Supplementary Information

Significance of the Connecting Position between Zn(II) Porphyrin and Re(I) Bipyridine Tricarbonyl Complex Units in Dyads for Room-Temperature Phosphorescence and Photocatalytic CO₂ Reduction: Unexpected Enhancement by Triethanolamine in Catalytic Activity

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Figure S1. ¹H NMR spectrum of H₂P-4py in CDCl₃ (400 MHz).



Figure S2. ¹³C NMR and DEPT135 spectra of H_2P-4py in CDCl₃ (100 MHz).



Figure S3. 1 H- 1 H COSY of H₂P-4py in CDCl₃ (400 MHz).



Figure S4. MALDI-TOF mass (matrix: dithranol) of H_2P-4py . Top: found, bottom: simulated by $[C_{52}H_{47}BrN_5]^+$ ($[M+H]^+$).



Figure S5. ¹H NMR spectrum of H_2P -5py in CDCl₃ (400 MHz).



Figure S6. ¹³C NMR and DEPT135 spectra of H_2P -5py in CDCl₃ (100 MHz).



Figure S7. 1 H- 1 H COSY of H₂P-5py in CDCl₃ (400 MHz).



Figure S8. MALDI-TOF mass (matrix: dithranol) of H_2P -5py. Top: found, bottom: simulated by $[C_{52}H_{47}BrN_5]^+$ ($[M+H]^+$).



Figure S9. 1 H NMR spectrum of H₂P-6py in CDCl₃ (400 MHz). Asterisks (*) indicate impurities.



Figure S10. 13 C NMR and DEPT135 spectra of H₂P-6py in CDCl₃ (100 MHz).



Figure S11. ${}^{1}\text{H}-{}^{1}\text{H}$ COSY of H_2P -6py in CDCl₃ (400 MHz).



Figure S12. MALDI-TOF mass (matrix: dithranol) of H_2P -6py. Top: found, bottom: simulated by $[C_{52}H_{47}BrN_5]^+$ ($[M+H]^+$).



Figure S13. Comparison of ¹H NMR spectra among H_2P -6py, H_2P -5py, and H_2P -4py in CDCl₃ (400 MHz).



Figure S14. ¹H NMR spectrum of ZnP-4py in CDCl₃ (400 MHz).



Figure S15. ¹³C NMR and DEPT135 spectra of **ZnP-4py** in CDCl₃ (100 MHz). Asterisks (*) indicate hexane.



Figure S16. 1 H- 1 H COSY of ZnP-4py in CDCl₃ (400 MHz).



Figure S17. MALDI-TOF mass (matrix: dithranol) of **ZnP-4py**. Top: found, bottom: simulated by $[C_{52}H_{44}BrN_5Zn]^+$ ($[M]^+$).



Figure S18. ¹H NMR spectrum of ZnP-5py in CDCl₃ (400 MHz).



Figure S19. ¹³C NMR and DEPT135 spectra of ZnP-5py in CDCl₃ (100 MHz + a drop of methanol- d_4).



Figure S20. ¹H-¹H COSY of ZnP-5py in CDCl₃ (400 MHz).



Figure S21. MALDI-TOF mass (matrix: dithranol) of **ZnP-5py**. Top: found, bottom: simulated by $[C_{52}H_{44}BrN_5Zn]^+$ ($[M]^+$).



Figure S22. ¹H NMR spectrum of ZnP-6py in CDCl₃ (400 MHz).



Figure S23. ¹³C NMR and DEPT135 spectra of ZnP-6py in CDCl₃ (100 MHz).



Figure S24. ¹H-¹H COSY of **ZnP-6py** in CDCl₃ (400 MHz).



Figure S25. MALDI-TOF mass (matrix: dithranol) of **ZnP-6py**. Top: found, bottom: simulated by $[C_{52}H_{44}BrN_5Zn]^+$ ($[M]^+$).



Figure S26. Comparison of ¹H NMR spectra among **ZnP-6py**, **ZnP-5py**, and **ZnP-4py** in CDCl₃ (400 MHz).



Figure S27. ¹H NMR spectrum of ZnP-4Bpy in CDCl₃ (400 MHz). Asterisks (*) indicate impurities.



Figure S28. 13 C NMR and DEPT135 spectra of ZnP-4Bpy in CDCl₃ (100 MHz).



Figure S29. 1 H- 1 H COSY of ZnP-4Bpy in CDCl₃ (400 MHz).



Figure S30. MALDI-TOF mass (matrix: dithranol) of **ZnP-4Bpy**. Top: found, bottom: simulated by $[C_{57}H_{49}N_6Zn]^+$ ($[M+H]^+$).



Figure S31. ¹H NMR spectrum of ZnP-5Bpy in CDCl₃ (400 MHz). Asterisks (*) indicate impurities.



Figure S32. ¹³C NMR and DEPT135 spectra of **ZnP-5Bpy** in CDCl₃ (100 MHz). Asterisks (*) indicate hexane.



Figure S33. ${}^{1}\text{H}-{}^{1}\text{H}$ COSY of ZnP-5Bpy in CDCl₃ (400 MHz).



Figure S34. MALDI-TOF mass (matrix: dithranol) of **ZnP-5Bpy**. Top: found, bottom: simulated by $[C_{57}H_{48}N_6Zn]^+$ ($[M]^+$) and $[C_{57}H_{49}N_6Zn]^+$ ($[M+H]^+$).



Figure S35. ¹H NMR spectrum of ZnP-6Bpy in CDCl₃ (500 MHz).



Figure S36. 13 C NMR and DEPT135 spectra of ZnP-6Bpy in CDCl₃ (125 MHz).



Figure S37. ¹H-¹H COSY of **ZnP-6Bpy** in CDCl₃ (500 MHz).



Figure S38. MALDI-TOF mass (matrix: dithranol) of **ZnP-6Bpy**. Top: found, bottom: simulated by $[C_{57}H_{49}N_6Zn]^+$ ($[M+H]^+$).



Figure S39. Comparison of ¹H NMR spectra among **ZnP-6Bpy**, **ZnP-5Bpy**, and **ZnP-4Bpy** in CDCl₃ (400 MHz).



Figure S40. ¹H NMR spectrum of **ZnP-4Bpy=Re^{Br}** in CDCl₃ (500 MHz). Asterisks (*) indicate impurities.



Figure S41. ¹³C NMR and DEPT135 spectra of ZnP-4Bpy=Re^{Br} in CDCl₃ (125 MHz).



Figure S42. ¹H-¹H COSY of ZnP-4Bpy=Re^{Br} in CDCl₃ (500 MHz).



Figure S43. MALDI-TOF mass (matrix: DCTB) of **ZnP-4Bpy=Re**^{Br}. Top: found, bottom: simulated by $[C_{60}H_{48}BrN_6O_3ReZn]^+$ ([M]⁺).



Figure S44. IR spectra of ZnP-4Bpy and ZnP-4Bpy=Re^{Br} in KBr pellet.



Figure S45. ¹H NMR spectrum of **ZnP-5Bpy=Re^{Br}** in CDCl₃ (400 MHz). Asterisks (*) indicate impurities.



Figure S46. ¹³C NMR and DEPT135 spectra of ZnP-5Bpy=Re^{Br} in CDCl₃ (100 MHz).


Figure S47. 1 H- 1 H COSY of ZnP-5Bpy=Re^{Br} in CDCl₃ (400 MHz).



Figure S48. MALDI-TOF mass (matrix: DCTB) of **ZnP-5Bpy=Re**^{Br}. Top: found, bottom: simulated by $[C_{60}H_{48}BrN_6O_3ReZn]^+$ ([M]⁺).



Figure S49. IR spectra of ZnP-5Bpy and ZnP-5Bpy=Re^{Br} in KBr pellet.



Figure S50. ¹H NMR spectrum of **ZnP-6Bpy=Re^{Br}** in CDCl₃ (500 MHz). Asterisks (*) indicate impurities.



Figure S51. ¹³C NMR and DEPT135 spectra of $ZnP-6Bpy=Re^{Br}$ in DMF- d_7 (125 MHz).



Figure S52. ¹H-¹H COSY of ZnP-6Bpy=Re^{Br} in DMF- d_7 (500 MHz).



Figure S53. MALDI-TOF mass (matrix: DCTB) of **ZnP-6Bpy=Re**^{Br}. Top: found, bottom: simulated by $[C_{60}H_{48}BrN_6O_3ReZn]^+$ ([M]⁺).



Figure S54. IR spectra of ZnP-6Bpy and ZnP-6Bpy=Re^{Br} in KBr pellet.



Figure S55. Comparison of ¹H NMR spectra among **ZnP-6Bpy=Re^{Br}** (500 MHz), **ZnP-5Bpy=Re^{Br}** (400 MHz), and **ZnP-4Bpy=Re^{Br}** (500 MHz) in CDCl₃. Asterisk marks (*) indicate toluene.



Figure S56. ¹H NMR spectrum of ZnP-5Bpy=Re^{MeCN} in CDCl₃ (400 MHz). Asterisks (*) indicate impurities.



Figure S57. ¹H-¹H COSY of ZnP-5Bpy=Re^{MeCN} in CDCl₃ (400 MHz).



Figure S58. IR spectra in the CO stretching region of **ZnP-5Bpy=Re**^{MeCN} and **ZnP-5Bpy=Re**^{Br} in CH₃CN (400 MHz).



Figure S59. ¹H NMR spectrum of ZnP-6Bpy=Re^{MeCN} in CDCl₃ (400 MHz). Asterisks (*) indicate impurities.



Figure S60. ¹H-¹H COSY of ZnP-6Bpy=Re^{MeCN} in CDCl₃ (400 MHz).



Figure S61. IR spectra in the CO stretching region of **ZnP-6Bpy=Re**^{MeCN} and **ZnP-6Bpy=Re**^{Br} in CH₃CN (400 MHz).



Figure S62. Comparison of ¹H NMR spectra among H₂P-4py, ZnP-4py, ZnP-4Bpy and ZnP-4Bpy=Re^{Br} in CDCl₃. Asterisk marks (*) indicate toluene.



Figure S63. Comparison of ¹H NMR spectra among H₂P-5py, ZnP-5py, ZnP-5Bpy, ZnP-5Bpy=Re^{Br} and ZnP-5Bpy=Re^{MeCN} in CDCl₃.



Figure S64. Comparison of ¹H NMR spectra among H₂P-6py, ZnP-6py, ZnP-6Bpy, ZnP-6Bpy=Re^{Br} and ZnP-6Bpy=Re^{MeCN} in CDCl₃.



Figure S65. IR spectral changes of (a) **ZnP-5Bpy=Re**^{MeCN} and (b) **ZnP-6Bpy=Re**^{MeCN} dissolved in Ar-saturated DMA for 2 h. Concentrations of the dyads: 11 mM.

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Figure S66. UV-vis absorption spectra in DMA of (a) ZnP-phen and ZnP-phen=Re, (b) ZnP-4Bpy and ZnP-4Bpy=Re^{Br}, (c) ZnP-5Bpy and ZnP-5Bpy=Re^{Br}, (d) ZnP-6Bpy and ZnP-6Bpy=Re^{Br}.



Figure S67. The center-to-center distances between the Zn and Re atoms in the dyads. Calculation method: B3LYP/LANL2DZ (Re) / 6-31G(d) (H, C, N, O, Br, Zn) using PCM with the default parameter for DMA. The Zn porphyrins without the DMA coordination were calculated.



Figure S68. UV-vis absorption spectra in DMA of (a) ZnP-5Bpy=Re^{Br} and ZnP-5Bpy=Re^{DMA}, (b) ZnP-6Bpy=Re^{Br} and ZnP-6Bpy=Re^{DMA}.



Figure S69. Fluorescence spectra in DMA ($\lambda_{ex} = 560 \text{ nm}$) of (a) ZnP-4Bpy and ZnP-4Bpy=Re^{Br}, (b) ZnP-5Bpy and ZnP-5Bpy=Re^{Br}, (c) ZnP-6Bpy and ZnP-6Bpy=Re^{Br}. (d) Overlay of all fluorescence spectra.



Figure S70. Fluorescence decay profiles of **ZnP***-n***Bpy** (n = 4, 5, and 6) in DMA. The excitation wavelength was 406 nm and instrumental response function was FWHM = 70 ps (blue lines). The decay profiles were fitted with one component (red lines).



Figure S71. Fluorescence decay profiles of **ZnP-4Bpy=Re**^{Br} and **ZnP-5Bpy=Re**^{Br} in DMA. The excitation wavelength was 406 nm and instrumental response function was FWHM = 70 ps (blue lines). The decay profiles were fitted with one component (red lines).



Figure S72. Fluorescence decay profiles of **ZnP-6Bpy=Re**^{Br} in DMA. The excitation wavelength was 406 nm and instrumental response function was FWHM = 70 ps (blue lines). The decay profiles were fitted with two components (red lines).



Figure S73. The fitting curves by changing the major component in Figure S70 (red lines) with 5 ps (black lines) and 25 ps (blue lines).



Figure S74. Emission spectra in DMA ($\lambda_{ex} = 560 \text{ nm}$) under air and Ar atmospheres at 298 K of (a) **ZnP-4Bpy=Re^{Br}**, (b) **ZnP-5Bpy=Re^{Br}**, and (c) **ZnP-6Bpy=Re^{Br}**. The long-lived excited state of the T₁ of the porphyrin is efficiently quenched by O₂ in air.



Figure S75. Emission spectra in Ar-saturated DMA ($\lambda_{ex} = 560 \text{ nm}$) of (a) ZnP-5Bpy=Re^{Br} and ZnP-5Bpy=Re^{DMA}, (b) ZnP-6Bpy=Re^{Br} and ZnP-6Bpy=Re^{DMA}.



Figure S76. (a) CVs (Scan rate =100 mV s⁻¹) and (b) DPVs of **ZnP-***n***Bpy=Re^{Br}**, **ZnP-***n***Bpy**, and *fac*-Re(bpy)(CO)₃Br (0.5 mM) in DMA under Ar atmosphere with 0.1 M ^{*n*}Bu₄NPF₆ as a supporting electrolyte.

	$E_{1/2}^{\text{red}}$ /V	$E(^{3}\text{ZnP*}/\text{ZnP}^{-})/\text{V}^{b}$
ZnP-4Bpy	-1.84, -2.24, -2.43	-0.20
ZnP-4Bpy=Re ^{Br}	-1.68, -1.83, -1.97, -2.42	n.d. ^c
ZnP-5Bpy	-1.85, -2.24, -2.44	-0.21
ZnP-5Bpy=Re ^{Br}	-1.64, -1.82, -2.34, -2.43	n.d. ^c
ZnP-6Bpy	-1.87, -2.26	-0.23
ZnP-6Bpy=Re ^{Br}	-1.76, -1.96, -2.45	n.d. ^c
ZnP-phen	-1.79, -2.10, -2.33	-0.15
ZnP-phen=Re	-1.71, -1.894, -2.23	n.d. ^c

 Table S1. Electrochemical properties in DMA at 298 K^a

^{*a*} $E_{1/2}$ vs. Fc/Fc⁺. ^{*b*} Excited state reduction potentials of the Zn porphyrin units were calculated from $E_{1/2}^{\text{red}} + E_{00}$ (1.64 eV, see: Y. Kuramochi, Y. Fujisawa, A. Satake, *J. Am. Chem. Soc.* 2020, **142**, 705). ^{*c*} Not determined.



Figure S77. (Left) Energy levels of the frontier orbitals of **ZnP-***n***Bpy=Re^{Br}** (n = 4 (green), 5 (blue), and 6 (red)) obtained from DFT calculations and redox potentials obtained from DPV measurement in DMA. The structures without (a, b) and with (c, d) the axial-coordinated DMA were optimized at the B3LYP/LANL2DZ/6-31G(d) level without (a, c) and with (b, d) using PCM with the default parameter for DMA. (Right) Redox potentials obtained from the DPV measurements. The trends of the HOMO energy levels among the 4-, 5- and 6-positions were well consistent with the experimental results when the solvent effect was considered.



Figure S78. Energy level diagrams and frontier orbitals of **ZnP-***n***Bpy=Re^{Br}** (n = 4, 5, and 6) with axial-coordinated DMA. The structures were optimized at the B3LYP/LANL2DZ/6-31G(d) level using PCM with the default parameter for DMA (isovalue = 0.02). DMA coordination to the Zn porphyrin can occur from above and below the direction of the Re complex units (the more stable structures are shown in this figure). The HOMO and LUMO energy levels are unaffected by the DMA coordination direction.



Figure S79. Spin density plots of the OERS of the ZnP-*n*Bpy=Re series with and without the Br ligand, the DMA adducts, and their TEOA and CO₂ adducts. The Zn porphyrin units have the axial-coordinated DMA. The structures were optimized at the B3LYP/6-31G+(d)/LANL2DZ levels using PCM with the default parameter for DMA.



Figure S80. (a) CVs (Scan rate =100 mV s⁻¹) and (b) DPVs of ZnT(^tBuP)P and ZnTPP (3.0 mM) in DMA under Ar atmosphere with 0.1 M ^{*n*}Bu₄NPF₆ as a supporting electrolyte. Due to the very low solubility of ZnTMP in DMA, the CV measurement could not be performed.



Figure S81. Energy diagrams of **ZnP**-*n***Bpy=Re**^{**Br**} (n = 4, 5, and 6) and **ZnP**-**phen=Re** (phen), and BIH in DMA at 298 K. The energy level of the T₁ of the zinc porphyrin (1.6 eV) was estimated from the value of **ZnP**-**phen=Re** (See: Y. Kuramochi, Y. Fujisawa, A. Satake, *J. Am. Chem. Soc.* 2020, **142**, 705). The energy levels of the charge-separated states from the ground state were calculated using $E(ZnP/ZnP^-) = -1.84$ V for **ZnP**-**4Bpy**, -1.85 V for **ZnP**-**5Bpy**, and -1.87 V for **ZnP**-**6Bpy**, $E(Re/Re^-) = -1.68$ V for **ZnP**-**4Bpy=Re**^{**Br**}, -1.64 V for **ZnP**-**5Bpy=Re**^{**Br**}, and -1.76 V for **ZnP**-**6Bpy=Re**^{**Br**}, and $E(BIH^+/BIH) = -0.10$ V vs. Fc/Fc⁺.



Figure S82. Formation of the CO_2 -TEOA zwitterionic adduct.



Figure S83. Emission spectral changes during the measurements in DMA ($\lambda_{ex} = 560 \text{ nm}$) of (a) **ZnP-5Bpy=Re**^{Br} (b) **ZnP-5Bpy=Re**^{DMA}, (c) **ZnP-6Bpy=Re**^{Br}, and (d) **ZnP-6Bpy=Re**^{DMA}. Each measurement (scan) takes approximately five minutes.



Figure S84. Emission spectral change during the measurements in DMA-TEOA (4:1 v/v) ($\lambda_{ex} = 560 \text{ nm}$) of **ZnP-5Bpy=Re^{DMA}**. Each measurement (scan) takes approximately five minutes. The sample was prepared by dissolving **ZnP-5Bpy=Re^{MeCN}** in DMA and then diluting with DMA-TEOA.


Figure S85. Time dependence of CO formation during irradiation at 420 nm by LED lamps (Input power: 30 mW), in a merry-go-round irradiation apparatus, of CO₂-saturated DMA solutions containing the dyad (0.05 mM) and BIH (0.05 M) in the presence of phenol (0.1 M). Green: ZnP-4Bpy=Re^{Br}, blue: ZnP-5Bpy=Re^{Br}, red: ZnP-6Bpy=Re^{Br}, black: ZnP-phen=Re. CO was selectively produced without forming detectable amounts of H₂, CH₄, and HCOOH.



Figure S86. Time dependence of H₂ formation during irradiation at 420 nm by LED lamps (Input power: 30 mW), in a merry-go-round irradiation apparatus, of CO₂-saturated DMA-TEOA (4:1 v/v) solutions containing the dyad (0.05 mM) and BIH (0.05 M). Green filled diamond: **ZnP-4Bpy=Re^{Br}**, blue filled square: **ZnP-5Bpy=Re^{Br}**, red filled triangle: **ZnP-6Bpy=Re^{Br}**, black filled circle: **ZnP-phen=Re**. Plot of **ZnP-phen=Re** (0.05 mM) in CO₂-saturated DMA containing BIH (0.05 M) and phenol (0.1 M) was shown as black open circles.



Figure S87. UV-vis absorption spectra of CO₂-saturated DMA-TEOA (4:1 v/v) solutions containing the dyad (0.05 mM) and BIH (0.05 M) after irradiation at 560 nm from LED lamps (input power: 30 mW) with a merry-go-round apparatus for 17 h.



Figure S88. UV-vis absorption spectral change during irradiation (0–60 min) at 420 nm (Xe lamp, 1.8×10^{-7} einstein s⁻¹) of CO₂ saturated DMA–TEOA (4:1 v/v) solutions containing BIH (0.05 M) and **ZnP-5Bpy=Re^{Br}** (0.05 mM). Purple dotted and solid lines show the spectra before and after the irradiation, respectively.



Figure S89. Plot of the Φ_{CO} versus the initial concentration of BIH in the photocatalytic CO₂ reduction (Xe lamp, 420 nm, 3.6×10^{-8} einstein s⁻¹) using the DMA solutions containing **ZnP-phen=Re** (0.05 mM) and phenol (0.1 M). The quenching efficiency relative to η_q at [BIH] = 50 mM was calculated using $\eta_q = [BIH] K_{SV} / (1 + [BIH] K_{SV})$.



Figure S90. A plausible reaction mechanism for the **ZnP-***n***Bpy=Re** series in the absence of TEOA. The catalytic cycle is based on the following literature: Y. Kou, Y. Nabetani, D. Masui, T. Shimada, S. Takagi, H. Tachibana, H. Inoue, *J. Am. Chem. Soc.* 2014, **136**, 6021–6030.



Figure S91. Turnover frequency (TOF_{CO}) as a function of Br ion concentration during irradiation at 420 nm by LED lamps (input power: 0.5 mW), in a merry-go-round irradiation apparatus, of CO₂-saturated DMA–TEOA (4:1 v/v) solutions containing **ZnP-5Bpy=Re^{Br}** (0.05 mM) and BIH (0.05 M) with various amounts (0–1.5 mM) of hexadecyltrimethylammonium bromide.



Iminoester complex

Figure S92. Formation of the iminoester complex.



Figure S93. IR spectral changes of (a) $ZnP-5Bpy=Re^{DMA}$ and (b) $ZnP-6Bpy=Re^{DMA}$ in Arsaturated DMA after addition of TEOA for 20 h to give a DMA-TEOA solution (400:1 v/v). Concentrations of the dyads: 9 mM.



Figure S94. UV-vis absorption spectra of $ZnP-5Bpy=Re^{Br}$ in DMA, DMA-TEOA (4:1 v/v), and dichloromethane.



Figure S95. UV-vis absorption spectral changes of (a) **ZnP-5Bpy=Re**^{DMA}, (b) **ZnP-5Bpy=Re**^{Br}, (c) **ZnP-5Bpy**, and (d) **ZnP-6Bpy=Re**^{DMA} (3 μ M) in Ar-saturated dichloromethane during addition of TEOA. Insets show magnifications of the Soret band region.



Figure S96. Comparison of the relative absorption changes at the Soret bands of ZnP-5Bpy=Re^{DMA}, ZnP-5Bpy=Re^{Br}, ZnP-5Bpy, and ZnP-6Bpy=Re^{DMA} in Ar-saturated dichloromethane during addition of TEOA. [TEOA] = (a) 0–20 μ M, (b) 0–100 μ M.



Figure S97. The Benesi-Hildebrand plots of (a) **ZnP-5Bpy=Re**^{DMA}, (b) **ZnP-5Bpy=Re**^{Br}, (c) **ZnP-5Bpy**, and (d) **ZnP-6Bpy=Re**^{DMA} in Ar-saturated dichloromethane during addition of TEOA.



Figure S98. UV-vis absorption spectral changes of (a) ZnP-5Bpy=Re^{Br}, (b) ZnP-5Bpy=Re^{DMA} (3 μ M) in Ar-saturated dichloromethane during addition of DMA. Insets show magnifications of the Soret band region. Absorption changes at the Soret bands of (c) ZnP-5Bpy=Re^{Br} and (d) ZnP-5Bpy=Re^{DMA}. Insets show the Benesi-Hildebrand plots. The apparent binding constants (K_{app}^{DMA}) were estimated to be 34 and 29 M⁻¹ for ZnP-5Bpy=Re^{Br} and ZnP-5Bpy=Re^{DMA}, respectively.

Proportion of Zn porphyrin with TEOA coordination in DMA-TEOA

The apparent binding constants of Zn porphyrins with TEOA and DMA were defined to be the following equations (S1) and (S2):

$$ZnP + TEOA \xrightarrow{K_{app}} ZnP-TEOA : K_{app} = \frac{[ZnP-TEOA]}{[ZnP][TEOA]}$$
(S1)
$$ZnP + DMA \xrightarrow{K_{app}} ZnP-DMA : K_{app}^{DMA} = \frac{[ZnP-DMA]}{[ZnP][DMA]}$$
(S2)

The apparent binding constants of **ZnP-5Bpy=Re^{DMA}** in dichloromethane were estimated to be $K_{app} = 330 \text{ M}^{-1}$ and $K_{app}^{DMA} = 29 \text{ M}^{-1}$ for TEOA and DMA, respectively. The equilibrium constant between the TEOA- and DMA-coordinated Zn porphyrins was defined to be equation (S3):

$$ZnP-TEOA + DMA \xrightarrow{K} ZnP-DMA + TEOA : K = \frac{[ZnP-DMA][TEOA]}{[ZnP-TEOA][DMA]}$$
 (S3)

In a mixed solvent of DMA-TEOA (4:1 v/v), the concentrations of DMA and TEOA were calculated to be 8.63 M and 1.51 M, respectively. Since [DMA], [TEOA] >> [ZnP-DMA], [ZnP-TEOA], the equation S3 became $K = [Zn-DMA]/[ZnP-TEOA] \times 0.18$. By using S1 and S2, $K = K_{app}^{DMA} / K_{app}$ and the ratio of the TEOA- and DMA-coordinated Zn porphyrins was expressed as equation S4.

$$\frac{[\text{ZnP-DMA}]}{[\text{ZnP-TEOA}]} = \frac{K_{app}^{DMA}}{K_{app}} \times 5.7$$
(S4)

Therefore, the proportions of the TEOA- and DMA-coordinated Zn porphyrins were estimated to be 67% and 33% in Ar-saturated DMA-TEOA (4:1 v/v), respectively. When the value under CO₂ atmosphere was used ($K_{app} = 760 \text{ M}^{-1}$), the proportion of the TEOA-coordinated Zn porphyrin increased to be 82% in CO₂-saturated DMA-TEOA (4:1 v/v). Here, the value of *K* estimated from the titrations in dichloromethane was much smaller than the value (*K* =1000) in DMA from the IR spectra, suggesting that TEOA is deprotonated and more strongly bound to the dyad in the DMA-TEOA mixed solution.



Figure S99. UV-vis absorption spectral changes of (a) ZnP-5Bpy=Re^{Br}, (b) ZnP-5Bpy=Re^{DMA} (3 μ M) in CO₂-saturated dichloromethane during addition of TEOA. Insets show magnifications of the Soret band region. Absorption changes at the Soret bands of (c) ZnP-5Bpy=Re^{Br} and (d) ZnP-5Bpy=Re^{DMA}. Insets show the Benesi-Hildebrand plots.



Figure S100. A plausible reaction mechanism for **ZnP-5Bpy=Re** in the presence of TEOA. The catalytic cycle is based on the following literature: K. Kamogawa, Y. Shimoda, K. Miyata, K. Onda, Y. Yamazaki, Y. Tamaki, O. Ishitani, Mechanistic Study of Photocatalytic CO₂ Reduction Using a Ru(ii)-Re(i) Supramolecular Photocatalyst. *Chem. Sci.* 2021, **12**, 9682–9693.