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Supporting Information

## Photocatalytic CO<sub>2</sub> Reductions Catalyzed by *meso*-(1,10-Phenanthroline-2-yl)-Porphyrins Having a Rhenium(I) Tricarbonyl Complex

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## Experimental section

**General procedure.** All chemicals and solvents were of commercial reagent quality and were used without further purification unless otherwise stated. The chloroform used contained 0.3–1% ethanol as a stabilizer. Zinc(II) tetraphenylporphyrin (ZnTPP) was prepared from tetraphenylporphyrin and zinc acetate by the method of Adler and coworkers,<sup>S1</sup> *fac*-Re(phen)(CO)<sub>3</sub>Br (phen = 1,10-phenanthroline)<sup>S2</sup>, and 1,3-dimethyl-2-phenyl-2,3-dihydro-1*H*-benzo[d]imidazole (BIH)<sup>S3</sup> were prepared according to the literatures. **H<sub>2</sub>P-phen**, **ZnP-phen** and **ZnP-phen=Re** were synthesized according to our previous report.<sup>S4</sup> *N,N*-Dimethylacetamide (DMA) was dried over molecular sieves of size 4 Å and distilled under reduced pressure. The silica-gels utilized for column chromatography were purchased from Kanto Chemical Co. Inc.: Silica-Gel 60N (Spherical, Neutral) 63–210 μm and 40–50 μm (Flash). The alumina used for column chromatography were purchased from Merck (aluminum oxide 90 standardized). <sup>1</sup>H and <sup>13</sup>C NMR, distortionless enhancement by polarization transfer 135 (DEPT 135), <sup>1</sup>H-<sup>1</sup>H correlation spectroscopy (COSY) spectra were recorded by using JEOL JNM-ECS-500. Chemical shifts were recorded in parts per million (ppm) relative to tetramethylsilane. UV-vis absorption spectra were collected using a square cell (path length = 1.0 cm) on JASCO V-650 spectrometer. Steady-state emission spectra were collected on Hitachi F-4500 spectrometer and corrected for the response of the detector system. The fluorescence intensities were normalized at the absorption of the excitation wavelength. Cyclic voltammogram (CV) and differential pulse voltammogram (DPV) were measured using ALS-H/CHI Model 612E electrochemical analyzer in a micro-cell equipped with a glassy carbon working electrode ( $\phi$  1.6 mm) and a Pt counter-electrode. The micro-cell was connected *via* a Luggin capillary with a reference electrode of Ag/AgNO<sub>3</sub> (10 mM in DMA). Tetrabutylammonium hexafluorophosphate (<sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub>) recrystallized from ethyl acetate was used as the supporting electrolyte. Ferrocene was used as an external standard, and all potentials are referenced to the ferrocene/ferrocenium couple ( $E_{1/2} = -0.097$  vs. Ag/AgNO<sub>3</sub>). FTIR spectra were recorded in KBr using JASCO FT/IR-4600. Elemental analyses were carried out with Perkin-Elmer 2400II CHNS/O analyzer. UV-vis spectral changes during irradiation were obtained using an Asahi Spectra PRA-201 apparatus equipped with a Xe lamp (Asahi Spectra, MAX-350).

**Synthesis of H<sub>2</sub>P-phen=Re.** In a 20 mL flask were placed **H<sub>2</sub>P-phen** (25 mg,  $2.9 \times 10^{-5}$  mol, 1 equiv),<sup>S4</sup> Re(CO)<sub>5</sub>Br (12 mg,  $2.9 \times 10^{-5}$  mol, 1 equiv), toluene (5.0 mL), and the mixture was heated to reflux for overnight under Ar atmosphere. The solvent was evaporated and the solid was recrystallized from CHCl<sub>3</sub>/ethanol/hexane, giving the titled compound as purple fine-needle

crystals (20 mg, 57%). TLC (silica gel, CHCl<sub>3</sub>:methanol = 10:1)  $R_f = 0.9$ ; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 9.32 (d,  $J = 5$  Hz, 1H, phen 9), 8.97 (d,  $J = 5$  Hz, 1H,  $\beta$ -pyrrole), 8.84–8.88 (m, 6H,  $\beta$ -pyrrole), 8.49 (d,  $J = 8$  Hz, 1H, phen 3), 8.38 (d,  $J = 8$  Hz, 1H, phen 7), 8.31 (d,  $J = 8$  Hz, 1H, phen 4), 8.25 (d,  $J = 8$  Hz, 1H, Ph(ortho)), 8.20 (d,  $J = 8$  Hz, 1H, Ph(ortho)), 8.18 (d, 1H,  $J = 5$  Hz, 1H,  $\beta$ -pyrrole), 8.14 (d,  $J = 8$  Hz, 1H, Ph(ortho)), 8.08 (d,  $J = 8$  Hz, 1H, Ph(ortho)), 8.05 (d,  $J = 8$  Hz, 1H, Ph(ortho)), 8.01 (d,  $J = 8$  Hz, 1H, Ph(ortho)), 7.92 (d,  $J = 8$  Hz, 1H, phen 6), 7.89 (d,  $J = 8$  Hz, 1H, phen 5), 7.68–7.76 (m, 7H, Ph(meta) and phen 8), 1.58 (s, 9H, *tert*-butyl), 1.57 (s, 9H, *tert*-butyl), 1.56 (s, 9H, *tert*-butyl), –2.49 (s, 2H, *N*-H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 197.15 (CO), 191.24 (CO), 188.72 (CO), 165.41 (C), 152.94 (CH), 150.64 (C), 150.56 (C), 150.51 (C), 148.39 (C), 146.20 (C), 139.13 (C), 138.81 (C), 138.69 (C), 137.69 (CH), 134.72 (CH), 134.66 (CH), 134.51 (CH), 134.43 (CH), 131.77 (C), 130.49 (CH), 127.77 (CH), 127.65 (CH), 125.42 (CH), 123.89 (CH), 123.85 (CH), 123.63 (CH), 123.51 (CH), 123.43 (CH), 122.23 (C), 121.45 (C), 121.27 (C), 115.76 (C), 34.89 (*tert*-butyl, C), 34.87 (*tert*-butyl, C), 31.67 (*tert*-butyl, CH<sub>3</sub>); FT-IR (KBr)  $\nu_{CO} = 1897, 1925, 2022$  cm<sup>–1</sup>; UV-vis absorption (DMA)  $\lambda_{max}/nm$  (log  $\epsilon$ ) = 427 (5.43), 520 (4.32), 556 (3.99), 594 (3.81), 651 (3.64). Anal. Calcd (%) for C<sub>65</sub>H<sub>56</sub>BrN<sub>6</sub>O<sub>3</sub>Re: C, 63.20; N, 6.80; H, 4.57. Found (%): C, 63.14; N, 6.84; H, 4.25.

**Energy levels of charge-separated states in ZnP-phen=Re and H<sub>2</sub>P-phen=Re.** From the electrochemical data, the energy levels of the charge-separated states in **ZnP-phen=Re** and **H<sub>2</sub>P-phen=Re** were calculated using the following equation (S1):<sup>S5</sup>

$$E_{CS} = e[E^0(D^+/D) - E^0(A/A^-)] - \frac{e^2}{4\pi\epsilon_0\epsilon_s} \frac{1}{R_{DA}} - \frac{e^2}{4\pi\epsilon_0} \left[ \left( \frac{1}{2r_{D^+}} + \frac{1}{2r_{A^-}} \right) \left( \frac{1}{\epsilon_{ref}} - \frac{1}{\epsilon_s} \right) \right] \quad (S1)$$

where  $e$  is the elementary charge,  $E^0(D^+/D)$  and  $E^0(A/A^-)$  are the first oxidation and reduction potentials for the electron donor and acceptor, respectively, measured in a solvent with  $\epsilon_{ref}$  (DMA: 38.3),  $r_{D^+}$  and  $r_{A^-}$  are the radii of the electron donor and electron acceptor,  $R_{DA}$  is the center-to-center donor–acceptor distance, respectively.

**Quenching experiments.** The Stern-Volmer relationship (equation (S2)) was obtained by the plots of the relative emission peak area ( $\Phi_0/\Phi$ ) versus the concentration of BIH:

$$\Phi_0/\Phi = 1 + K_{SV} [BIH] = 1 + k_q \tau [BIH] \quad (S2)$$

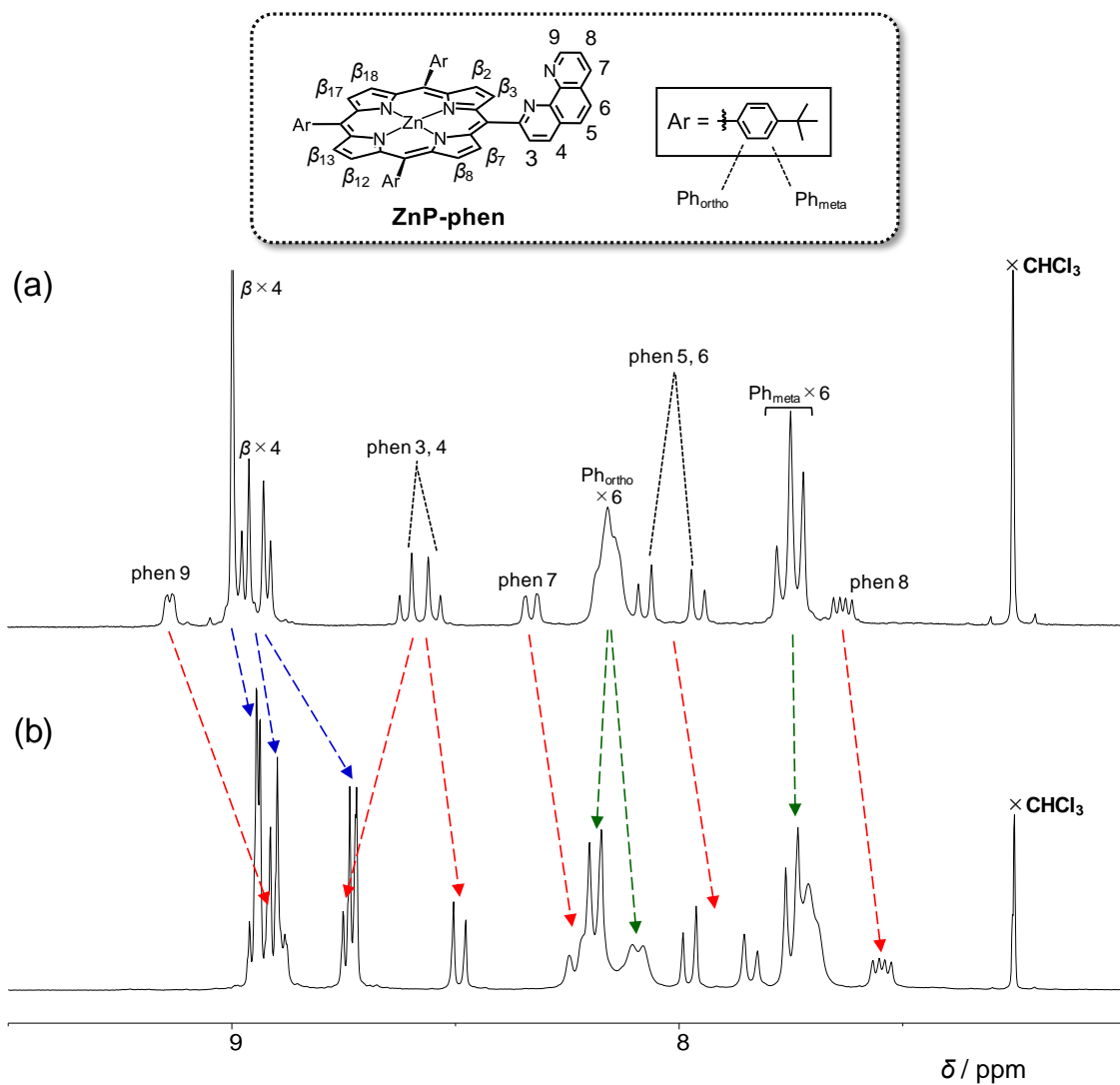
where  $\Phi_0$  and  $\Phi$  represent the emission peak area in the absence and presence of BIH, respectively, and  $K_{SV}$ ,  $k_q$ ,  $\tau$  are the Stern-Volmer constant, the quenching rate constant, and the emission lifetime, respectively. The Ar-saturated DMA solutions containing the porphyrins in square quartz cells ( $l = 1.0$  cm) were bubbled with Ar gas and the emission spectra of each samples were measured.

**Photocatalytic CO<sub>2</sub> reduction** In glass tubes (8.0 mL, i.d. = 10 mm), 1.0 mL of CO<sub>2</sub>-saturated DMA solutions containing BIH was added by 1.0 mL of Ar-saturated DMA solutions containing a mixture of ZnTPP and *fac*-Re(phen)(CO)<sub>3</sub>Br or the dyad (**ZnP-phen=Re** or **H<sub>2</sub>P-phen=Re**), and the reaction solutions were bubbled with CO<sub>2</sub> gas for 20 min. In the experiment adding proton sources, less than 1.0 mL of CO<sub>2</sub>-saturated DMA solutions containing BIH was added by 1.0 mL of Ar-saturated DMA solutions containing the dyad, and the reaction solutions were bubbled with CO<sub>2</sub> gas for 20 min. After the bubbling, the proton source was added so that the total amount of the solution was 2.0 mL, and then the CO<sub>2</sub>-bubbling was performed for a few minutes. Otherwise, 1.9 mL of Ar-saturated DMA solutions containing a mixture of ZnTPP and *fac*-Re(phen)(CO)<sub>3</sub>Br or the dyad (**ZnP-phen=Re** or **H<sub>2</sub>P-phen=Re**) were bubbled with CO<sub>2</sub> gas for 20 min, and then 0.1 mL of TEA was added to each of the solutions and the reaction solutions were bubbled with CO<sub>2</sub> gas for 30 sec. Photo-irradiations were carried out using a merry-go-round irradiation apparatus (Iris-MG, Cell Systems) equipped with LED lamps at  $\lambda = 419.7$  nm (30 mW, FWHM = 18.4 nm) and 447.7 nm (40 mW, FWHM = 17.2 nm). Reaction quantum yield was determined with an Asahi Spectra PRA-201 apparatus equipped with a Xe lamp (Asahi Spectra, MAX-350) and calculated according to equation (S3):

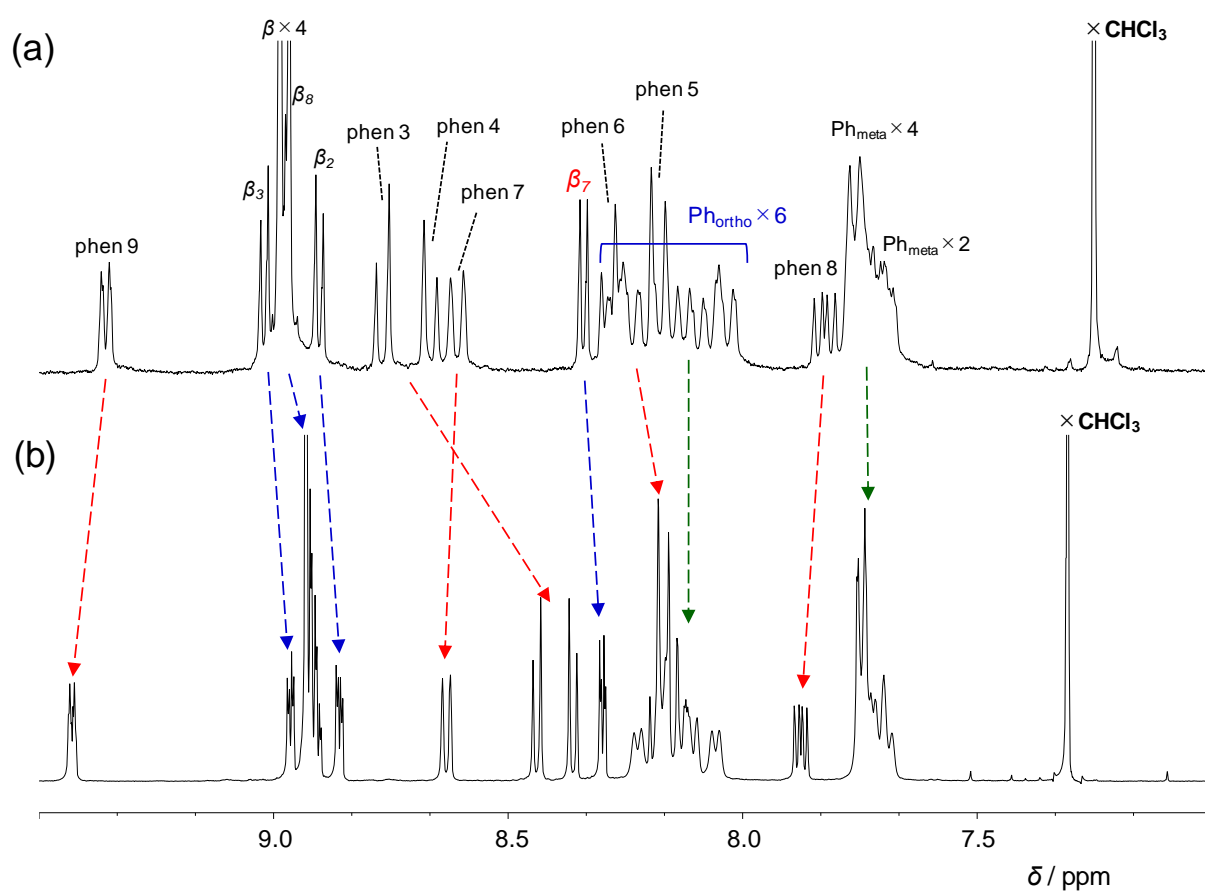
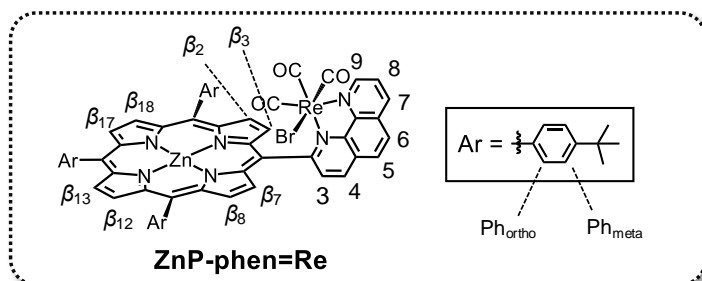
$$\Phi = \frac{[CO]}{[incident\ photons]} \quad (S3)$$

The solutions in 7 mL quartz cubic cells (optical path length: 1.0 cm) were irradiated with light at 420 nm using a bandpass filter. The gaseous reaction products (CO and H<sub>2</sub>) were quantified with a gas chromatography system (GC-2014, Shimadzu Science) equipped with a Shincarbon column (i.d. 3.0 mm×3.0 m) and a thermal conductivity detector (TCD). The product (formate) in the solutions was analyzed with a capillary electrophoresis system (Otuka Electronics Co. CAPI-3300I).

**Computational Methods.** DFT calculations were carried out using the Gaussian 09 package of programs.<sup>S6</sup> Each structure was fully optimized using the B3LYP functional using the 6-31G(d) basis set for all atoms except Re and the standard double- $\zeta$  type LANL2DZ basis set with the effective core potential of Hay–Wadt for Re. The calculation was carried out by using the polarizable continuum model (PCM) with a default parameter for *N,N*-dimethylacetamide. The stationary points were verified using the vibrational analysis.



**Figure S1.**  $^1\text{H}$  NMR spectra of **ZnP-phen** in (a)  $\text{CDCl}_3$  (300 MHz) and (b)  $\text{CDCl}_3$  + a drop of  $\text{CD}_3\text{OD}$  (300 MHz).



**Figure S2.**  $^1\text{H}$  NMR spectra of **ZnP-phen=Re** in (a)  $\text{CDCl}_3$  (300 MHz) and (b)  $\text{CDCl}_3$  + a few drops of  $\text{CD}_3\text{OD}$  (500 MHz).

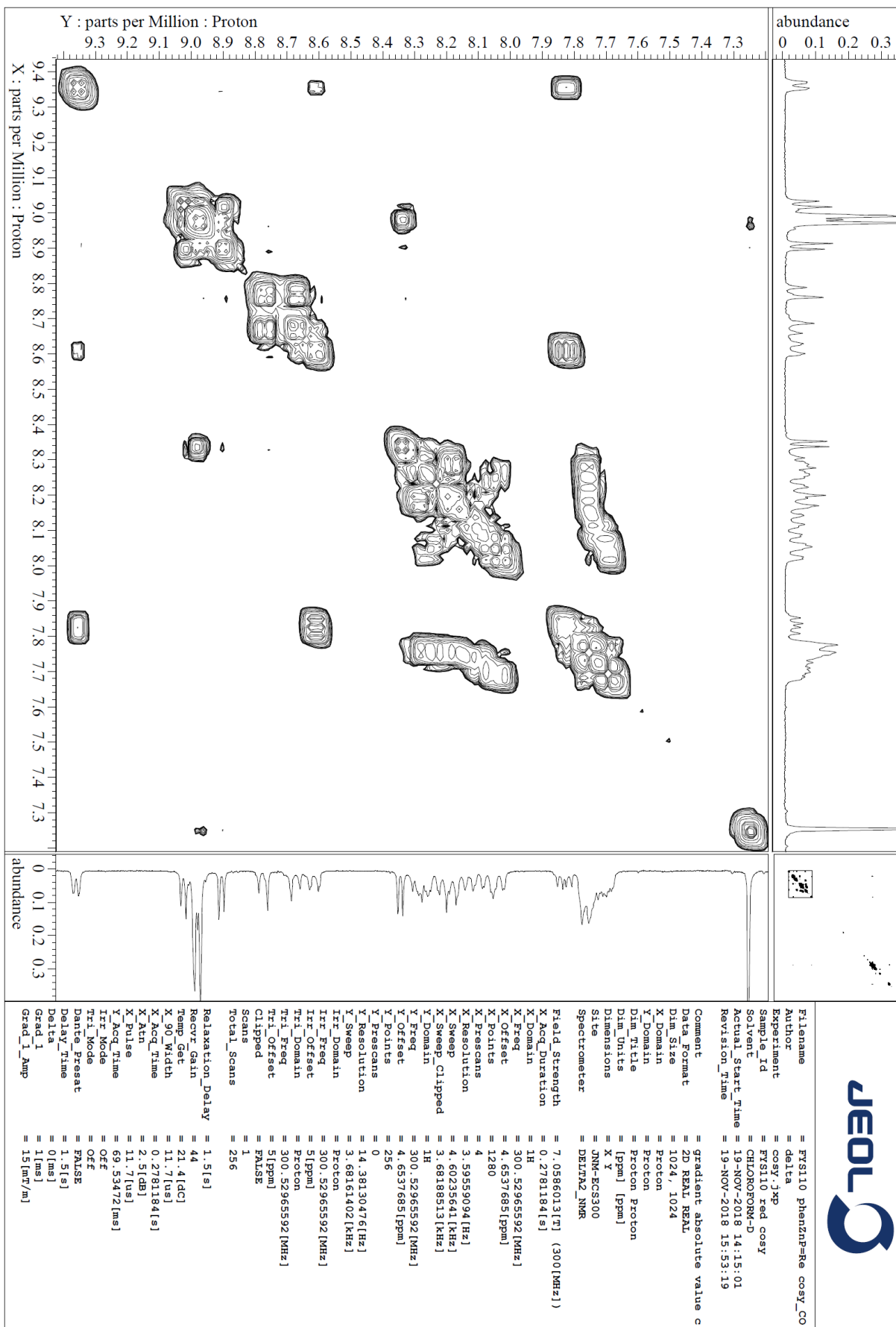
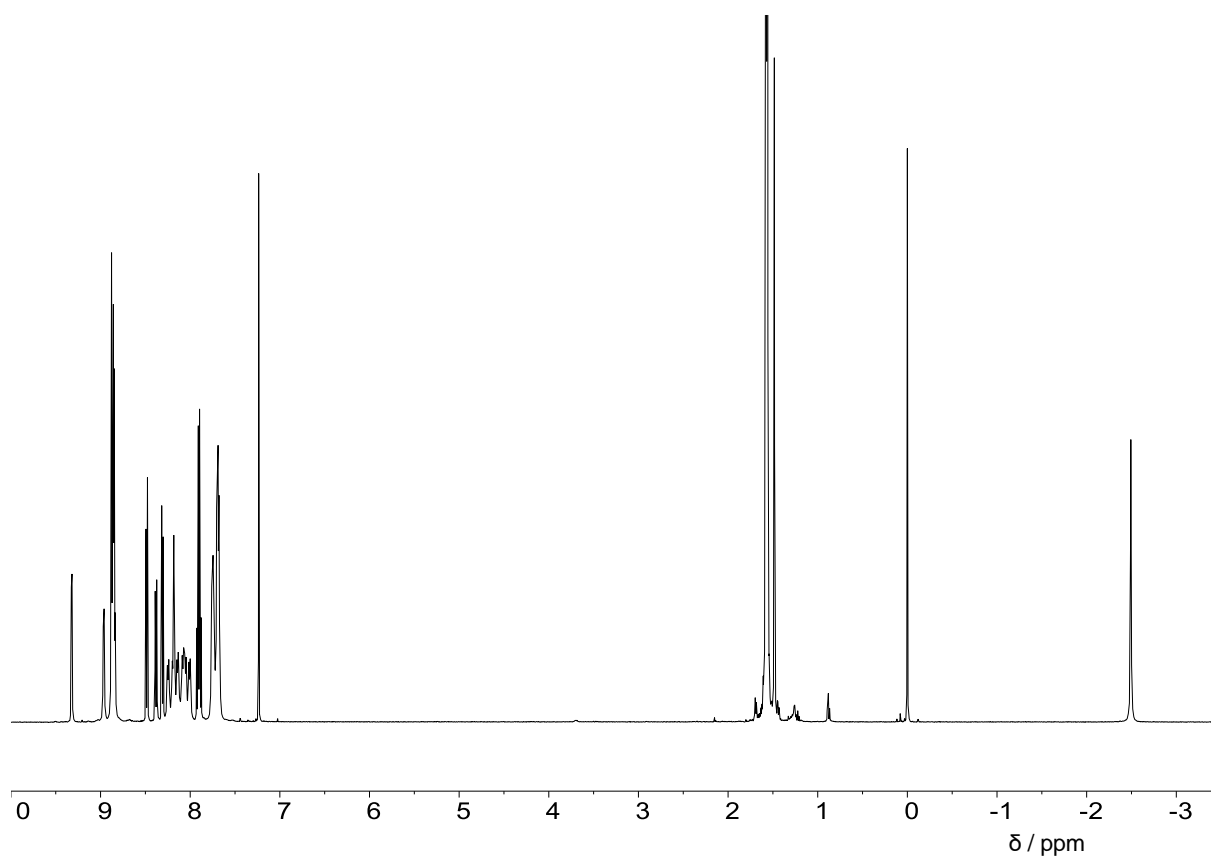
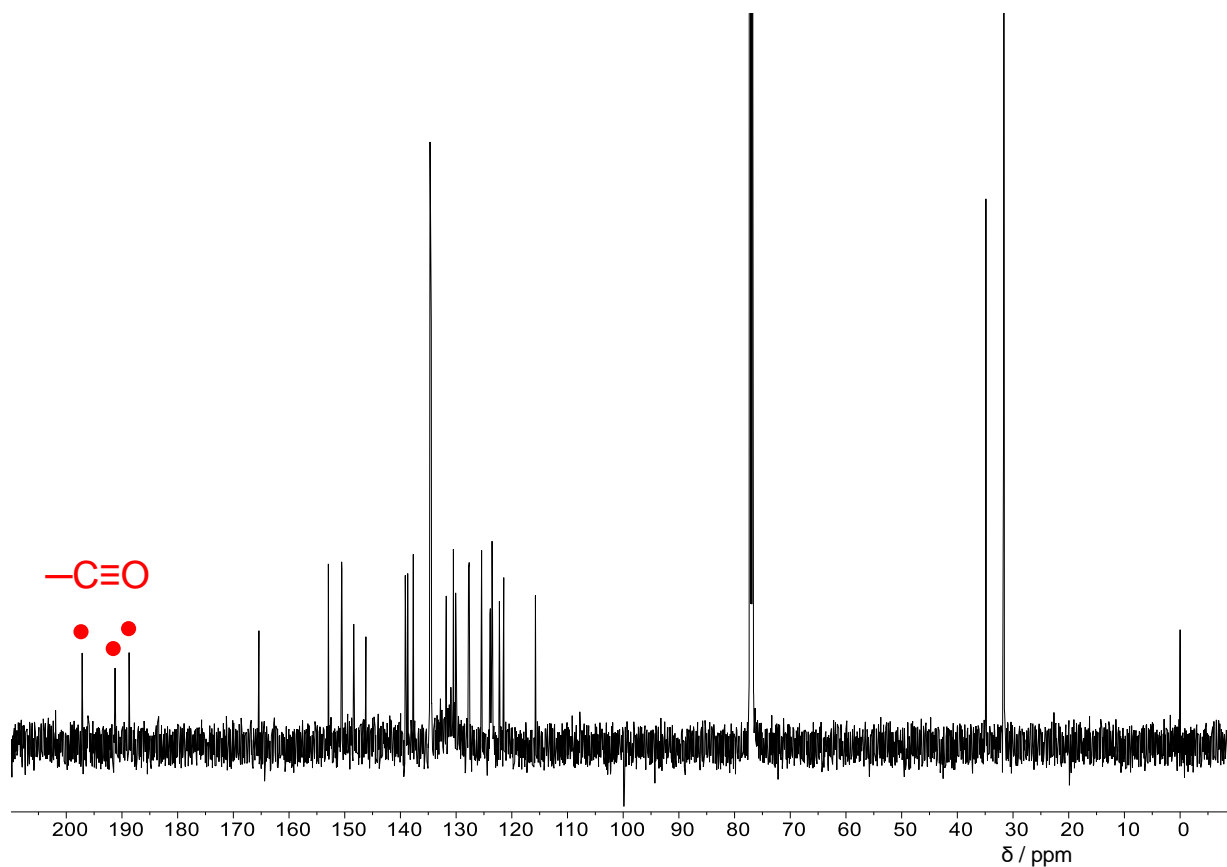


Figure S3.  $^1\text{H}$ - $^1\text{H}$  COSY ( $\text{CDCl}_3$ , 500 MHz) of ZnP-phen=Re.

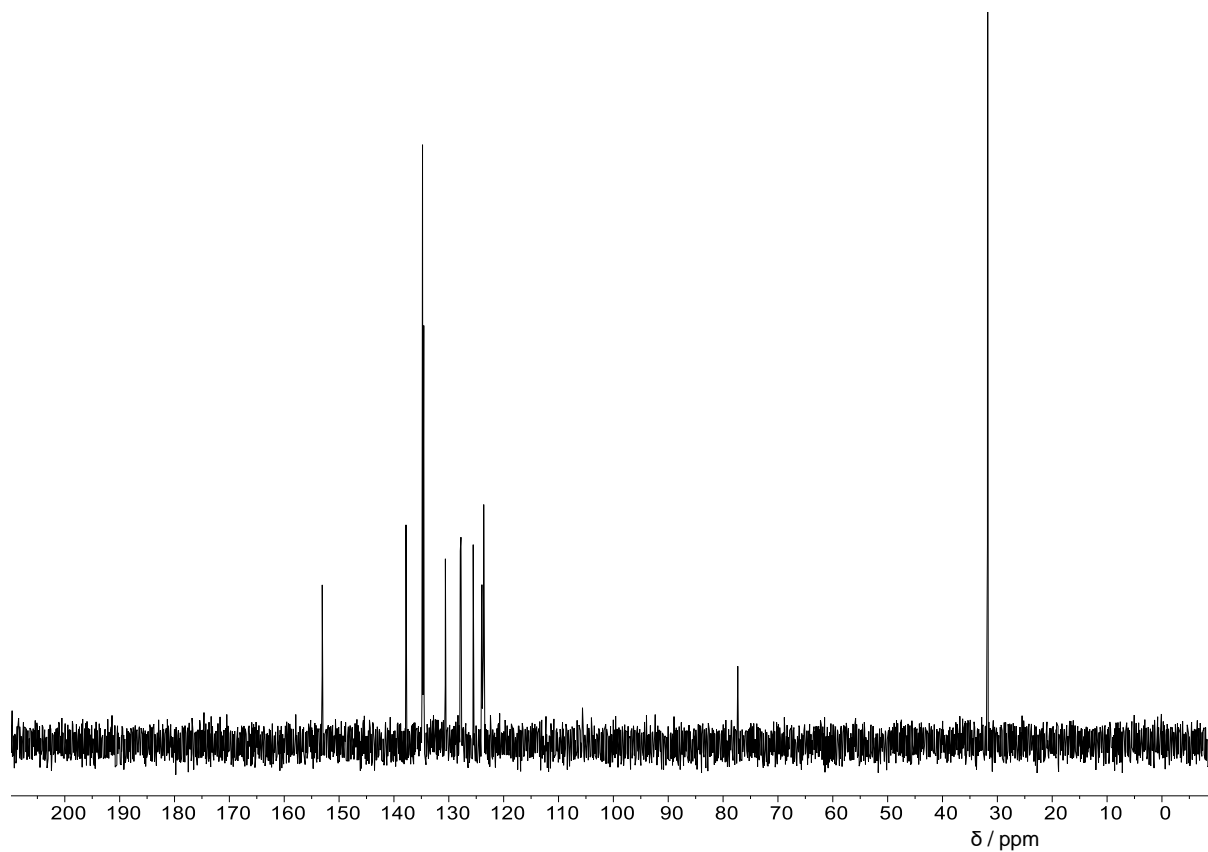


**Figure S4.**  $^1\text{H}$  NMR spectrum of  $\text{H}_2\text{P-phen=Re}$  in  $\text{CDCl}_3$  (500 MHz).

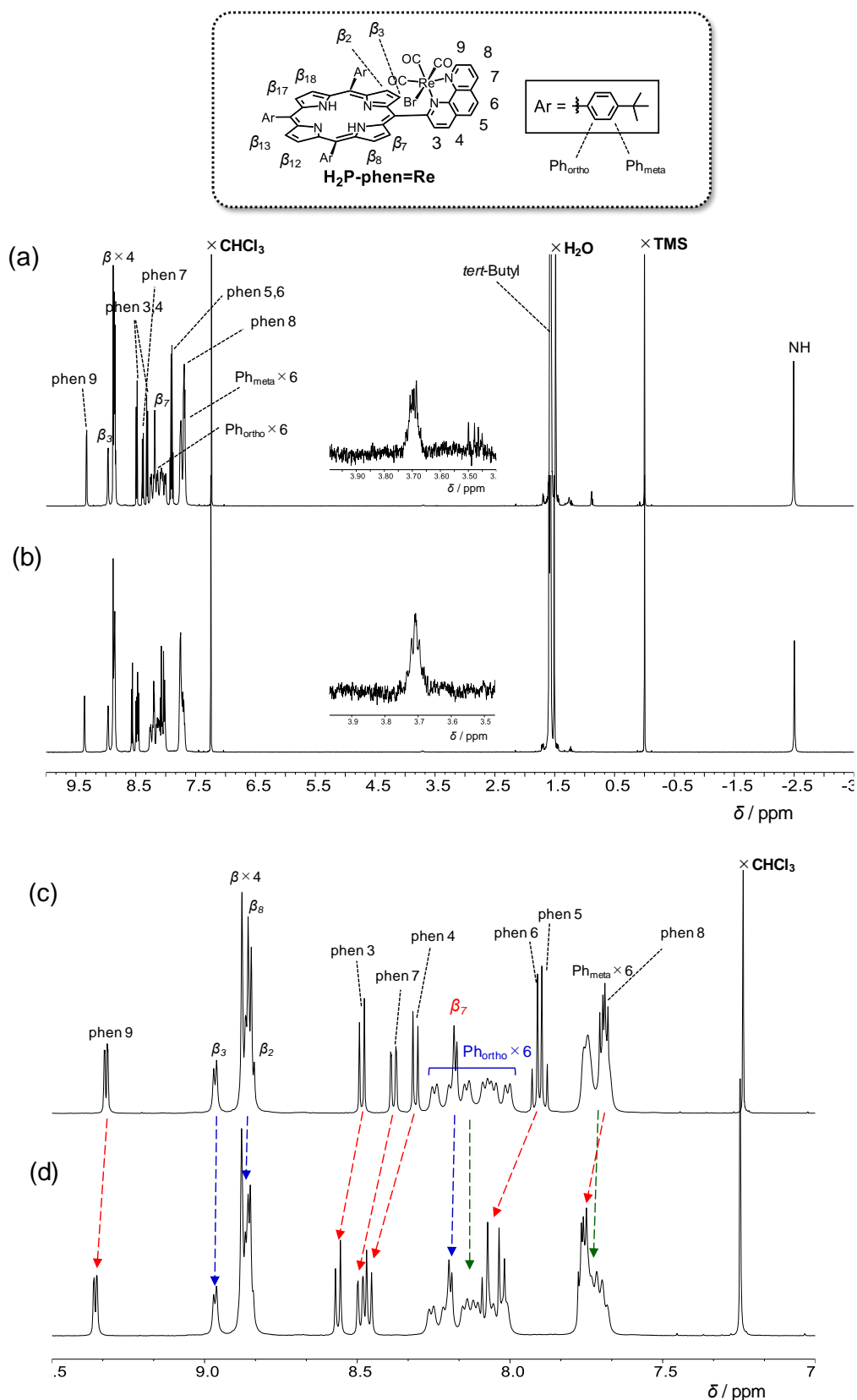




**Figure S5.**  $^{13}\text{C}$  NMR spectrum ( $\text{CDCl}_3$ , 125 MHz) of  $\text{H}_2\text{P-phen=Re}$  used in Figure S4.



**Figure S6.** Distortionless enhancement by polarization transfer (DEPT)135 spectrum ( $\text{CDCl}_3$ , 125 MHz) of  $\text{H}_2\text{P-phen=Re}$  used in Figure S4.



**Figure S7.**  $^1\text{H}$  NMR spectra of two different batch samples of  $\text{H}_2\text{P-phen=Re}$  in  $\text{CDCl}_3$  (500 MHz). The spectra of (a) and (c) correspond to Figure S4, and the spectra of (b) and (d) were obtained with a different batch sample. Judging from the peak integrations at 3.7 ppm, the amounts of free ethanol included in the samples of (a) and (b) are estimated to be 0.5 and 3 mol% of  $\text{H}_2\text{P-phen=Re}$ , respectively.

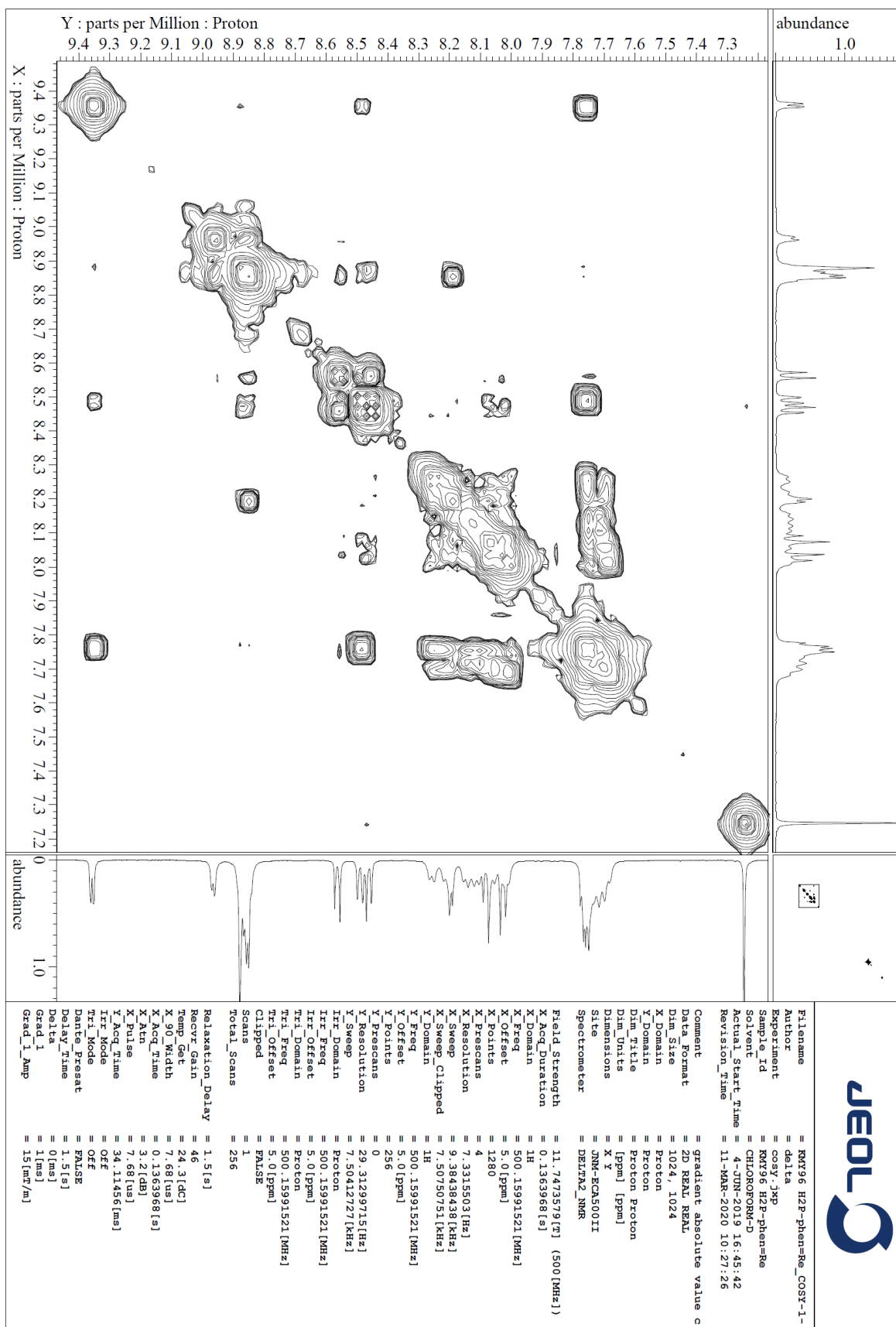
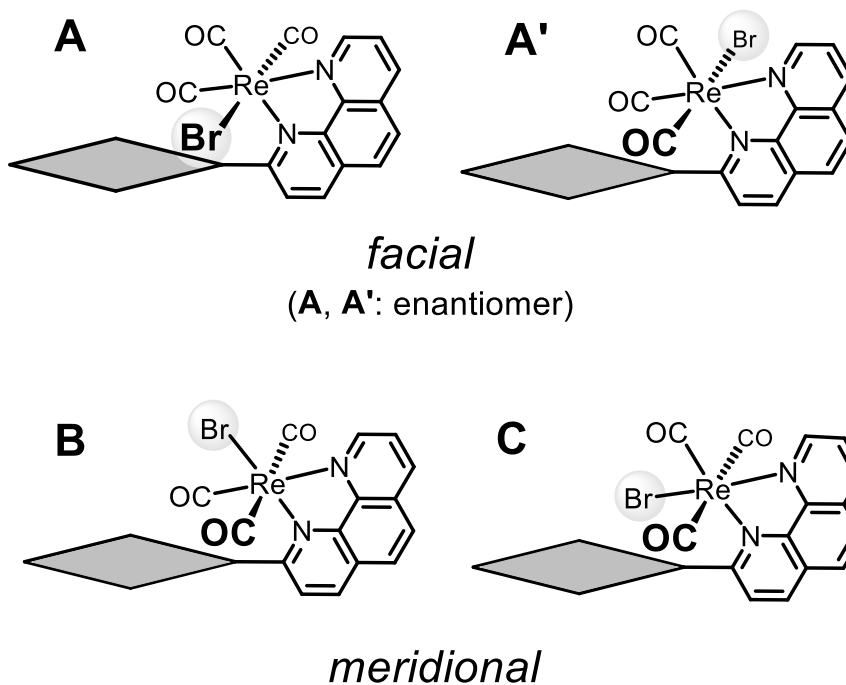
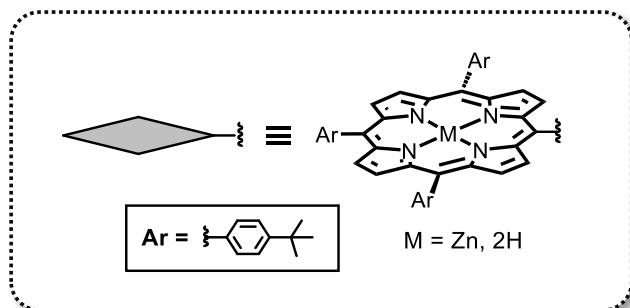
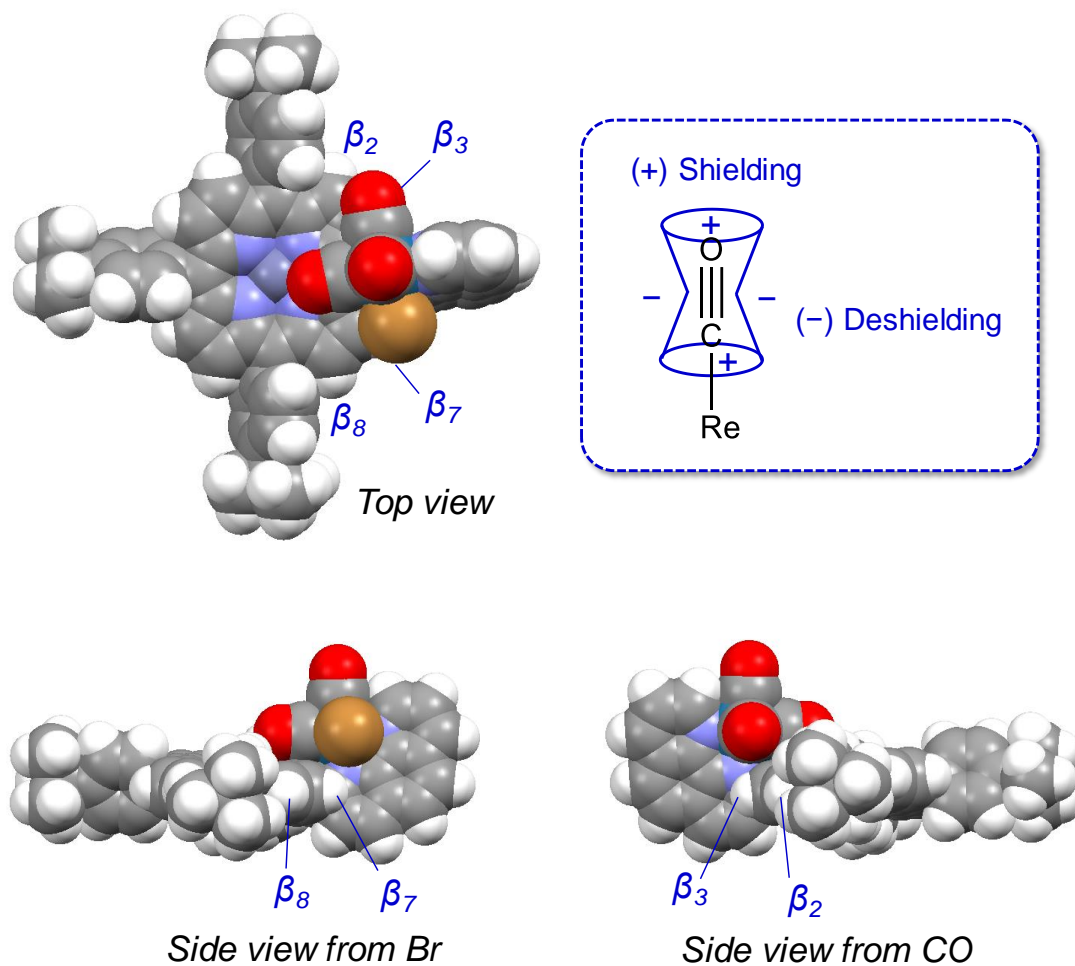


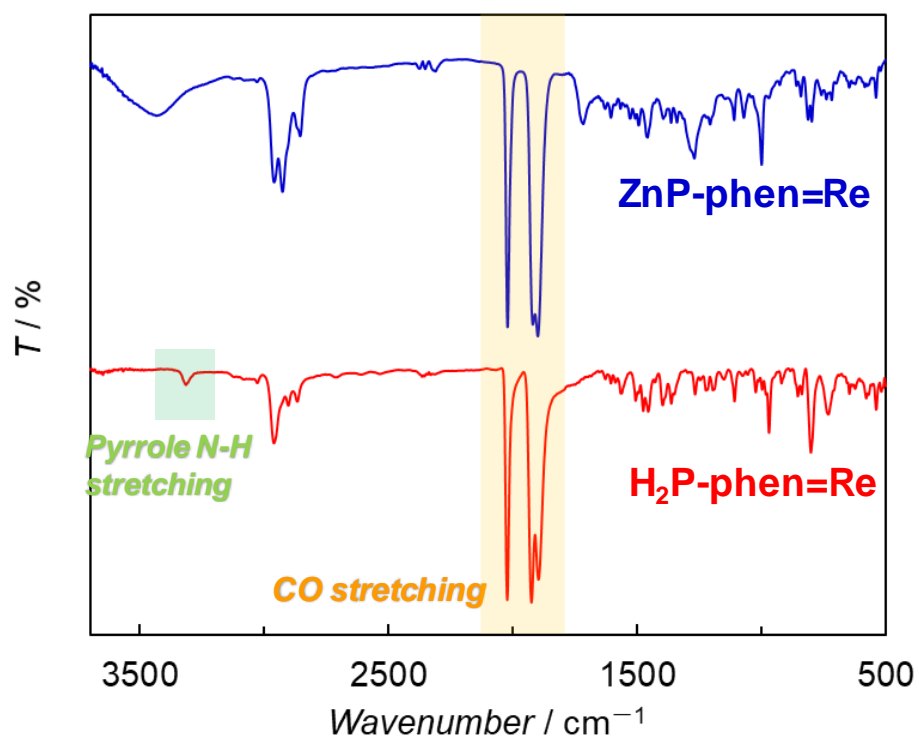
Figure S8.  $^1\text{H}$ - $^1\text{H}$  COSY (CDCl<sub>3</sub>, 500 MHz) of H<sub>2</sub>P-phen=Re used in Figure S7b and S7d.



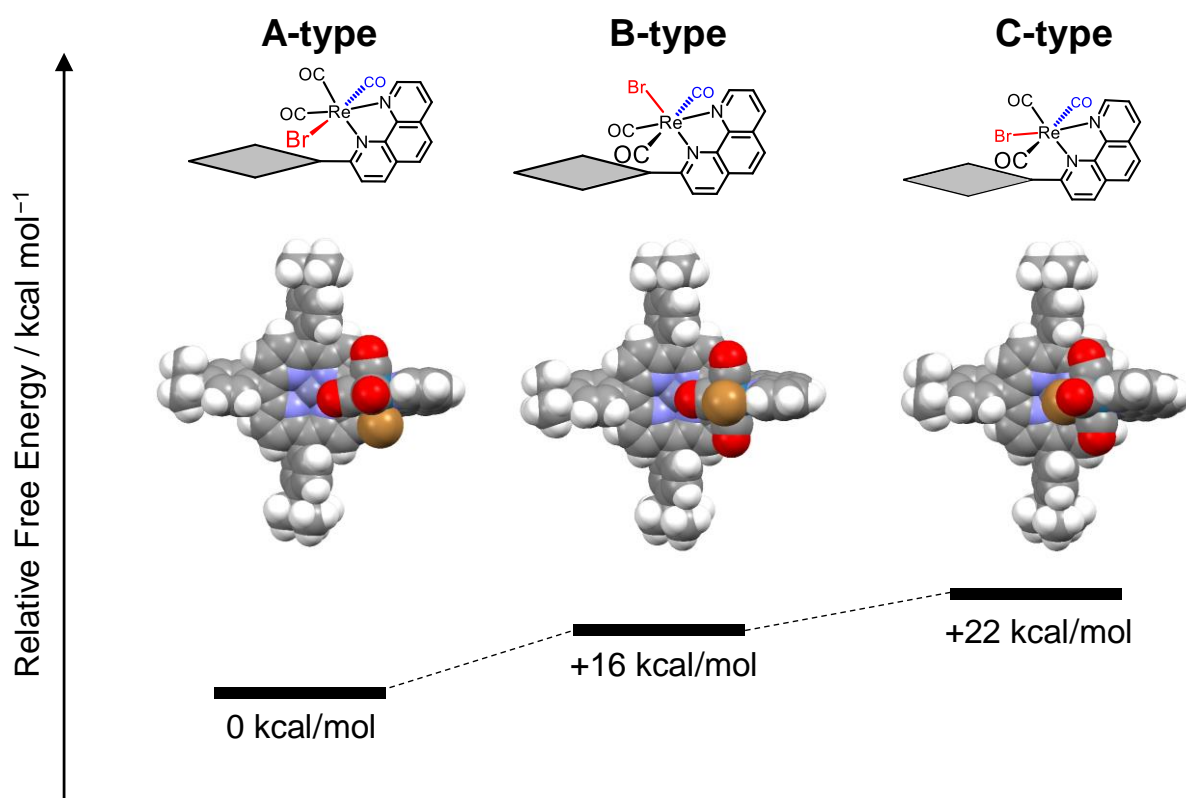
**Figure S9.** Possible stereoisomers of the dyads. The gray-colored squares indicate the porphyrins. **A** and **A'** are enantiomers of each other.



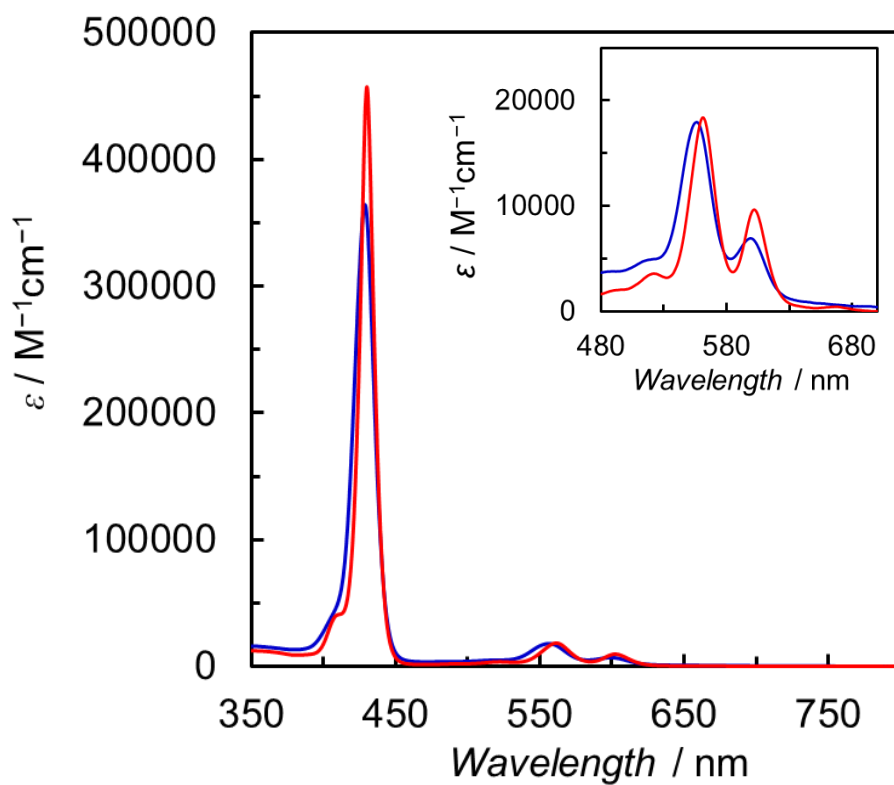
**Figure S10.** Molecular models (top and side views) of **ZnP-phen=Re** optimized by a DFT calculation using the B3LYP/LANL2DZ/6-31G(d) level, and schematic diagram of a shielding cone for the carbonyl group.



**Figure S11.** IR spectra of **ZnP-phen=Re** and **H<sub>2</sub>P-phen=Re** in KBr pellet. The peaks at 1900–2020  $\text{cm}^{-1}$  correspond to the CO stretching signals on the Re parts. The peak at 3310  $\text{cm}^{-1}$  in **H<sub>2</sub>P-phen=Re** corresponds to the NH stretching signal on the porphyrin part.<sup>S7</sup>

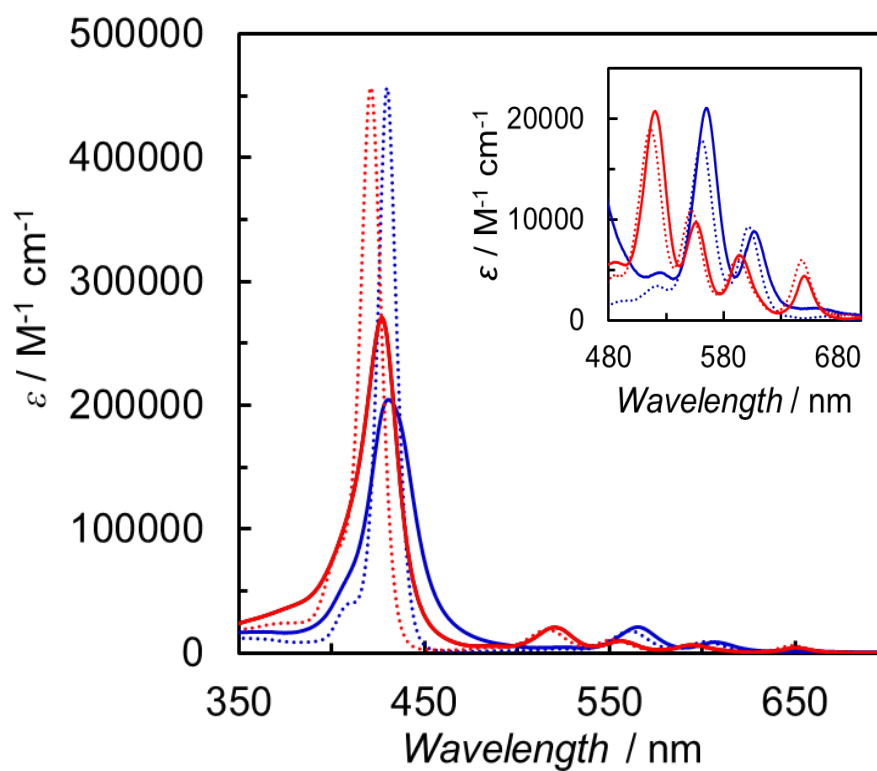


**Figure S12.** Gibbs free energy profile of the stereoisomers of  $\text{ZnP-phen=Re}$ . The structures were optimized at the B3LYP/LANL2DZ/6-31G(d) level.

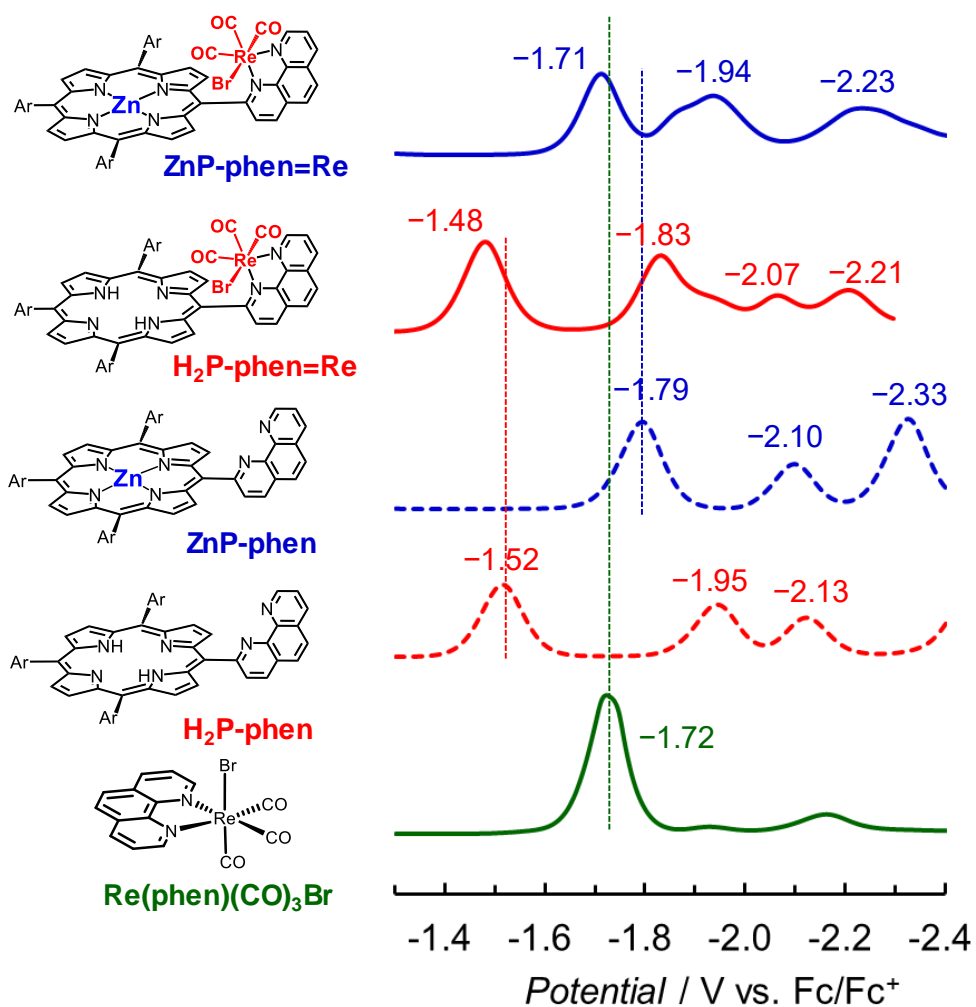


**Figure S13.** UV-vis absorption spectra of **ZnP-phen** in CHCl<sub>3</sub> (blue line) and DMA (red line). The inset shows the magnification of the Q-band region.

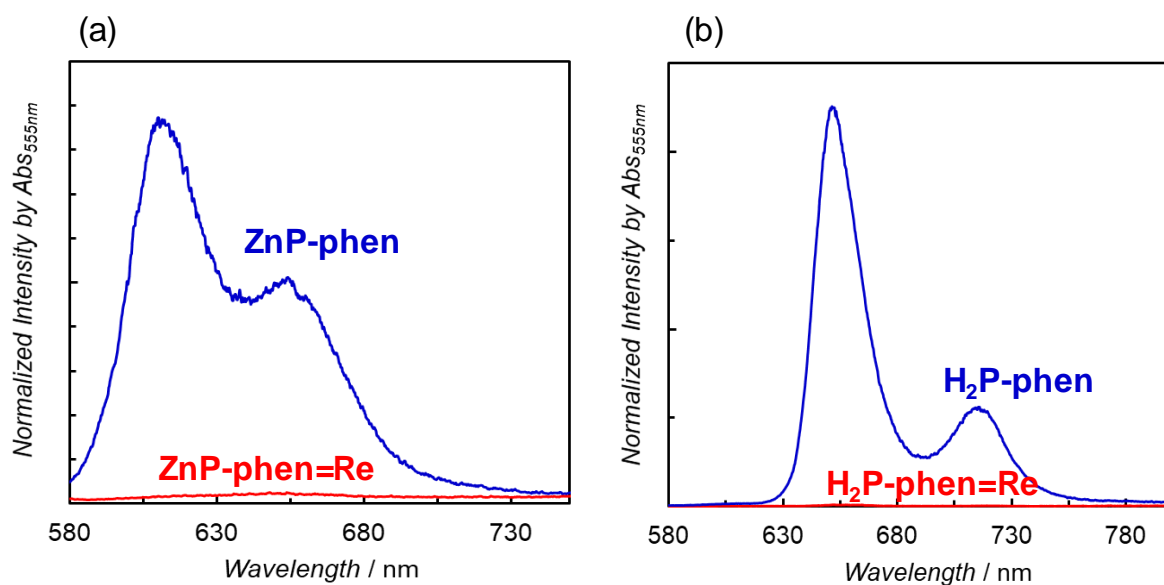




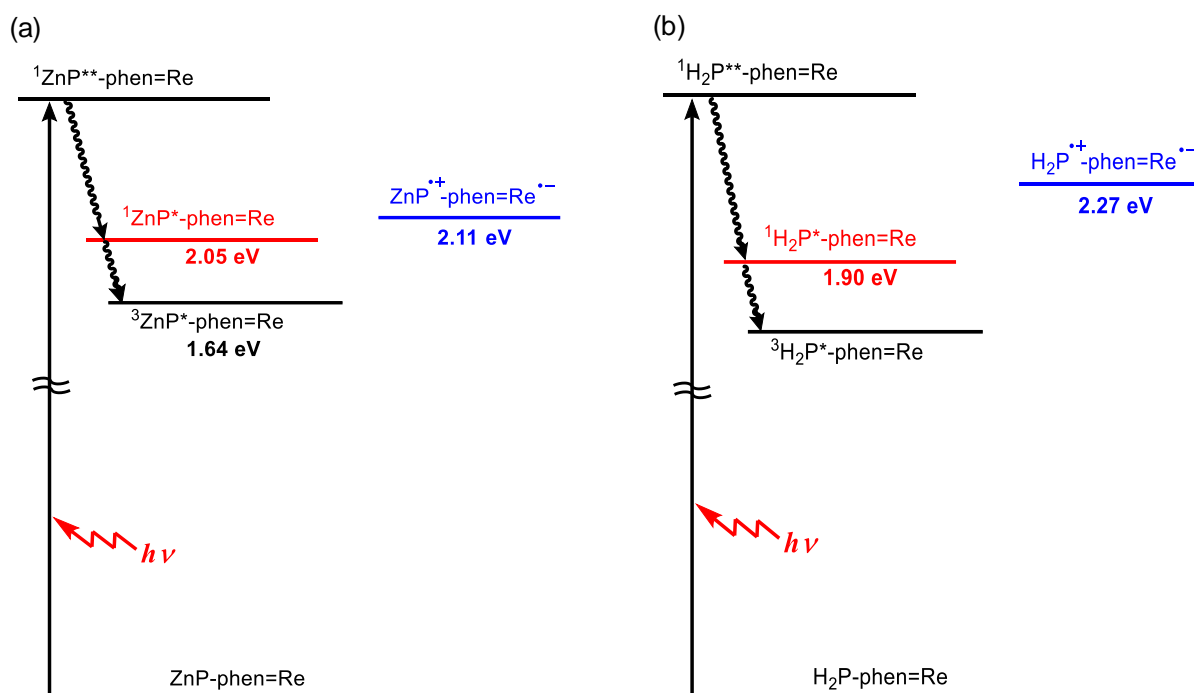
**Figure S14.** UV-vis absorption spectra of **H<sub>2</sub>P-phen** (red dotted line), **ZnP-phen** (blue dotted line), **H<sub>2</sub>P-phen=Re** (red solid line) and **ZnP-phen=Re** (blue solid line) in DMA. The inset shows the magnification of the Q-band region.



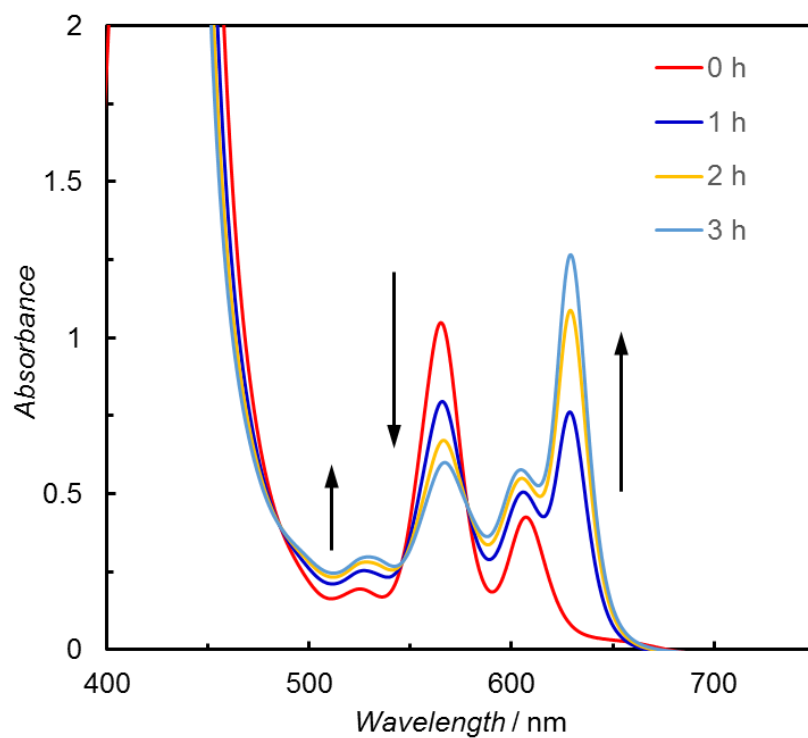
**Figure S15.** DPVs of the dyads, the porphyrins and *fac*-Re(phen)(CO)<sub>3</sub>Br (0.5 mM) in Ar-saturated DMA with 0.1 M <sup>n</sup>Bu<sub>4</sub>NPF<sub>6</sub> as a supporting electrolyte.



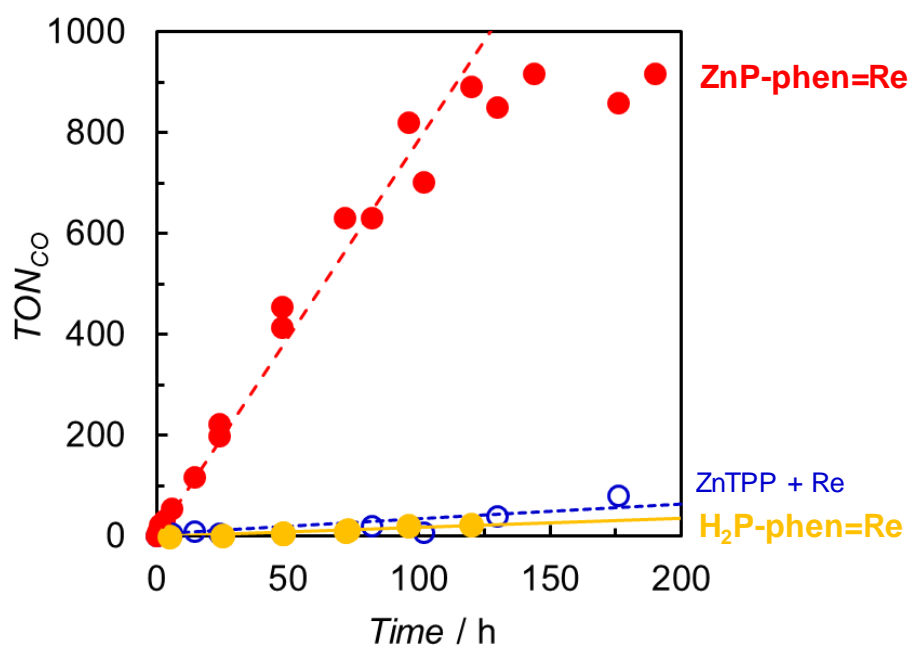
**Figure S16.** Fluorescence spectra of (a) **ZnP-phen** (blue line) and **ZnP-phen=Re** (red line), and (b) **H<sub>2</sub>P-phen** (blue line) and **H<sub>2</sub>P-phen=Re** (red line) in DMA at 298 K. Excited at 555 nm. The spectra of (a) correspond to Figure S14a in ref. S4.



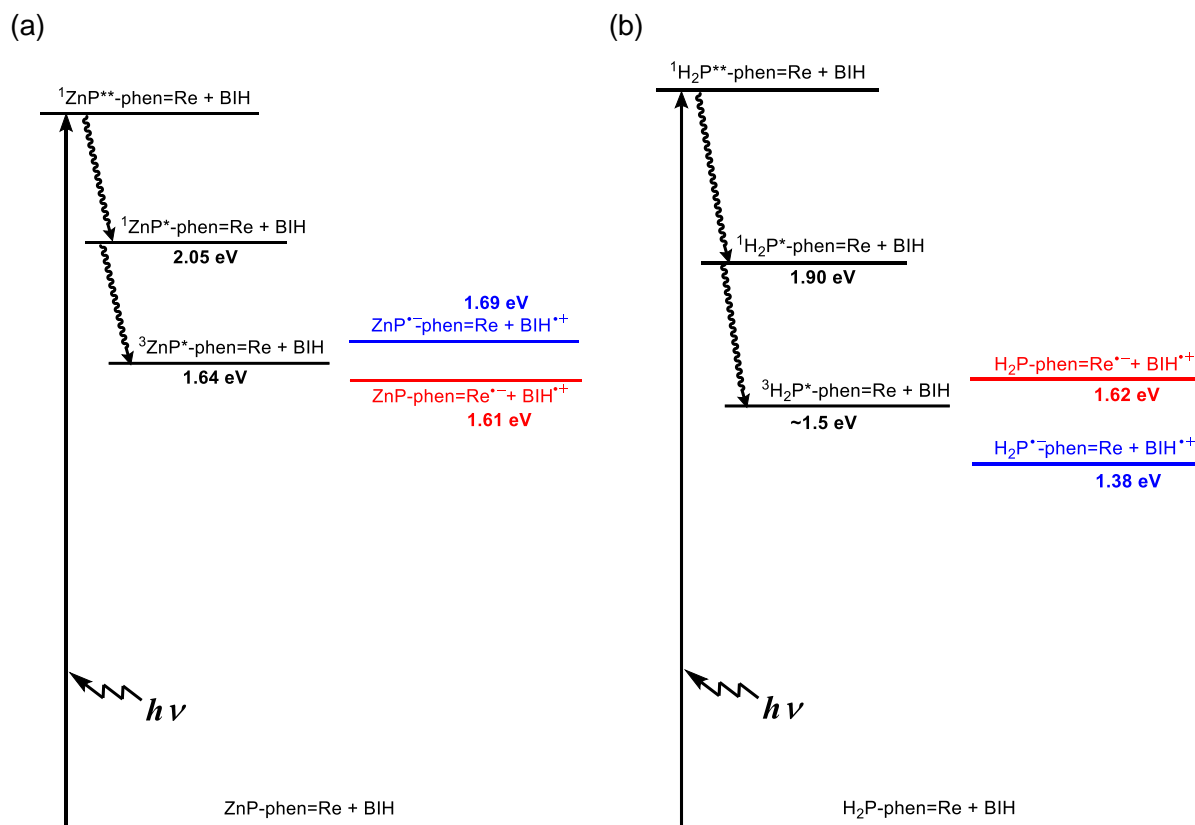
**Figure S17.** Energy diagrams of (a) **ZnP-phen=Re** and (b) **H<sub>2</sub>P-phen=Re** in DMA at 298 K. <sup>1</sup>ZnP<sup>\*\*</sup> and <sup>1</sup>H<sub>2</sub>P<sup>\*\*</sup> represent the upper excited singlet states (S<sub>2</sub>), and <sup>1</sup>ZnP<sup>\*</sup> and <sup>1</sup>H<sub>2</sub>P<sup>\*</sup> represent the lowest excited singlet states (S<sub>1</sub>) of the porphyrins. The energy levels of S<sub>1</sub> were estimated from the intersection between normalized absorption and fluorescence bands. The charge-separated states were calculated using equation (S1).<sup>S4</sup>



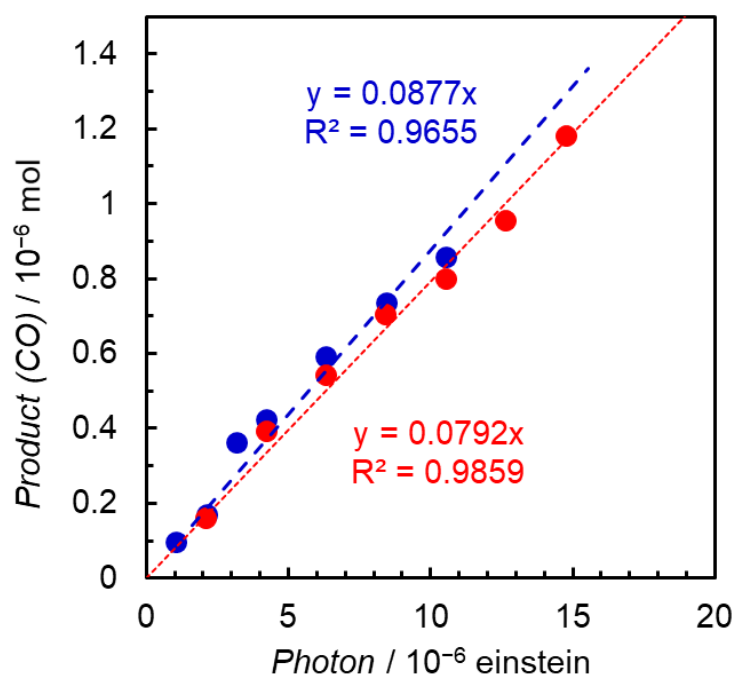
**Figure S18.** UV-vis absorption spectral change during the photo-irradiation ( $\lambda_{\text{ex}} = 420 \text{ nm}$ , Xe lamp) of  $\text{CO}_2$ -saturated DMA (3.0 mL) containing 5 vol% TEA in the presence of **ZnP-phen=Re** (0.05 mM).



**Figure S19.** Time dependences of CO formation during irradiation at 560 nm in 2.0 mL of CO<sub>2</sub>-saturated DMA solutions containing 0.05 M BIH and 0.05 mM **ZnP-phen=Re** and 0.05 mM **H<sub>2</sub>P-phen=Re**, and a mixed system of 0.05 mM ZnTPP and 0.05 mM *fac*-Re(phen)(CO)<sub>3</sub>Br. The plots for **ZnP-phen=Re** and the mixed system correspond to Figure S22 in ref. S4 with additional data.

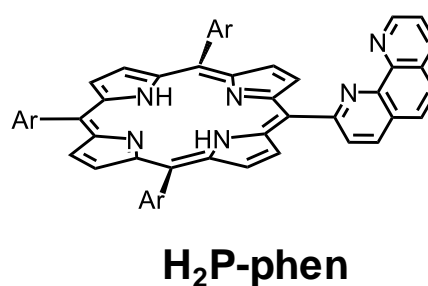
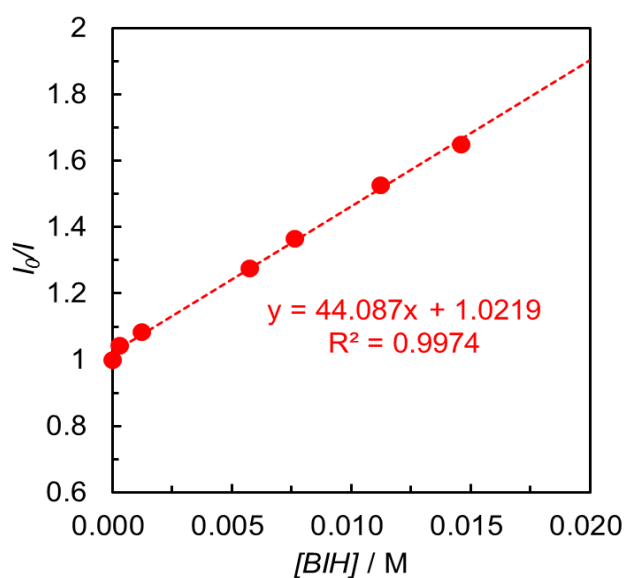


**Figure S20.** Energy diagrams of (a) **ZnP-phen=Re** and (b) **H<sub>2</sub>P-phen=Re** in the presence of BIH in DMA at 298 K. The diagram of (a) corresponds to Figure S28 in ref. S4. The  $T_1$  of the free-base porphyrin (~1.5 eV) was estimated from the difference between the phosphorescence peaks of ZnTPP and H<sub>2</sub>TPP.<sup>S8</sup> The energy levels of the charge-separated states from the ground state were calculated using  $E(\text{H}_2\text{P}/\text{H}_2\text{P}^-) = -1.48$  V,  $E(\text{Re}/\text{Re}^-) = -1.72$  V, and  $E(\text{BIH}^+/\text{BIH}) = -0.10$  V vs. Fc/Fc+ (Figure S15).<sup>S5b</sup>

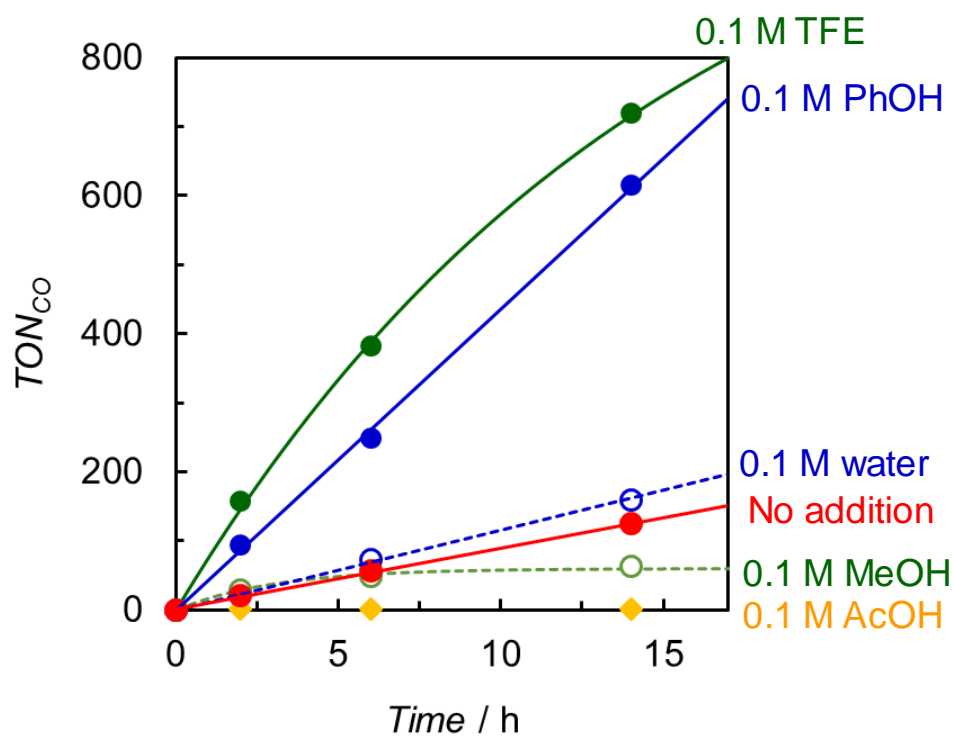


**Figure S21.** Formations of CO during irradiation at  $\lambda_{\text{ex}} = 420 \text{ nm}$  ( $3.5 \times 10^{-9} \text{ einstein s}^{-1}$ ) using BIH (red circles, 0.05 M; blue circles, 0.01 M) and phenol (0.1 M) in  $\text{CO}_2$ -saturated DMA containing **ZnP-phen=Re** (0.05 mM).

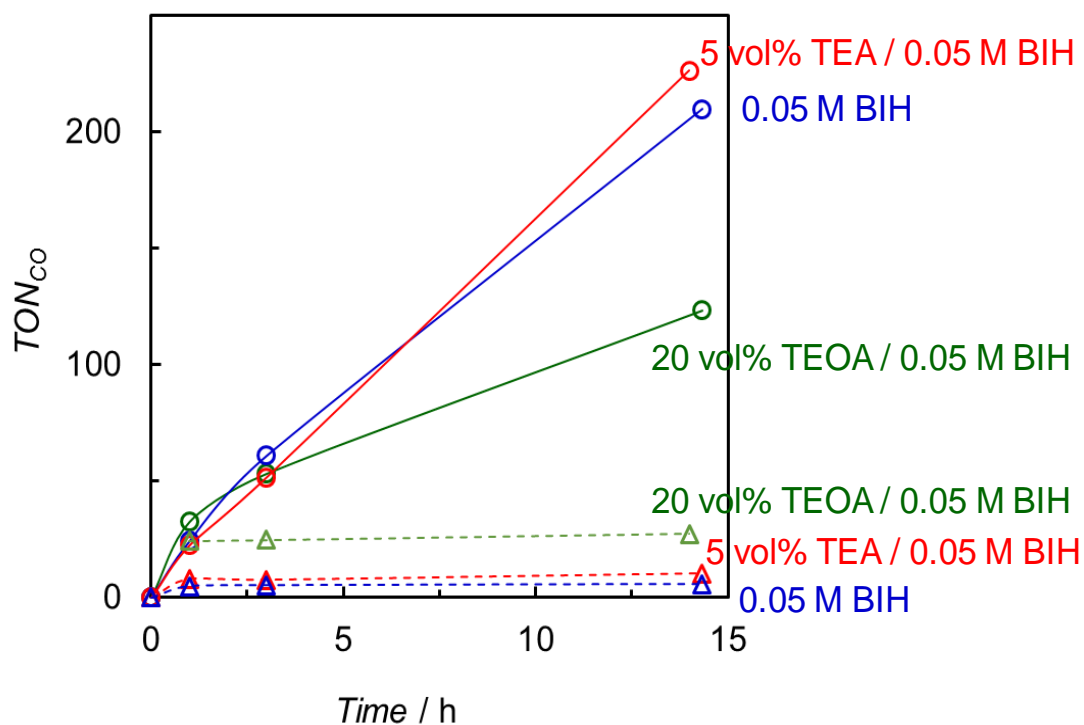




**Figure S22.** Stern–Volmer plots for fluorescence quenching of **H<sub>2</sub>P-phen** by BIH in DMA at 298 K. From the slope of the plots ( $K_{SV} = 44 \text{ M}^{-1}$ ) and the emission lifetime ( $\tau_{em}$ ), the quenching rate constant ( $k_q$ ) was obtained ( $k_q = K_{SV}/\tau_{em}$ ). Assuming that the fluorescence lifetime of free-base porphyrin was ca. 10 ns,<sup>S9</sup> the value of  $k_q$  was estimated to be  $4 \times 10^9 \text{ M}^{-1}$ . Judging from the value in the order of  $10^9 \text{ M}^{-1} \text{ s}^{-1}$ , the electron transfer from BIH to the S<sub>1</sub> of the porphyrin is a diffusion-controlled process.



**Figure S23.** Time dependence of CO formation during the irradiation at 420 nm in 2.0 mL of CO<sub>2</sub>-saturated DMA solutions containing 0.05 M BIH and 0.05 mM **ZnP-phen=Re** in the absence of acid (red) and in the presence of AcOH (yellow filled diamonds), PhOH (blue filled circles), TFE (green filled circles), MeOH (green open circles), and water (blue open circles).



**Figure S24.** Time dependence of CO formation during the irradiation at 420 nm in 2.0 mL of CO<sub>2</sub>-saturated DMA solutions containing 0.05 mM **ZnP-phen=Re** (circles, solid lines) and a mixed system of 0.05 mM ZnTPP and 0.05 mM *fac*-Re(phen)(CO)<sub>3</sub>Br (triangles, dotted lines) in the presence of 0.05 M BIH. The blue plots indicate the reactions in the absence of amine (blue). The green and red plots indicate the reactions in the presence of 20 vol% TEOA and 5 vol% TEA, respectively.

## References

- S1. A. D. Adler, F. R. Longo, J. D. Finarelli, J. Goldmacher, J. Assour, L. Korsakoff, *J. Org. Chem.* **1967**, *32*, 476–476.
- S2. E. W. Abel, P. J. Heard, K. G. Orrell, *Inorg. Chim. Acta* **1997**, *255*, 65–71.
- S3. (a) X.-Q. Zhu, M.-T. Zhang, A. Yu, C.-H. Wang, J.-P. Cheng, *J. Am. Chem. Soc.* **2008**, *130*, 2501–2516. (b) E. Hasegawa, T. Seida, N. Chiba, T. Takahashi, H. Ikeda, *J. Org. Chem.* **2005**, *70*, 9632–9635.
- S4. Y. Kuramochi, Y. Fujisawa, A. Satake, *J. Am. Chem. Soc.* **2020**, *142*, 705–709.
- S5. (a) Y. Kuramochi, Y. Kawakami, A. Satake, *Inorg. Chem.* **2017**, *56*, 11008–11018. (b) G. J. Kavarnos, *Fundamentals of Photoinduced Electron Transfer*; VCH: Weinheim, New York, 1993.
- S6. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, G. A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A. V. Marenich, J. Bloino, B. G. Janesko, R. Gomperts, B. Mennucci, H. P. Hratchian, J. V. Ortiz, A. F. Izmaylov, J. L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V. G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. J. Bearpark, J. J. Heyd, E. N. Brothers, K. N. Kudin, V. N. Staroverov, T. A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. P. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, J. M. Millam, M. Klene, C. Adamo, R. Cammi, J. W. Ochterski, R. L. Martin, K. Morokuma, O. Farkas, J. B. Foresman, and D. J. Fox, *Gaussian 09*, revision D.01; Gaussian, Inc.: Wallingford, CT, 2009.
- S7. Z.-C. Sun, Y.-B. She, Y. Zhou, X.-F. Song, K. Li, *Molecules* **2011**, *16*, 2960–2970.
- S8. A. Harriman, *J. Chem. Soc., Faraday Trans 1*, **1980**, *76*, 1978-1985.
- S9. M. Montalti, A. Credi, L. Prodi, M. T. Gandolfi. *Handbook of Photochemistry*, 3<sup>rd</sup> ed., CRC Press, Boca Raton 2006.