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# A Red Light-Driven CO-releasing Complex: Photochemical and Photophysical Properties of Highly-Distorted Tricarbonyl Rhenium Phthalocyanines

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**Abstract:** A complex comprising one  $[\text{Re}(\text{CO})_3]^+$  unit and a phthalocyanine (Pc) ligand (**Re<sub>1</sub>Pc**) is shown to function as a photo-induced CO-releasing molecule (photoCORM) in the presence of  $\text{O}_2$  and a coordinative solvent under irradiation with red light, which can deeply penetrate living tissues. Transient absorption spectroscopic measurements indicate very short excited-state lifetimes and ultrafast intersystem crossing for **Re<sub>1</sub>Pc** and **Re<sub>2</sub>Pc**, which contains two  $[\text{Re}(\text{CO})_3]^+$  units. The excited-state properties are ascribed to efficient spin-orbit coupling and large Franck-Condon factors originating from the complexes' distorted structures, i.e., unsymmetric coordination of  $[\text{Re}(\text{CO})_3]^+$  unit(s), one of which was confirmed via single-crystal X-ray analysis of a symmetrically-substituted Pc with two  $[\text{Re}(\text{CO})_3]^+$  units. **Re<sub>1</sub>Pc** represents a promising red light-driven photoCORM that can be applied in biological environments or therapeutic applications.

## Introduction

Carbon monoxide (CO) is a well-known toxic molecule that can cause accidental carbon monoxide poisoning. Until the early 1990s, it was theorized that CO might also play a physiological role owing to its vasorelaxation effect, which is similar to that of nitric oxide (NO).<sup>[1,2]</sup> More recently, a large amount of evidence has confirmed that endogenously-produced CO is a bifunctional molecule that can contribute to homeostatic control of cardiovascular effects in various vascular components; clinical trials involving CO have also been conducted.<sup>[3-8]</sup> As a result, investigations of various CO-releasing molecules (CORMs) have attracted significant attention. It is crucial that CORMs can safely deliver and release CO to targeted living tissues while maintaining

stability in biological systems. Metal complexes have been studied for this purpose because CO is inactivated when it coordinates to the metal center owing to strong  $\pi$ -back donation, and CO is released only after a trigger is introduced.<sup>[9-12]</sup> The photodissociation of CO is another promising phenomenon that can be exploited by activating CORMs with light of an appropriate wavelength, i.e., photoCORMs. It is advantageous to be able to photo-control the release of CO and, therefore, CO photodissociation using UV light has been investigated with numerous metal carbonyl complexes.<sup>[13-25]</sup> Ligand modifications enable the metal carbonyl complexes to release CO via visible light irradiation.<sup>[26-36]</sup> The major challenge involved in developing photoCORMs based on metal carbonyl complexes is releasing CO upon irradiation with red or near-infrared (NIR) light, which can deeply penetrate living tissues. Some metal carbonyl complexes that can release CO under red light conditions have been developed.<sup>[30,36]</sup> With the goal of using red or NIR light, phthalocyanine (Pc) molecules and their analogues are promising because of the large absorption coefficients ( $>10^5$ ) of the Q absorption bands in the red or NIR spectral regions.<sup>[37]</sup> Ruthenium Pc and naphthalocyanine (Nc) complexes containing one CO as the axial ligand were shown to function as photoCORMs under red light irradiation via stepwise two-photon excitation using nanosecond pulsed laser sources.<sup>[38]</sup> However, wider applications of RuPc and RuNc complexes are limited because they require expensive pulsed lasers. Thus, it is strongly desired to develop new Pc-based CORMs driven by continuous-wavelength (CW) red light, which is a more conventional light source. In this case, it is important to balance the complex's stability under ambient

light with its facile release of CO under relatively intense CW red light.

Herein, we report a novel CW red light-triggered photoCORM comprising a Pc complex with one tricarbonyl rhenium(I),  $[\text{Re}(\text{CO})_3]^+$  unit ((tetra-*tert*-butylphthalocyaninato)tricarbonyl rhenium(I); **Re<sub>1</sub>Pc**), as shown in Figure 1. The photochemical and photophysical properties of the two rhenium(I) Pc complexes (**Re<sub>1</sub>Pc** and **Re<sub>2</sub>Pc**; Figure 1) were investigated, revealing characteristic properties, including sharp, intense Q-bands, which enabled the use of red/NIR light (745 and 798 nm for **Re<sub>1</sub>Pc** and **Re<sub>2</sub>Pc**, respectively) and high stability against oxidation.<sup>[39]</sup> As expected, **Re<sub>1</sub>Pc** behaves as a photoCORM, simultaneously releasing three CO molecules in the presence of CW red light, molecular oxygen, and a coordinative solvent, e.g., pyridine or acetonitrile. Importantly, **Re<sub>1</sub>Pc** is stable during synthetic, purification, and measurement processes under ambient conditions. Furthermore, transient absorption measurements indicated that the excited-state lifetimes of **Re<sub>1</sub>Pc** and **Re<sub>2</sub>Pc** were very short because of ultrafast intersystem crossing (ISC). These observations are quantitatively explained based on (i) efficient spin-orbit coupling (SOC) due to the heavy atom effect of Re ions and (ii) the distorted structures with unsymmetric coordination of the  $[\text{Re}(\text{CO})_3]^+$  unit(s). Thus, a stable, Pc-derived, CW red light-driven CORM was successfully developed and provides a basis for designing photoCORMs for biological or therapeutic applications.

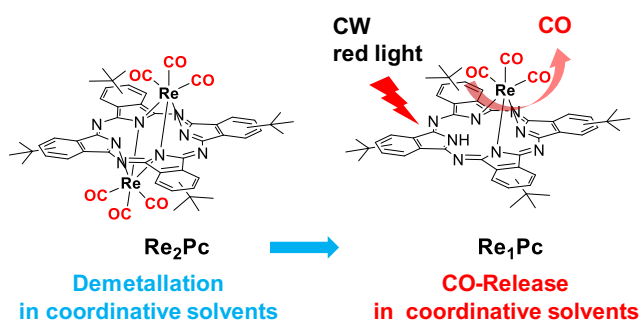


Figure 1. Concept image of **Re<sub>2</sub>Pc** and **Re<sub>1</sub>Pc**.

## Results and Discussion

**Single-crystal X-ray structural analysis:** The Re(I) Pc complexes are characterized by structural distortions due to the coordination of isoindole units, which cause the  $[\text{Re}(\text{CO})_3]^+$  unit(s) to protrude from the Pc plane; these structures were computed using density functional theory (DFT).<sup>[39]</sup> Single crystals were obtained for X-ray structural analyses to experimentally confirm the predicted structural distortions. **Re<sub>2</sub>Pc** may contain isomers because of the substitution pattern of four *tert*-butyl groups on the Pc ring<sup>[39,40]</sup>; therefore, a Pc ligand symmetrically substituted with eight *n*-butoxyl groups (i.e., 2,3,9,10,16,17,23,24-octabutoxyphthalocyanine; H<sub>2</sub>ObPc) was used for crystallization.<sup>[41-46]</sup> **Re<sub>2</sub>ObPc** was synthesized by heating a decalin solution containing  $\text{Re}_2(\text{CO})_{10}$  and H<sub>2</sub>ObPc under a nitrogen atmosphere, and its single crystal was successfully obtained by vapor diffusion. Although some disorder was observed in the butoxyl substituents,<sup>[47]</sup> the single crystal obtained was sufficient for X-ray structural analysis, providing a final  $R_1$  of 0.0384 ( $I > 2\sigma(I)$ ).

In the **Re<sub>2</sub>ObPc** crystal, the two  $[\text{Re}(\text{CO})_3]^+$  units are located on different sides of the Pc plane and are coordinated by the oppositely-inclined isoindole units (Figure 2). The other two isoindole units adjacent to the coordinating isoindole units are not inclined. Thus, the Pc skeleton in **Re<sub>2</sub>ObPc** is clearly distorted, as shown in the side view of the crystal structure (Figure 2b). The single-crystal structure is consistent with the optimized structure calculated by DFT, and it is also analogous to the crystal structure previously reported for  $[\text{Re}(\text{CO})_3]_2\text{TPP}$  (TPP: tetraphenylporphyrin).<sup>[48]</sup> The data for single-crystal X-ray structural analysis are summarized in Tables S1 and S2.

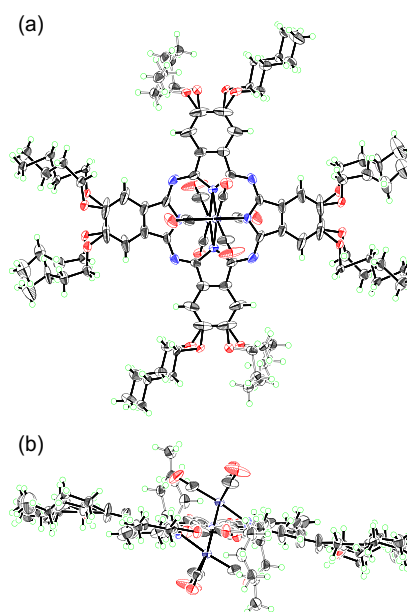
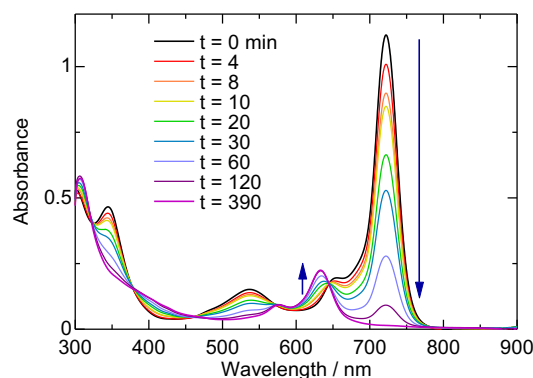


Figure 2. (a) Top and (b) side views of the single crystal structure of **Re<sub>2</sub>ObPc**.

**Photodissociation of CO:** To investigate the possibility of CO photodissociation, the photochemical properties of **Re<sub>1</sub>Pc** and **Re<sub>2</sub>Pc** were investigated. Figure 3 shows the spectral changes in a solution of **Re<sub>1</sub>Pc** in pyridine (0.01 mM, 3 mL) under CW red light irradiation. Upon increasing the irradiation time, the Q-band of **Re<sub>1</sub>Pc** at 722 nm decreased in intensity, while a new absorption band grew at 633 nm. After 390 min of red light irradiation, no further spectral changes occurred. Isosbestic points were observed at 324, 379, 466, 571, and 646 nm during the irradiation, which indicated a direct conversion of **Re<sub>1</sub>Pc** to its photochemical product. Similar spectral changes were observed in acetonitrile (Figure S2a), indicating that a similar product was formed.

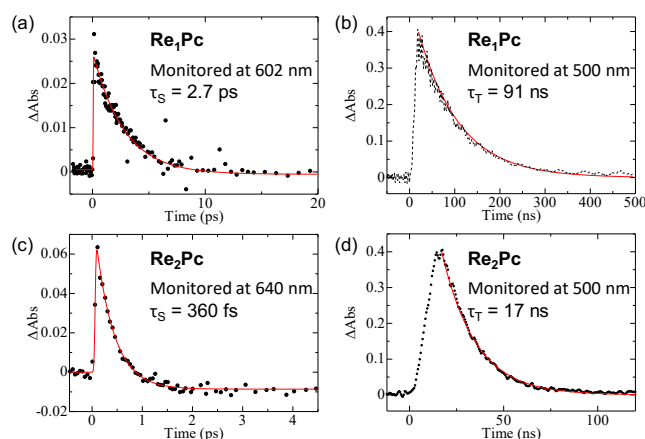
Notably, the reactivity of **Re<sub>1</sub>Pc** strongly depends on the experimental conditions (Table S3). Under an N<sub>2</sub> atmosphere, no spectral changes were observed upon irradiation with CW red light in pyridine, which indicated that molecular oxygen was necessary for the photochemical CO dissociation reaction involving **Re<sub>1</sub>Pc**.<sup>[17,18,22,49]</sup> Solvent effects were also identified; specifically, **Re<sub>1</sub>Pc** photochemical reactions occurred in solvents with coordination abilities, e.g., pyridine or acetonitrile, whereas the spectra did not change in non-coordinating solvents, e.g., toluene or chloroform. Therefore, three essential parameters were identified for the photochemical reactions of **Re<sub>1</sub>Pc**: CW red light, molecular oxygen, and a coordinative solvent.



**Figure 3.** Electronic absorption spectral changes for **Re<sub>1</sub>Pc** (0.01 mM, 3mL, stirring) in pyridine upon CW red light irradiation (Xe lamp with >640 nm filter; light intensity = 0.260 W).

To better understand the photochemical reactions involving **Re<sub>1</sub>Pc**, gas chromatography (GC) measurements were carried out. CO was detected by GC in the reaction vessel's gaseous headspace, which indicated that the CO-releasing reaction occurred and confirmed the successful preparation of a new CW red light-driven Pc-based CORM. Additionally, electrospray ionization mass spectrometry (ESI-MS) measurements were performed to identify the photoproduct in solution. After completion of the photodecarbonylation reaction of **Re<sub>1</sub>Pc** in pyridine and purification by thin-layer chromatography (TLC; CHCl<sub>3</sub>:*n*-hexane = 3:1 as the eluent), the peak observed at *m/z* = 1081.5 in the ESI-MS (positive) spectrum was attributed to [RePc(py)<sub>2</sub>]<sup>+</sup> (**RePc(py)<sub>2</sub>**: bis(pyridine)(tetra-*tert*-butylphthalocyaninato) rhenium). This result indicated that **RePc(py)<sub>2</sub>** was the final photoproduct, wherein the Re ion was situated in the Pc plane with two axial pyridine ligands after releasing all three CO from **Re<sub>1</sub>Pc** upon CW red light irradiation. The structure of **RePc(py)<sub>2</sub>** was supported by magnetic circular dichroism (MCD) results (Figure S3). In contrast to the quasi-Faraday A term observed for unsymmetric **Re<sub>1</sub>Pc**, a Faraday A term was observed in the Q-band region of the **RePc(py)<sub>2</sub>** spectrum, which indicated that the Pc-based π-conjugated system adopted D<sub>4h</sub> symmetry. Therefore, the spectral changes following CW red light irradiation in pyridine (722 → 633 nm) were assigned to the photodissociation of CO from **Re<sub>1</sub>Pc**, resulting in the formation of **RePc(py)<sub>2</sub>**. Interestingly, the corresponding CO-releasing reaction was not observed in **Re<sub>2</sub>Pc** under similar experimental conditions; instead, a demetallation reaction occurred in coordinative solvents, such as pyridine.<sup>[50]</sup>

**Excited-state properties:** To better understand the Pc-based CORM, the excited-state properties of **Re<sub>1</sub>Pc** and **Re<sub>2</sub>Pc** were investigated by transient absorption spectroscopy. The time profiles of the excited states are shown in Figure 4. For **Re<sub>1</sub>Pc**, the excited-state lifetimes were 2.7 ps and 91 ns for the lowest excited singlet (S<sub>1</sub>) and triplet (T<sub>1</sub>) states, respectively. For **Re<sub>2</sub>Pc**, the S<sub>1</sub> and T<sub>1</sub> lifetimes were 360 fs and 17 ns, respectively. Notably, diamagnetic **Re<sub>1</sub>Pc** and **Re<sub>2</sub>Pc** have very short S<sub>1</sub> lifetimes compared with other Pc complexes.<sup>[51,52]</sup> In particular, the S<sub>1</sub> lifetime (360 fs) of **Re<sub>2</sub>Pc** is the shortest among diamagnetic Pcs. For example, the S<sub>1</sub> lifetimes of H<sub>2</sub>Pc and ZnPc, which are

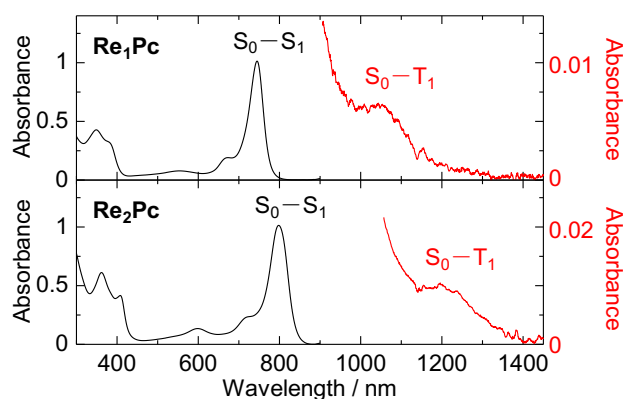


**Figure 4.** Time profiles of transient absorption signals for **Re<sub>1</sub>Pc** in the (a) S<sub>1</sub> and (b) T<sub>1</sub> states and **Re<sub>2</sub>Pc** in the (c) S<sub>1</sub> and (d) T<sub>1</sub> states in toluene (black dot or broken lines). The fitting curves are shown by red solid lines.

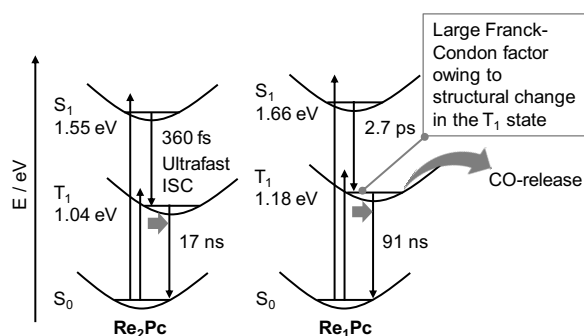
commonly studied diamagnetic Pcs, are on the order of several ns. The much shorter S<sub>1</sub> lifetimes in **Re<sub>1</sub>Pc** and **Re<sub>2</sub>Pc** is compatible with ultrafast S<sub>1</sub> → T<sub>1</sub> intersystem crossing (ISC), resulting from the heavy atom effect of Re, i.e., SOC. The T<sub>1</sub> lifetimes of **Re<sub>1</sub>Pc** and **Re<sub>2</sub>Pc** are also very short – much shorter than those of H<sub>2</sub>Pc and ZnPc, which are each several 100 μs. In particular, the T<sub>1</sub> lifetime of **Re<sub>1</sub>Pc** (91 ns) is shorter than that of **IrPcCl(py)** (760 ns), despite the fact that d<sup>6</sup> Ir(III) is heavier than d<sup>6</sup> Re(I).<sup>[53]</sup> Surprisingly, although the excited-state spin multiplicities in paramagnetic CuPc are changed dramatically because of the unpaired electron spin in d<sup>9</sup> Cu(II), the shortest excited-state lifetime of diamagnetic **Re<sub>2</sub>Pc** (17 ns) is comparable to that of CuPc (22–65 ns).<sup>[51,52]</sup> The very short excited-state lifetimes and ultrafast ISC in **Re<sub>1</sub>Pc** and **Re<sub>2</sub>Pc** can be explained by the efficient SOC owing to the distorted structures, as follows.

First, **Re<sub>1</sub>Pc** and **IrPcCl(py)** were compared from the viewpoint of their characteristic SOC; the differences in their optimized structures are presented in Figure S5. Time-dependent DFT calculations for **Re<sub>1</sub>Pc** and **IrPcCl(py)** indicate that the S<sub>1</sub> and T<sub>1</sub> states mainly originate from the HOMO (π, a<sub>1u</sub>) → LUMO (π\*, e<sub>g</sub>).<sup>[39,53]</sup> Additionally, two excited states, i.e., <sup>1</sup>E<sub>ux</sub> and <sup>1</sup>E<sub>uy</sub> (or <sup>3</sup>E<sub>uy</sub> and <sup>3</sup>E<sub>ux</sub>), are nearly degenerate in the S<sub>1</sub> (or T<sub>1</sub>) region because of the nearly degenerate LUMOs (e<sub>gx</sub> and e<sub>gy</sub>); this was confirmed by the Faraday A term in the MCD spectra. In the case of **IrPcCl(py)** where the heavy Ir ion sits in the Pc plane, the z-component of SOC between the <sup>1</sup>E<sub>ux</sub> and <sup>3</sup>E<sub>uy</sub> (or <sup>1</sup>E<sub>uy</sub> and <sup>3</sup>E<sub>ux</sub>) states is significant, owing to the orbital angular momentum between the Ir ion's d<sub>yz</sub> and d<sub>xz</sub> orbitals, which can be admixed only with the e<sub>gy</sub> and e<sub>gx</sub> π\* orbitals of the Pc ligand, respectively (Figure S6).<sup>[51,53]</sup> Thus, the triplet <sup>3</sup>E<sub>uy</sub> (or <sup>3</sup>E<sub>ux</sub>) state can contain singlet <sup>1</sup>E<sub>ux</sub> (or <sup>1</sup>E<sub>uy</sub>) character, which leads to efficient ISC and a short T<sub>1</sub> lifetime (760 ns). In contrast, the heavy Re atom is situated out from the Pc plane in **Re<sub>1</sub>Pc**. Therefore, in addition to the d<sub>xz</sub> and d<sub>yz</sub> orbitals, the p<sub>y</sub> orbital of Re can contribute to the e<sub>gy</sub>' orbital of the Pc ligand, while the p<sub>x</sub>, p<sub>z</sub>, d<sub>xy</sub>, and d<sub>x<sup>2</sup>-y<sup>2</sup></sub> orbitals of Re can be admixed with the e<sub>gx</sub>' orbital of the Pc ligand (detailed analyses are summarized in Tables S6 and S7).<sup>[54]</sup> In this way, the distorted structure allows for the x-, y-, and z-components of SOC, as shown in Figure S7. Similarly, for **Re<sub>2</sub>Pc**, the e<sub>gy</sub>' orbital of Pc interacts with the p<sub>y</sub>, d<sub>xz</sub>, and d<sub>yz</sub> orbitals of Re, whereas the e<sub>gx</sub>' orbital of Pc interacts with the p<sub>x</sub>, p<sub>z</sub>, d<sub>xz</sub>, d<sub>yz</sub>, d<sub>xy</sub>, d<sub>x<sup>2</sup>-y<sup>2</sup></sub>, and d<sub>z<sup>2</sup></sub>

orbitals of Re. Thus, the RePc complexes' distorted structures lead to efficient  $x$ -,  $y$ -, and  $z$ -components of SOC, which is confirmed by the spin-forbidden singlet–triplet ( $S$ – $T$ ) absorption spectra of highly-concentrated **Re<sub>1</sub>Pc** and **Re<sub>2</sub>Pc** solutions (Figure 5). In the NIR region, absorption bands attributable to the spin-forbidden  $S_0$ – $T_1$  transition were observed at approximately 1050 and 1200 nm for **Re<sub>1</sub>Pc** and **Re<sub>2</sub>Pc**, respectively, in agreement with efficient SOC. Notably, the full widths at half maximum (FWHM) of the  $S_0$ – $T_1$  transitions were  $\sim 1400$   $\text{cm}^{-1}$  for **Re<sub>1</sub>Pc** and  $\sim 1600$   $\text{cm}^{-1}$  for **Re<sub>2</sub>Pc**, which were much broader than the  $S_0$ – $T_1$  transition (959 nm, 470  $\text{cm}^{-1}$ ) of **IrPcCl(py)**. This indicates a deviation in the minimum position between the  $S_0$  and  $T_1$  states, which can increase the vibrational overlap, i.e., the Franck-Condon factor (Figure 6); this is one of the characteristics of distorted porphyrins.<sup>[55,56]</sup> The deviation in the minimum position between the  $S_0$  and  $T_1$  states was verified based on the time-resolved infrared (TRIR) spectra (Figure S8). In the TRIR spectrum of **Re<sub>1</sub>Pc** in the  $T_1$  state at 150 ps, transient absorption signals were observed at 2014 and 1902  $\text{cm}^{-1}$  in the region of  $\nu(\text{CO})$ , in addition to the bleaching of the  $S_0$  state (2020 and 1918  $\text{cm}^{-1}$ ). This indicates structural changes between the  $S_0$  and  $T_1$  states, including an increase in  $\pi$ -back donation in the  $T_1$  state. In the case of **Re<sub>2</sub>Pc**, the TRIR spectrum of the  $T_1$  state showed transient absorption (2017, 1926, and 1913  $\text{cm}^{-1}$ ) and bleaching (2023  $\text{cm}^{-1}$ ) of the  $S_0$  state, thus revealing a similar tendency as in **Re<sub>1</sub>Pc**. Therefore, the very short excited-state lifetimes and ultrafast ISC in **Re<sub>1</sub>Pc** and **Re<sub>2</sub>Pc** can be reasonably explained by their efficient SOC and large Franck-Condon factors, both originating from their distorted structures.

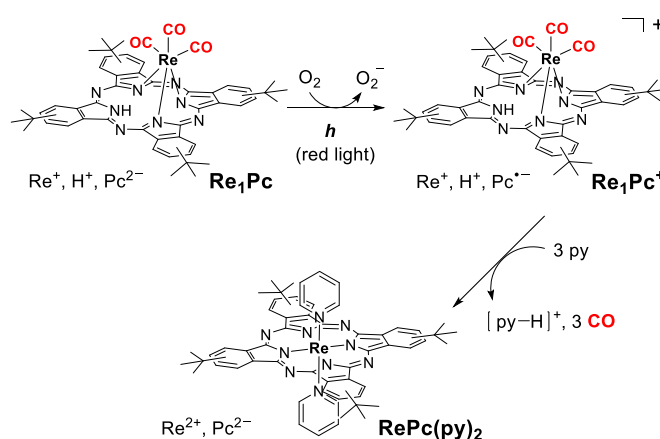


**Figure 5.** Singlet-singlet (black) and singlet–triplet absorption (red) spectra of (a) **Re<sub>1</sub>Pc** and (b) **Re<sub>2</sub>Pc**.



**Figure 6.** Summary of the excited-state properties of **Re<sub>1</sub>Pc** and **Re<sub>2</sub>Pc**.

**Mechanism of CO-release:** Three important parameters were identified for the photo-induced CO-release from **Re<sub>1</sub>Pc**: CW red light, molecular oxygen, and coordinative solvents, such as pyridine or acetonitrile. From this, a plausible photochemical reaction mechanism is proposed for **Re<sub>1</sub>Pc** (Scheme 1). After excitation with CW red light, the excited **Re<sub>1</sub>Pc** undergoes intersystem crossing and is oxidized in the presence of molecular oxygen.<sup>[39,40,57,58]</sup> Photo-induced electron transfer is considered to be initiated from the  $T_1$  state because of the very short  $S_1$  lifetime due to ultrafast ISC (see Table S4).<sup>[59]</sup> Next, the pyrrole undergoes deprotonation as the Pc ligand is oxidized from  $\text{Pc}^{2-}$  to  $\text{Pc}^{\cdot-}$ . Intramolecular electron transfer from Re to Pc decreases the electron density on Re, which weakens the  $\pi$ -back donation between the Re and CO moieties. Under these conditions, CO molecules are released, and a new bond between the Re and Pc ligand is formed. After releasing CO, two solvent molecules coordinate to the Re ion as axial ligands to form **RePc(py)<sub>2</sub>** as the final photoproduct when the reaction is conducted in pyridine.



**Scheme 1.** Mechanism of **Re<sub>1</sub>Pc** photoCORM behavior in pyridine.

## Conclusion

This study investigated the photochemical and photophysical properties of **Re<sub>1</sub>Pc** and **Re<sub>2</sub>Pc**, which revealed that **Re<sub>1</sub>Pc** can function as a photoCORM under CW red light irradiation. Thus, a novel, stable, CW red light-driven CORM was developed, which demonstrates CW red light-driven photoCORM behavior that is promising for applications in biological environments. The very short excited-state lifetimes of **Re<sub>1</sub>Pc** and **Re<sub>2</sub>Pc** were explained by the efficient SOC and large Franck-Condon factors caused by these complexes' distorted structures. A plausible photochemical reaction mechanism was proposed for **Re<sub>1</sub>Pc**, and therefore, this study provides key insights and a foundation for designing photoCORMs for biological or therapeutic applications.

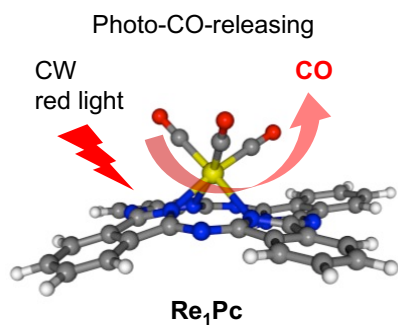
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**Keywords:** carbonyl ligands • CO-releasing molecule • continuous-wavelength red light • phthalocyanines • rhenium

- [1] H. Lin, J. J. McGrath, *Drug Chem. Toxicol.*, **1988**, *11*, 371–385.
- [2] R. Wang, L. Wu, Z. Wang, *Eur. J. Physiol.*, **1997**, *434*, 285–291.
- [3] *Carbon monoxide and Cardiovascular Functions*, (Ed.: R. Wang), CRC Press, New York, **2001**.
- [4] *Signal Transduction and the Gasotransmitters: NO, CO, and H<sub>2</sub>S in Biology and Medicine*, (Ed.: R. Wang), (Ed.): Humana Press, New Jersey, **2004**.
- [5] R. Motterlini, J. E. Clark, R. Foresti, P. Sarathchandra, B. E. Mann, C. J. Green, *Circ. Res.*, **2002**, *90*, e17–e24.
- [6] J. E. Clark, P. Naughton, S. Shurey, C. J. Green, T. R. Johnson, B. E. Mann, R. Foresti, R. Motterlini, *Circ. Res.*, **2003**, *93*, e2–e8.
- [7] J. H. Jaggari, A. Li, H. Parfenova, J. Liu, E. S. Umstot, A. M. Dopico, C. W. Leffler, *Circ. Res.*, **2005**, *97*, 805–812.
- [8] R. Motterlini, L. Otterbein, *Nat. Rev. Drug Discov.*, **2010**, *9*, 728–743.
- [9] C. C. Romão, W. A. Blättler, J. D. Seixas, G. J. Bernardes, *Chem. Soc. Rev.*, **2012**, *41*, 3571–3583.
- [10] R. Alberto, R. Motterlini, *Dalton Trans.*, **2007**, *17*, 1651–1660.
- [11] A. C. Kautz, P. C. Kunz, C. Janiak, *Dalton Trans.*, **2016**, *45*, 18045–18063.
- [12] U. Schatzschneider, *Br. J. Pharmacol.*, **2015**, *172*, 1638–1650.
- [13] J. Niesel, A. Pinto, H. W. P. N'Dongo, K. Merz, I. Ott, R. Gust, U. Schatzschneider, *Chem. Commun.*, **2008**, *15*, 1798–1800.
- [14] C. R. Child, S. Kealey, H. Jones, P. W. Miller, A. J. White, A. D. Gee, N. J. Long, *Dalton Trans.*, **2011**, *40*, 6210–6215.
- [15] H. Pfeiffer, A. Rojas, J. Niesel, U. Schatzschneider, *Dalton Trans.*, **2009**, *22*, 4292–4298.
- [16] U. Schatzschneider, *Inorg. Chim. Acta*, **2011**, *374*, 19–23.
- [17] U. Sachs, G. Schaper, D. Winkler, D. Kratzert, P. Kurz, *Dalton Trans.*, **2016**, *45*, 17464–17473.
- [18] H.-M. Berends, P. Kurz, *Inorg. Chim. Acta*, **2012**, *380*, 141–147.
- [19] N. E. Brueckmann, M. Wahl, G. J. Reiss, M. Kohns, W. Watjen, P. C. Kunz, *Eur. J. Inorg. Chem.*, **2011**, *29*, 4571–4577.
- [20] C. S. Jackson, S. Schmitt, Q. P. Dou, J. J. Kodanko, *Inorg. Chem.*, **2011**, *50*, 5336–5338.
- [21] P. C. Kunz, W. Huber, A. Rojas, U. Schatzschneider, B. Spingler, *Eur. J. Inorg. Chem.*, **2009**, *35*, 5358–5366.
- [22] R. D. Rimmer, H. Richter, P. C. Ford, *Inorg. Chem.*, **2010**, *49*, 1180–1185. Light oxidation
- [23] A. E. Pierri, A. Pallaoro, G. Wu, P. C. Ford, *J. Am. Chem. Soc.*, **2012**, *134*, 18197–18200.
- [24] I. Chakraborty, J. Jimenez, W. M. C. Sameera, M. Kato, P. K. Mascharak, *Inorg. Chem.*, **2017**, *56*, 2863–2873.
- [25] K. Koike, J. Tanabe, S. Toyama, H. Tsubaki, K. Sakamoto, J. R. Westwell, F. P. A. Johnson, H. Hori, H. Saitoh, O. Ishitani, *Inorg. Chem.*, **2000**, *39*, 2777–2783.
- [26] R. Kretschmer, G. Gessner, H. Görls, S. H. Heinemann, M. Westerhausen, *J. Inorg. Biochem.*, **2011**, *105*, 6–9.
- [27] R. D. Rimmer, A. E. Pierri, P. C. Ford, *Coord. Chem. Rev.*, **2012**, *256*, 1509–1519.
- [28] M. A. Wright, J. A. Wright, *Dalton Trans.*, **2016**, *45*, 6801–6811.
- [29] I. Chakraborty, S. J. Carrington, P. K. Mascharak, *ChemMedChem*, **2014**, *9*, 1266–1274.
- [30] E. Kottelat, A. Ruggi, F. Zobi, *Dalton Trans.*, **2016**, *45*, 6920–6927.
- [31] K. Ishii, S. Hoshino, N. Kobayashi, *Inorg. Chem.*, **2004**, *43*, 7969–7971.
- [32] I. Chakraborty, S. J. Carrington, P. K. Mascharak, *Acc. Chem. Res.*, **2014**, *47*, 2603–2611.
- [33] T. Slanina, P. Šebej, *Photochem. Photobiol. Sci.*, **2018**, *17*, 692–710.
- [34] E. Kottelat, Z. Fabio, *Inorganics*, **2017**, *5*, 24.
- [35] P. C. Ford, *Coord. Chem. Rev.*, **2018**, *376*, 548–564.
- [36] Z. Li, A. E. Pierri, P.-J. Huang, G. Wu, A. V. Iretskii, P. C. Ford, *Inorg. Chem.*, **2017**, *56*, 11, 6094–6104.
- [37] K. Ishii, *Chem. Lett.*, **2019**, *48*, 1452–1461.
- [38] K. Ishii, M. Shiine, Y. Shimizu, S. Hoshino, H. Abe, K. Sogawa, N. Kobayashi, *J. Phys. Chem. B*, **2008**, *112*, 3138–3143.
- [39] K. Murata, Y. Koike, K. Ishii, *Chem. Commun.*, **2020**, *56*, 13760–13763.
- [40] M. Wang, K. Murata, K. Ishii, *Chem. Eur. J.*, **2021**, *27*, 8994–9002.
- [41] C. F. van Nostrum, S. J. Picken, A.-J. Schouten, R. J. M. Nolte, *J. Am. Chem. Soc.*, **1995**, *117*, 9957–9965.
- [42] Z. Li, M. Lieberman, *Supramolecular Science*, **1998**, *5*, 485–489.
- [43] M. A. Filatov, S. Balushev, I. Z. Ilieva, V. Enkelmann, T. Miteva, K. Landfester, S. E. Aleshchenkov, A. V. Cheprakov, *J. Org. Chem.*, **2012**, *77*, 11119–11131.
- [44] Z. Li, M. Lieberman, *Supramolecular Science*, **1998**, *5*, 485–489.
- [45] Y. B. Platonova, A. N. Volov, L. G. Tomilova, *J. Catal.*, **2019**, *373*, 222–227.
- [46] R. Li, X. Zhang, P. Zhu, D. K. P. Ng, N. Kobayashi, J. Jiang, *Inorg. Chem.*, **2006**, *45*, 2327–2334.
- [47] Crystallization success was attributed to the symmetry of the Pc ligand and the length of the alkyl substituents. A Re<sub>2</sub>Pc bearing eight ethoxy substituents was also synthesized, but it was not sufficiently soluble in organic solvents. In the case of butoxy substituents, the solubility improved, although some disorder was introduced in the substituents.
- [48] M. Tsutsui, C. P. Hsung, D. Ostfeld, T. S. Srivastava, D. L. Cullen, E. F. Meyer Jr, *J. Am. Chem. Soc.*, **1975**, *97*, 3952–3965.
- [49] The importance of oxidation for CO-release was also confirmed by electrochemical oxidation reactions. Under an N<sub>2</sub> atmosphere and an applied potential in the range of 1.3–1.6 V for 2 h, CO was detected by GC. CO was considered to be released by removing an electron from the Re ion, which decreases the π-back donation.
- [50] The demetallation reaction of **Re<sub>2</sub>Pc** in pyridine was reported previously (ref 39). No spectral changes were observed in a solution containing a mononuclear Re(I) tetraazaporphyrin complex (**Re<sub>1</sub>TAP**; ref 40) in the presence of CW red light, molecular oxygen, and coordinative solvents (Figure S2b).
- [51] K. Ishii, Y. Kitagawa, in *Handbook of Porphyrin Science Vol. 32* (Eds.: K. M. Kadish, K. M. Smith, R. Guilard), World Scientific Pub Co. Inc., **2014**, Chap. 168.
- [52] K. Ishii, N. Kobayashi in *The Porphyrin Handbook Vol. 16* (Eds.: K. M. Kadish, R. M. Smith, R. Guilard), Academic Press, New York, **2003**, Chap. 102.
- [53] K. Murata, K. Ishii, *Eur. J. Inorg. Chem.*, **2017**, *44*, 5103–5107.
- [54] For **IrPcCl(py)** (D<sub>4h</sub> symmetry of a π-conjugated system), the HOMO and nearly degenerate LUMOs are a<sub>1u</sub> (π) and e<sub>g</sub> (π\*) (or e<sub>g</sub>x (π\*)) orbitals, respectively. In **Re<sub>1</sub>Pc** and **Re<sub>2</sub>Pc**, whose π-conjugated systems deviate significantly from D<sub>4h</sub> symmetry owing to structural distortion, the HOMO is predominantly a Pc-centered a<sub>1u</sub>-like π orbital (a<sub>1u</sub>'), while the LUMO and LUMO+1 correspond to the Pc-centered e<sub>g</sub>'- and e<sub>g</sub>x'-like π\* orbitals (e<sub>g</sub>' and e<sub>g</sub>x'), respectively.
- [55] S. Gentemann, C. J. Medforth, T. P. Forsyth, D. J. Nurco, K. M. Smith, J. Fajer, D. Holten, *J. Am. Chem. Soc.*, **1994**, *116*, 7363–7368.
- [56] S. Gentemann, S. H. Leung, K. M. Smith, J. Fajer, D. Holten, *J. Phys. Chem.*, **1995**, *99*, 4330–4334.
- [57] Based on its oxidation potential (+0.32 V vs. Fc/Fc<sup>+</sup>), **Re<sub>1</sub>Pc** in the ground state cannot be oxidized by O<sub>2</sub> or <sup>1</sup>O<sub>2</sub>. Thus, **Re<sub>1</sub>Pc** is considered to be oxidized in the excited-state.
- [58] Based on its oxidation potential (+0.74 V vs. Fc/Fc<sup>+</sup>), **Re<sub>1</sub>TAP** oxidation is more difficult than **Re<sub>1</sub>Pc** oxidation. Additionally, **Re<sub>1</sub>TAP** did not undergo photodecarbonylation under similar conditions. These results are consistent with the mechanism proposed herein.
- [59] Theoretical calculations were performed to investigate the oxidation of **Re<sub>1</sub>Pc** in the T<sub>1</sub> state with molecular oxygen. In pyridine, the ΔG<sup>0</sup> value was calculated to be +13.8 kcal/mol, and therefore, this oxidation reaction is considered to proceed.

## Entry for the Table of Contents



The  $[\text{Re}(\text{CO})_3]^+$  unit and phthalocyanine (Pc) ligand in **Re<sub>1</sub>Pc** enable it to function as a photo-induced CO-releasing molecule (photoCORM) under continuous-wavelength red light irradiation, thus providing insights for applicable in biological environments. The distorted structures generated from unsymmetric  $[\text{Re}(\text{CO})_3]^+$  coordination result in very short excited-state lifetimes and ultrafast intersystem crossing.