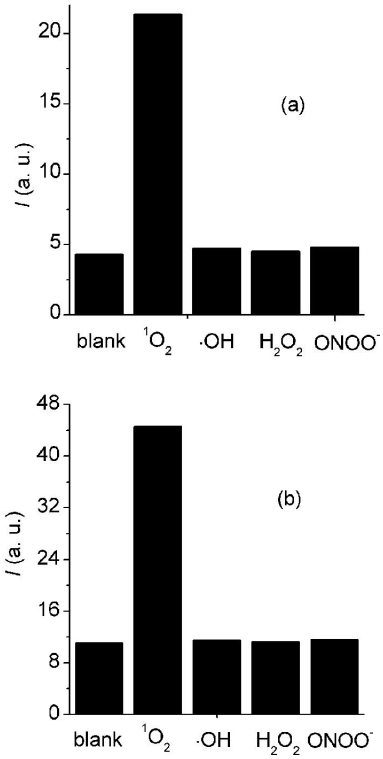

Figure 8. Luminescent intensities of the Re^I complex in the absence and presence of different ROS ([ROS] = 40 mM) in (a) neutral ([Re] = 2.01×10^{-5} M) and (b) alkaline media ([Re] = 2.87×10^{-5} M).

The luminescence properties of the Re^I complex studied in this work and some representative $^1O_2$ luminescence probes are summarized in Table 1. The excitation wavelength for the Re^I complex is within the visible region (410 nm), which probably allows for the application of the Re^I complex in biosystems, while the excitation wavelengths used by previously reported probes are within the ultraviolet region (316–390 nm). Moreover, the Re^I complex studied here may hold prospects for further applications in many biosystems as a result of its good water solubility and comparatively low detection limits of 4.9–10.5 nM for $^1O_2$.

Table 1. The luminescence properties of the Re^I complex and some representative $^1O_2$ fluorescent probes.

Complex[a]	λ_{ex} [nm]	Detection limit [nM]	Enhancement factor, Φ/Φ_0	Ref.
daet[b]	390	76	54	[24]
atta–Eu^{3+}[c]	335	2.8	17	[26]
mtta–Eu^{3+}[c]	335	3.8	15.3	[27]
Pata–Tb^{3+}[c]	316	10.8	22.8	[28]
$Re(CO)_3Cl(aeip)$[c]	410	4.9	18.7	this work

[a] daet = 4,5-dimethylthio-4′-[2-(9-anthryloxy)ethylthio]tetrathiafulvalene; atta = [4′-(9-anthryl)-2,2′:6′,2′′-terpyridine-6,6′′-diyl] bis(methylenenitrilo)tetrakis(acetic acid); mtta = [4′-(10-methyl-9-anthryl)-2,2′:6′,2′′-terpyridine-6,6′′-diyl] bis(methylenenitrilo)tetrakis(acetic acid); pata = *N*,*N*,*N*′,*N*′-[2,6-bis(3′-aminomethyl-1′-pyrazolyl)-4-(9′′-anthryl)pyridine]tetrakis(acetic acid). [b] In neutral medium. [c] In alkaline medium.

Conclusions

An anthryl-moiety-containing Re^I complex has been synthesized. The new complex can specifically react with $^1O_2$ to form its endoperoxide, which leads to a remarkable luminescence enhancement in both neutral and alkaline media. These characteristics could be used for the detection of $^1O_2$, with high sensitivity and selectivity. Importantly, the Re^I complex has an advantage over previously reported fluorescent probes because it can be excited by visible light, which suggests that it should be very useful for the detection of $^1O_2$ in not only chemical but also biological systems.

Experimental Section

General: Unless otherwise noted, materials obtained from commercial sources were used without further purification. Elemental analyses were performed on a Vario EL elemental analyzer. Infrared spectra were measured on a Nicolet Avatar 360 FTIR spectrometer in KBr disks. ^1H NMR spectra were obtained on a Bruker DRX-500 spectrometer. The matrix-assisted laser desorption ionization mass spectrum (MALDI-TOF MS) was run on an API Q-star pulsar (applied Biosystems) mass spectrometer. UV/Vis absorption spectra were recorded on a GBC Cintra 10e UV/Vis spectrophotometer. Emission spectra were recorded on a Shimadzu RF-5301PC spectrofluorimeter. The luminescence quantum yields were calculated by using Equation (1), where Φ_s and Φ_{std} are the quantum yields of unknown and standard samples {Φ_{std} = 0.028 for aerated $[Ru(bpy)_3]^{2+}$, aqueous solution}, A_s and A_{std} (<0.1) are the solution absorbance at the excitation wavelength (λ_{ex}), I_s and I_{std} are the integrated emission intensities, and η_s and η_{std} are the refractive indices of the solvents.

$$\Phi_s = \Phi_{std}(A_{std}/A_s)(I_s/I_{std})(\eta_s/\eta_{std})^2 \quad (1)$$

Synthesis of aeip·0.25H_2O: A suspension of NaH (0.27 g, 5.6 mmol) and 2-(anthracen-9-yl)-imidazo[4,5-*f*] [1,10]phenanthroline[42] (1.59 g, 4.0 mmol) in anhydrous dmf (15 mL) was heated under N_2 at 100–110 °C for 1 h, and then cooled to room temperature. After addition of bromoethane (1.09 g, 10.0 mmol), the solution was further heated at 100–110 °C for 24 h. Upon cooling to room temperature, NaBr that precipitated was filtered off, and the solvent was driven off under reduced pressure. The resulting solid was chromatographed over silica gel by using CH_2Cl_2/CH_3OH (15:1, v/v) as eluent, then crystallized from CH_2Cl_2 and *n*-hexane, and dried under vacuum to afford a light yellow solid. Yield 0.679 g (40%). IR (KBr): $\tilde{\nu}_{max}$ = 3440 (vs), 2984 (w), 2924 (w), 1632 (m), 1604 (m), 1524 (w), 1502 (w), 1482 (w), 1469 (w), 791 (w), 739 (s) cm^{-1}. ^1H NMR ([D_6]dmso): δ = 9.11–9.15 (m, 2 H), 8.89–8.97 (m, 3 H), 8.29 (d, J = 8.5 Hz, 2 H), 7.63–7.85 (m, 2

H), 7.62 (t, J = 6.7 Hz, 2 H), 7.49–7.54 (m, 4 H), 4.28–4.32 (m, 2 H), 1.18 (t, J = 7 Hz, 3 H) ppm. $C_{29}H_{20}N_4 \cdot 0.25H_2O$ (429.0): calcd. C 81.25, H 4.82, N 13.06; found C 81.41, H 4.54, N 12.80.

Synthesis of $Re(CO)_3Cl(aeip)$: A mixture of $Re(CO)_5Cl$ (0.44 g. 0.12 mmol) and aeip (0.051 g, 0.12 mmol) in toluene (5 mL) was heated at reflux under N_2 at 115 °C for 6 h. After the solution was cooled to room temperature, most of the solvent was removed under reduced pressure. The solid precipitated was filtered and was washed with diethyl ether and dried under vacuum to give a yellow solid. Yield 0.069 g (79%). IR (KBr): $\tilde{\nu}_{max}$ = 3430 (s), 2974 (w), 2923 (w), 2027 (vs), 1921 (vs), 1871 (vs), 1607 (w), 1595 (w), 1530 (w), 1499 (w), 1444 (w), 732 (w) cm^{-1}. ^1H NMR ($CDCl_3$): δ = 9.49 (d, J = 4.84 Hz, 1 H), 9.44 (d, J = 4.5 Hz, 1 H), 9.39 (d, J = 8.12 Hz, 1 H), 8.93 (d, J = 8.19 Hz, 1 H), 8.80 (s, 1 H), 8.20 (m, 2 H), 7.98 (d, J = 4.80 Hz, 2 H), 7.59 (d, J = 7.56 Hz, 2 H), 7.48 (m, 1 H), 7.29 (s, 3 H), 4.36 (m, 2 H), 1.36 (t, J = 7.00 Hz, 3 H) ppm. $C_{32}H_{20}ClN_4O_3Re$ (730.2): calcd. C 52.49, H 3.03, N 7.65; found C 52.66, H 3.11, N 7.62. ESI-MS: m/z = 731.1 $[M + H^+]^+$.

Preparation of ROS: $^1O_2$ was chemically generated from the H_2O_2/MoO_4^{2-} system in alkaline media or from the H_2O_2/NaOCl system in neutral media. In alkaline media, the reaction was performed in a 0.1 M carbonate buffer with a pH of 10.5; H_2O_2 solutions were added.[28] In neutral media, the reaction was performed in a 50 mM phosphate buffer with a pH of 7.0; H_2O_2 solutions were added.[25] Prior to use, hydrogen peroxide was diluted immediately from a stabilized 30-% solution and was assayed by using its molar absorption coefficient of 43.6 $M^{-1} cm^{-1}$ at 240 nm.[43] The hydroxyl radical (·OH) was generated through the reaction of ferrous ammonium sulfate and hydrogen peroxide.[44] $ONOO^-$ was synthesized from NO_2^- and H_2O_2, and the concentration of $ONOO^-$ was determined by measuring the absorbance at 302 nm with a molar extinction coefficient of 1670 $M^{-1} cm^{-1}$.[45]

Detection of $^1O_2$ in Aqueous Media

In neutral medium: To a 10 mL of 50 mM phosphate buffer solution (pH 7.0) containing 10 mM NaOCl was added 200 μL of 1 mM $Re(CO)_3Cl(aeip)$ in dmso. After addition of different amounts of H_2O_2, the reactions were monitored by luminescence and UV/Vis spectroscopy.

In alkaline medium: To a 10 mL of 0.1 M carbonate buffer solution (pH 10.5) containing 10 mM Na_2MoO_4 was added 150 μL of 1.9 mM $Re(CO)_3Cl(aeip)$ in dmso. After addition of different amounts of H_2O_2, the reactions were monitored by luminescence and UV/Vis spectroscopy.

Acknowledgments

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