Supporting Information for

Light-Driven Redox Activation of CO₂- and H₂-Activating Complexes in a Self-Assembled Triad

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1. Synthetic Procedures

CH₂Cl₂, toluene, MeOH and diethyl ether for synthesis were HPLC grade (Fisher). Anhydrous methanol (Acros, >99.8 %, Extra Dry) was used as received. The dyad **ZnP–Re**⁺ was prepared by a modification of the literature procedure.² In order to avoid porphyrin-porphyrin coordination and aggregation, the free-base 5,10,15-triphenyl-20-(*p*-pyridyl)porphyrin (**H**₂**P**) was used to prepare the **H**₂**P–Re**⁺ dyad, which was subsequently metallated under mild conditions. The compounds W(C-4,4'-C₆H₄CCC₅H₄N)(dppe)₂Cl (**W**; dppe = 1,2-bis(diphenylphosphino)ethane),³ 5,10,15-triphenyl-20-(*p*-pyridyl)porphyrin (**H**₂**P**),⁴ W(CC₆H₄-4-CCPh)(dppe)₂Cl (**WPh**),⁵ and [Re(bpy)(CO)₃(dmso-O)][CF₃SO₃]⁶ were prepared according to standard procedures. All other reagents were obtained from commercial sources and used as received.

Preparation of [H₂P–Re][CF₃SO₃]. The dyad was prepared by a modification of a previously reported procedure.⁷ A solution of [Re(bpy)(CO)₃(dmso-O)][CF₃SO₃] (0.1516 g, 0.232 mmol) and H₂P (0.160 g, 0.256 mmol) in CH₂Cl₂ (50 mL) was refluxed in the dark for 7 d, at which point unreacted [Re(bpy)(CO)₃(dmso)][CF₃SO₃] was not detectable by ¹H NMR spectroscopy. It was found that use of a slight excess of porphyrin was necessary for all [Re(bpy)(CO)₃(dmso)][CF₃SO₃] to be consumed; unreacted H₂P is much easier to separate from the reaction mixture than unreacted [Re(bpy)(CO)₃(dmso)][CF₃SO₃]. The reaction mixture was reduced to dryness on a rotary evaporator and the remaining purple solid dissolved in a minimum volume of CH₂Cl₂ (6 mL), to which was then added toluene (500 mL). The mixture was allowed to stand in an open beaker for 4 h until purple microcrystals formed. These were isolated by filtration, washed with toluene and Et₂O, and dried under vacuum. Yield: 0.204 g (71% yield). Use of THF instead of CH₂Cl₂ as the solvent for the initial reaction was found to lead to decomposition. ¹H NMR (400 MHz, CD₂Cl₂): 9.35 (δ, 2 H, 6,6'-bpy), 8.88 (m, 8 H, porphyrin β), 8.65 (d, 2 H,

3,3'-bpy), 8.60 (d, 2 H, 2,6-pyridyl), 8.45 (t, 2 H, 4,4'-bpy), 8.20 (m, 8 H, *ortho*-phenyl, 3,5-pyridyl), 7.89 (t, 2 H, 5,5'-bpy), 7.79 (m, 9 H, *meta/para* phenyl), -2.19 (s, 2H, NH).

Preparation of ZnP–Re[CF₃SO₃]. The dyad was prepared by a modification of the literature procedure.² A solution of [H₂P–Re][CF₃SO₃] (0.100 g, 0.081 mmol) in CH₂Cl₂ (30 mL) was combined with a solution of Zn(OAc)₂·2H₂O (0.075 g, 342 mmol; Sigma-Aldrich, 99.999% trace metals basis) in MeOH (10 mL) and stirred for 5 d at room temperature; heating at reflux was found to degrade the compounds. The reaction mixture was reduced to dryness by rotary evaporation, and the remaining red-purple solid was dissolved in CH₂Cl₂ (50 mL). The solution was washed with H₂O (6 × 150 mL), dried over K₂CO₃, gravity filtered and evaporated to dryness by rotary evaporation. The solid was dissolved in 10 mL CH₂Cl₂ and layered with 30 mL pentane. After one week, purple crystals formed which were collected by filtration, washed with pentane and dried. Yield: 0.049 g (43% yield). ¹H NMR (400 MHz, CD₂Cl₂): 9.37 (δ, 2 H, 6,6'-bpy), 8.98–8.93 (m, 6 H, porphyrin β), 8.82 (d, 2H, 3,3'-bpy), 8.72 (d, 2 H, porphyrin β), 8.57 (d, 2 H, 3,5-pyridyl), 8.45 (t, 2 H, 4,4'-bpy), 8.19 (m, 8 H, *ortho*-phenyl, 2,6-pyridyl), 7.90 (t, 2 H, 5,5'-bpy), 7.78 (m, 9 H, *meta+para* phenyl). IR (CH₂Cl₂): v(CO), 2041 (sharp), 1936 (broad) cm⁻¹.

2. Spectroscopic Procedures

All optical experiments were performed under a nitrogen atmosphere using standard Schlenk and glovebox techniques. CH₂Cl₂ for photophysical experiments (Fisher, HPLC grade stored under nitrogen) was passed through two 4.5 in × 24 in. (1 gal) columns of activated A2 aluminum under nitrogen pressure.¹ Solution samples for UV/vis/NIR experiments were prepared on a vacuum line in sealable cuvettes of path length 1 cm (absorption/emission) or 2 mm (fsTA), degassed with five freeze–pump–thaw cycles, and sealed under purified nitrogen. Solution samples for IR

experiments were prepared in a glovebox in a demountable IR cell (Specac) equipped with CaF_2 windows and a 500 μ m PTFE spacer.Electronic absorption spectra were recorded on a Cary 300 spectrometer. FTIR spectra were recorded on a Nicolet 6700 FTIR spectrometer.

Visible and Near-IR Transient Absorption Spectroscopy. Experiments were performed at the Center for Nanoscale Materials, Argonne National Laboratory. The instrument employed a femtosecond Ti:sapphire oscillator regeneratively amplified at 1.7 kHz. The white-light continuum probe was generated using 5% of the output (sapphire crystal in the visible region, sapphirecontaining proprietary material in the near-infrared region). The remaining output was used to drive an optical parametric amplifier that produced a tunable 35-femtosecond excitation (pump) pulses. The pump and probe output entered a transient-absorption spectrometer (Helios, Ultrafast Systems), where the delay of the probe relative to the pump was varied using a mechanical delay line. The pump beam was chopped at one-half the repetition rate of the laser so that an absorption change ($\Delta A = -[log(I_p/I_0)]$) could be measured as a function of delay, where I_p and I_0 are the intensities of the transmitted probe with the pump on and off. Spectral content of the probe in the regions 440–700 nm and 830–1400 nm was collected as a function of delay using separate spectrographs. Second-order diffractions were removed from the near-infrared by passing the probe through an 850 nm long-pass filter before entering the detector. The data were chirpcorrected to within 200 fs over the spectral range by fitting the solvent response of a pure-solvent standard (under identical conditions) to a polynomial function. The photochemical stability of samples was established by comparing electronic absorption spectra obtained before and after transient-absorption measurements. Global kinetic analyses of spectra were performed using OriginPro.

Time-resolved IR (TR-IR) Spectroscopy. Experiments were performed at the Center for Nanoscale Materials, Argonne National Laboratory. The instrument employed a femtosecond Ti:sapphire oscillator regeneratively amplified at 2 kHz. The 35 fs, 2 mJ, 800 nm output of the titanium:sapphire laser was beamsplit 50:50 and used to pump two optical parametric amplifiers (OPA). Mid-infrared probe pulses, generated via difference frequency mixing of signal and idler beams in a AgGaS₂ crystal, were focused to a 250 micron-diameter spot on the sample, directed to a 190-mm imaging spectrograph, dispersed with a 150 groove/mm grating, and detected with a HgCdTe array detector and boxcar integrator. Pump pulses, produced via either second harmonic generation of the laser fundamental or OPA signal beam, were mechanically delayed relative to the probe pulse, mechanically chopped at 1 kHz, and overlapped with the probe pulse on the sample. Global kinetic analyses of spectra were performed using OriginPro. The wavelength of the detector was calibrated by comparison to an FTIR absorbance scan of Re(bpy)(CO)₃Cl in CH₃CN. Kinetic traces were first corrected by setting the average of all points at t < 0 to zero. Next, the baseline drift was determined by measuring the kinetic trace in regions containing no transient signal, averaging those traces, and subtracting the result from all the kinetic traces analyzed. Baseline drift was measured at several wavelengths to ensure the uniformity of baseline drift. The sample was moved back and forth across the laser beams to reduce the risk of sample degradation due to overexposure.

3. Spectral and Kinetic Analysis Methods

Determination of the extent of formation of 1 in solution. The extent of coordination of $ZnP-Re^+$ by W to form 1 in TA samples was determined by fitting their electronic-absorption spectra to a linear combination of the spectra of W, $ZnP-Re^+$, and $Zn_{py}P-Re^+$ (which was assumed to be identical to the porphyrinic chromophore of 1). A known volume of a solution of

 $ZnP-Re^+$ was diluted with 1% pyridine, and a spectrum acquired and scaled appropriately to produce a hypothetical spectrum of $Zn_{py}P-Re^+$, which was assumed to be equivalent to the spectrum of the porphyrinic component of 1. These spectra were then used as basis spectra for a linear combination fit in Igor Pro. The equation for the best-fit spectrum F is:

$$F(\lambda) = A1(\lambda) + B2(\lambda) + C3(\lambda)$$

Values of *A*, *B*, and *C* from the fit then represented the concentrations of **W**, $ZnP-Re^+$, and **1** in solution. The extent of selective excitation of **1** at 565 nm was then determined by comparing the absorbance at that wavelength by a solution of **1** at the concentration C to the total sample absorbance. The residual from the fit represents the unaccounted-for extent to which the spectrum of ligated **W** differs from that of ligated **W**.

As described previously for W-ZnTPP,^{3, 8} it is possible to identify conditions under which the complex may be selectively excited. At the concentrations used for TA experiments, the porphyrin species present are approximately 78–91% 1 and the balance $ZnP-Re^+$. Owing to the Q band red shift and the loss of Q(1,0) intensity in 1 relative to $ZnP-Re^+$, excitation at 565 nm, the wavelength used in our TA experiments, produces 89–96% excited 1.

Shown in Figure S1 are example fits to representative visible/NIR and mid-IR TA samples, showing the extent of ligation as well as the selectivity of excitation at 565 nm.



Figure S1. Spectra (blue) and fits (red) for representative TA samples, corrected to 1 cm pathlengths, showing extent of ligation of $ZnP-Re^+$ by W.

Kinetic Analysis of the fsIR spectra of ZnP–Re⁺. The intensities of the bleaches at 2041 cm⁻¹ and 1945 cm⁻¹ and S₁ absorption bands at 2035 cm⁻¹ were fit to a single exponential, with the kinetic parameter shared across all three wavelengths. The duration of the experiment (1.6 ns) was too short to accurately determine the S₁ lifetime. The kinetic data with the best fit line obtained from the fit, where $\tau = 776 \pm 26$ ps, is shown in Figure S2b.

The intensity of the band at 2014 cm⁻¹ attributable to the **Re•** fragment of ZnP^+ –**Re•** was fit to a biexponential expression to model its growth and decay:

$$\Delta A(t) = A_{rise}(e^{-t/\tau_{rise}}) + A_{decay}(e^{-t/\tau_{decay}}) + A_0$$

Forcing τ_{rise} and τ_{decay} to lie anywhere within the range $\tau_{rise} = 40 \pm 30$ ps and $\tau_{decay} = 600 \pm 200$ ps did not markedly decrease the observed quality of the fit. The data and the best fit as determined, with $\tau_{rise} = 40 \pm 3$ ps and $\tau_{decay} = 601 \pm 76$ ps, is shown in Figure 2.

Kinetic Analysis of S_1 Transient-Absorption Data of 1. The kinetic analysis of 1 was performed on the data in the wavelength regions of the S_1 absorption features. The features were fit to a biexponential expression:

$$\Delta A(t) = A_{S_1, background}(e^{-t/\tau_{S_1}}) + A_{S_1}(e^{-t/\tau_{decay}}) + A_0$$

where the term with the $_{S1, background}$ subscript is a fixed background process with a lifetime of 1700 ps, and the term with the $_{S1}$ subscript corresponds to the decay of the S₁ transient features. The data were fit using an unweighted global analysis in OrginPro at six different wavelengths covering both transient absorption features (~590–594 nm and 1259–1325 nm⁹). The time constant τ_{S1} was shared between all kinetic profiles; the other variables were unconstrained. A representative fit is shown in Figure S2.



Figure S2. Fits to the transient-absorption band of 1 at 594 nm (left) and 1297 nm (right) provided by global kinetic analysis of the spectrum ($\tau_{S1} = 106 \pm 1$ ps). Inset: Residuals from global fit.

Kinetic Analysis of the fsIR spectra of 1. The kinetic traces of the induced absorption features at 2012, 1901, 1898 and 1881 cm⁻¹ were fit to a single exponential, with the kinetic parameter shared across all three wavelengths. Kinetic data and the fit obtained with $\tau = 102 \pm 4$ ps are shown in Figure 5b. The kinetic trace of the bleach feature at 2035 cm⁻¹ was fit to a single exponential. Kinetic data and the fit obtained with $\tau = 114 \pm 6$ ps is shown in Figure 6c.

4. Calculations

Excited-State Energy Levels. The energy levels presented in Figures 1 and 7 and shown below in Table S1 were determined as follows. For unligated $ZnP-Re^+$, the S₁ energy level is taken from the report by Casanova et al.² For ligated $Zn_{py}P-Re^+$ and 1, the energy shift of the S₁ state upon coordination is estimated from the redshift of the Q(0,0) absorption band from 592 nm to 611 nm. The T₁ energy for unligated $ZnP-Re^+$ is assumed to be equal to the T₁ energy for ZnTPP, and the decrease in T₁ energy upon pyridine coordination in ZnTPP(py) is used to compute the T₁ energy for $Zn_{py}P-Re^+$ and 1.¹⁰

Tuble 51. Excited state energy levels for Zill ite with various inguitus.					
Ligand	$S_1 (eV)$	$T_1 (eV)$	$ZnPor^{+}-Re(bpy \bullet -) (eV)$		
none	2.04	1.61	1.99		
pyridine	1.98	1.57	1.88		
W	1.98	1.57	1.88 (see below for further discussio	n)	

Table S1. Excited-state energy levels for ZnP-Re⁺ with various ligands.

The energy of the charge-shift state $W-ZnP^+-Re^{\bullet}$ is taken from the literature report on the model pyridine adduct, $Zn_{py}P-Re^{+.2}$ This report relies on the observation by Gust and coworkers that coordination of pyridine to ZnTPP lowers the oxidation potential of ZnTPP by 0.11 V in the absence of a coordinating electrolyte.¹¹ The energy of the ZnP^+-Re^{\bullet} state in 1 is assumed to be identical (see discussion below).

The energy of the W^+ – ZnP^- –Re charge-separated state and the W^+ –ZnP–Re• chargeshift state are taken from Table S3 (see discussion below). The excited-state energies of the ${}^{1,3}[(d_{xy})^1(\pi^*)^1]$ (${}^{1,3}[d\pi^*]$) states of W are taken from a study of the photophysics of W–ZnTPP in toluene and fluorobenzene.^{3, 8}

Gibbs' Free Energy Change for Electron Transfer Events. In 1 there are three distinct redox states that are potentially accessible from the porphyrin S_1 state: (i) oxidized porphyrin/reduced rhenium ($W-ZnP^+-Re^+$), (ii) oxidized tungsten/reduced porphyrin ($W^+-ZnP^ -Re^+$), and (iii) oxidized tungsten/reduced rhenium ($W^+-ZnP-Re^+$). States (i) and (iii) are charge shift processes and (ii) is a charge separation process. The Gibbs free energy change for an excitedstate charge shift is estimated by the following equation:¹²

$$\Delta G_{CS} = e[E_{ox} - E_{red}] - E_{00} \tag{1}$$

where *e* is the elementary charge, E_{ox} and E_{red} are the oxidation potential of the donor and the reduction potential of the donor, respectively, and E_{00} is the excited-state energy (2.02 eV).²

In the relevant charge-separation process in this dyad, three electrostatic interactions must be accounted for. Two of these are attractive stabilization terms (oxidized tungsten/reduced porphyrin and reduced porphyrin/cationic rhenium) and the third is a repulsive destabilizing term (oxidized tungsten/cationic rhenium). The Gibbs free energy change for an excited-state charge separation in this system is estimated by the following equation:¹²

$$\Delta G_{CS} = e[E_{ox} - E_{red}] - \frac{e^2}{4\pi\varepsilon_0\varepsilon R_{WZn}} - \frac{e^2}{4\pi\varepsilon_0\varepsilon R_{ZnRe}} + \frac{e^2}{4\pi\varepsilon_0\varepsilon R_{WRe}} - E_{00}$$
(2)

where *e* is the elementary charge, E_{ox} and E_{red} are the oxidation potential of the donor and the reduction potential of the donor, respectively, E_{00} is the excited-state energy (2.02 eV),² ε_s is the solvent dielectric constant (CH₂Cl₂ ε_s = 8.93),¹³ and R_{WZn} , R_{ZnRe} , and R_{WRe} are the distances between the three metal centers. The relevant oxidation and reduction potentials of the dyads and respective model compounds are laid out in Table S2. Because compound **W** was found to adsorb to the electrodes and produce erratic electrochemical data, model compound **WPh** (shown in Chart S1) was used in its place. This substitution is not predicted to result in a change in oxidation or reduction potentials, as described by O'Hanlon et al. in a study of tungsten–benzylidyne compounds with different length oligo-phenylene-ethynylene substituents.¹⁴

Table S2. Redox Potentials for Triad Compounds and Model Complexes^a

compound	$E_{1/2}^{0/-}, V$	$E_{1/2}^{0/+}, V$
WPh	-2.95 ^b	-0.59°
$\text{Re(bpy)(CO)}_3(\text{py})^+ d$	-1.59	+1.28
ZnP–Re ^{+d}	-1.62	+0.26 ^e

^a CH₂Cl₂ solution (except as noted), room temperature, V vs. $FeCp_2^{0/+}$. ^b THF solution (ref.¹⁴)^c Ref. ^{11d} Values from ref.², converted from SCE to $FeCp_2^{0/+}$ using ref.¹⁵. ^eE_{1/2}^{0/+} adjusted by -0.11 V to account for stabilization of the ZnPor⁺ state upon pyridine coordination. ⁶



Chart S1. Model compound WPh, used to determine redox potentials of compound W.

The donor-acceptor distance between the tungsten and porphyrin is taken from DFT calculations ($R_{WZn} = 15.2$ Å).³ In order to determine the donor–acceptor distances for the other two relevant charge-separated states we present the DFT model for **ZnP–Re**⁺ in Figure S3. Since the first rhenium reduction is bipyridine based,¹⁶ the average zinc-bipyridine carbon distance is used for the zinc-rhenium donor-acceptor distance ($R_{ZnRe} = 10.5$ Å). The oxidized tungsten/reduced rhenium distance was determined geometrically ($R_{WRe} = 19.6$ Å) using the law of cosines c² = a² + b² – 2ab cos γ , with the system considered a triangle with the three nodes located at the tungsten center, zinc center in **ZnP–Re**⁺, and one of the 1,1′ bpy carbons in **ZnP–Re**⁺. The parameters were a = 15.2 Å, b = 10.5 Å, and $\gamma = 98^{\circ}$. Presented in Table S3 are the Gibbs free energy change for photochemical charge separation for the relevant charge-shifted and charge-separated states in **3**, determined from Equations 1 and 2.

Relevant Charge-Separated States.							
charge-separated state	ΔG_{CS} (ZnPor S ₁),	$-\Delta G_{CR}, eV^b$	Process				
	eV ^a						
W–ZnP ⁺ –Re•	-0.10	1.88	Charge Shift				
W ⁺ -ZnP ⁻ -Re	-0.88	1.14	Charge Separation				
W ⁺ -ZnP-Re•	-0.98	1.00	Charge Shift				

Table S3. Gibbs Free Energy for Photochemical Charge Separation and State Energy for Relevant Charge-Separated States.

^{*a*} Equations 1 (Charge Shift) and 2 (Charge Separation). ^{*b*} $-\Delta G_{CR} = E_{00} + \Delta G_{CS}$.



Figure S3. Calculated (DFT) model structure of **ZnP–Re**⁺. The average Zn–bpy(C) distance is 10.5 Å. Calculations performed in Gaussian 09¹⁷ with the B3P86 functional and 6-31G* (H, C, N, O)¹⁸⁻¹⁹ and LANL2DZ (Zn, Re)²⁰⁻²¹ basis sets. LANL2DZ effective-core potentials were used for Zn and Re.²⁰⁻²¹

Solvent correction for rates of FRET and reductive quenching. The rate constants of FRET and reductive quenching have been reported for W–ZnTPP in toluene (FRET) and C₆H₅F (reductive quenching). In order to use the measured values to estimate the rates of FRET and reductive quenching in 1 in CH₂Cl₂, it is necessary to apply a correction.

The rate of FRET in different solvents depends almost entirely on the refractive index η of each solvent. The rate of FRET is determined by the following equation:

$$k_{FRET} = \frac{9000 \ln(10) \kappa^2 \Phi_D J_F}{128 \pi^5 \eta^4 N_A \tau_D R_{DA}^6}$$

In this equation, the porphyrin radiative lifetime (φ_D/τ_D), dyad geometry (which determines R_{DA} , the donor-acceptor distance, and κ^2 , the dipole orientation factor), and spectral-overlap integral (J_F) are nearly or completely solvent-independent. Consequently, the FRET rate constant in dichloromethane ($k_{FRET, DCM}$) can be related to the rate constant measured in toluene by the following equation:

$$k_{FRET,DCM} = k_{FRET,tol} \frac{\eta_{tol}^4}{\eta_{DCM}^4}$$

where $k_{FRET, tol} = 1.63 \times 10^9 \text{ s}^{-1.4}$, $\eta_{tol} = 1.4941$, 9 and $\eta_{DCM} = 1.4242$. This provides an energy-transfer rate of $k_{FRET,DCM} = 1.97 \times 10^9 \text{ s}^{-1}$.

To estimate the rate of reductive quenching, we must first consider the factors that influence the observed electron transfer rate in C_6H_5F , and how changing those parameters when switching to CH_2Cl_2 will affect the rate. We begin with the equation from Marcus theory for the rate of electron transfer:

$$k_{ET} = \sqrt{\frac{\pi}{\hbar^2 \lambda k_b T}} \left| V \right|^2 e^{\frac{-(\Delta G^\circ + \lambda)^2}{4 \lambda k_b}}$$

where V is the donor-acceptor electronic coupling, λ is the total reorganization energy, T is the temperature, k_B is the Boltzmann constant, and \hbar is the Planck constant ($\hbar = h/2\pi$). The driving force, ΔG° , is -0.71 eV in C₆H₅F³ and -0.88 in CH₂Cl₂ (see above). The total reorganization energy λ can be divided into two terms, the solvent-independent inner-sphere reorganization energy λ_i and the solvent-dependent outer-sphere reorganization energy λ_o , which can be estimated using the dielectric continuum model

$$\lambda = \lambda_i + \lambda_o = \lambda_i + \frac{e^2}{4\pi\varepsilon_0} \left(\frac{1}{r} - \frac{1}{R_{cc}}\right) \left(\frac{1}{\eta^2} - \frac{1}{\varepsilon_s}\right)$$

where *r* is the average radius of the donor and acceptor (5.0 Å, taken from DFT models)⁴, *R_{CC}* is the center-to-center distance between the donor and acceptor (15.4 Å, see above), η is the solvent refractive index (see above), and ε_s is the solvent dielectric constant (PhF: $\varepsilon_s = 5.465$, DCM: $\varepsilon_s =$ 8.93).⁹ The inner-sphere reorganization energy has not been measured for W=CR–ZnTPP donoracceptor pairs, but is assumed to be roughly 0.2 eV by analogy with ZnP/AuP⁺ donor-acceptor pairs (varying this value in the range 0.1–0.5 eV has a negligible effect on the final estimate of k_{RedQ} in CH₂Cl₂). With the exception of Δit and λ_o , none of the parameters are expected to change between C₆H₅F and CH₂Cl₂. For C₆H₅F, $\lambda_o = 0.55$ eV, and for CH₂Cl₂, $\lambda_o = 0.74$ eV. Using the Marcus equation above, we find that $k_{ET, DCM} = k_{ET, PhF} \times 0.91 = 1.1 \times 10^9$ s⁻¹.

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