Supplementary Information

## Photocatalytic CO<sub>2</sub> Reduction Sensitized by a Special-Pair Mimic Porphyrin Connected with a Rhenium(I) Tricarbonyl Complex

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#### 5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bipyridine (5Bpy-B(OR)2).



In a 100 mL three necked flask were placed 5-bromo-2,2'-bipyridine (1.0 g, 4.3 mmol) and dry diethyl ether (50 mL). The solution degassed by freeze-thaw cycles was cooled to -78 °C under Ar atmosphere, and *n*–BuLi (1.57 M in hexane, 4.1 mL, 6.6 mmol) was slowly added to it. After stirred for 1.5 h at -78 °C, the mixture was added by triisopropylborate (1.5 mL, 6.5 mmol) and was slowly warmed to room temperature. The solution was quenched by adding 2 M HCl aqueous solution (ca. 30 mL) to pH =1 and then the pH was adjusted to pH = 11 by careful addition of 3 M NaOH aqueous solution. The aqueous solution was washed with CHCl<sub>3</sub> (ca. 50 mL×3) and adjusted to pH = 6 by adding HCl aqueous solution, and the solvent was evaporated in vacuo. Pinacol (580 mg, 4.9 mmol) was added to the residue and refluxed in toluene (250 mL) for overnight. The insoluble material was removed by filtration and the solvent was evaporated to dryness, giving a pale brawn solid (960 mg, 79%). <sup>1</sup>H NMR (300 Hz, CDCl<sub>3</sub>)  $\delta$ /ppm = 9.03 (s, 1H), 8.70 (dd, *J* = 4.8, 1.5 Hz, 1H), 8.46 (d, *J* = 7.8 Hz, 1H), 8.39 (d, *J* = 7.8 Hz, 1H), 8.21 (dd, *J* = 7.8, 1.5 Hz, 1H), 7.32 (ddd, *J* = 7.8, 4.8, 1.5 Hz, 1H), 1.37 (s, 12H).

5-(4-Iodophenyl)-15-(1-methylimidazol-2-yl)-10,20-bis(3-allyloxypropyl)porphyrin (Im<sup>Me</sup>-H<sub>2</sub>P-PhI).



Im<sup>Me</sup>-H<sub>2</sub>P-PhI

In a three-necked 1 L flask were placed 1-methyl-imidazole-2-carbaldehyde (220 mg, 2.0 mmol), 4-iodobenzaldehyde (470 mg, 2.0 mmol), and *meso*-(3-allyloxypropyl)dipyrromethane (990 mg, 4.1 mmol), and CHCl<sub>3</sub> (500 mL). The mixture was degassed by bubbling with Ar gas for 15 min and then trifluoroacetic acid (TFA, 0.47 mL, 6.1 mmol) in CHCl<sub>3</sub> (ca. 2 mL) was slowly added. The reaction mixture was stirred at room temperature in dark and the reaction progress was monitored with silica gel TLC. After being stirred for 3 h, TFA (0.15 mL, 2.0 mmol) was further

added because the starting materials remained. After stirred for overnight, the mixture was added by triethylamine (1.1 mL, 8.0 mmol) and p-chloranil (2.0 g, 8.2 mmol) and stirred at room temperature for overnight. The resulting mixture was concentrated and passed through a Celite column. The solvent of the filtrate was evaporated to dryness and the residue was purified with an alumina column (eluent:  $CHCl_3/acetone = 10/1$ ) and a silica gel column (eluent:  $CHCl_3/acetone$ =  $10/1 \rightarrow 2/1$ ). The collected solution was evaporated to dryness, giving a purple solid (250 mg, 16% yield). TLC (silica gel, CHCl<sub>3</sub>/acetone = 10/1)  $R_f = 0.2$ ; MALDI-TOF-mass (dithranol) m/z  $[M+H]^+$  789.2458, calcd for  $[C_{42}H_{42}IN_6O_2]^+$  789.2408; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 9.54 (d, J = 4.8 Hz, 2H,  $\beta$ -pyrrole), 9.50 (d, J = 4.9 Hz, 2H,  $\beta$ -pyrrole), 8.85 (d, J = 4.8 Hz, 2H,  $\beta$ pyrrole), 8.80 (d, J = 4.9 Hz, 2H,  $\beta$ -pyrrole), 8.12 (d, J = 8.0 Hz, 1H, phenylene), 8.09 (d, J = 8.0Hz, 1H, phenylene), 7.97 (d, J = 8.0 Hz, 1H, phenylene), 7.87 (d, J = 8.0 Hz, 1H, phenylene), 7.69 (d, J = 1.5 Hz, 1H, Im), 7.48 (d, J = 1.5 Hz, 1H, Im), 6.08 (m, 2H, -CH=), 5.42 (dd, J = 17, 1.7) Hz, 2H, =CH<sub>2</sub>), 5.27 (dd, J = 10, 1.7 Hz, 2H, =CH<sub>2</sub>), 5.11 (t, J = 7.4 Hz, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 4.07 (dd, J = 5.5, 1.7 Hz, 4H, -OCH<sub>2</sub>-), 3.65 (t, J = 5.7 Hz, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 3.40 (s, 3H, CH<sub>3</sub>), 2.80 (quin, J = 6.5 Hz, 4H, -CH<sub>2</sub>CH<sub>2</sub>-), -2.71 (s, 2H, NH); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 148.81 (C), 143-148 (C, br), 142.02 (C), 135.92 (CH), 135.64 (CH), 134.98 (CH), 131.70 (CH, br), 130.58 (CH, br), 129.20 (CH, br), 128.34 (CH), 127.93 (CH, br), 121.35 (CH), 119.47 (C), 118.98 (C), 116.83 (CH<sub>2</sub>), 104.52 (C), 94.09 (C), 71.95 (CH<sub>2</sub>), 69.07 (CH<sub>2</sub>), 37.77 (CH<sub>2</sub>), 34.47 (CH<sub>3</sub>), 31.25 (CH<sub>2</sub>).

Zinc(II) 5-(4-iodophenyl)-15-(1-methylimidazol-2-yl)-10,20-bis(3-allyloxypropyl)porphyrin ([Im<sup>Me</sup>-ZnP-PhI]<sub>2</sub>).



[Im<sup>Me</sup>-ZnP-Phl]<sub>2</sub>

Zinc(II) acetate (110 mg, 0.57 mmol) in methanol (ca. 3 mL) was added to a solution of  $Im^{Me}$ -H<sub>2</sub>P-PhI (58 mg, 0.073 mmol) in CHCl<sub>3</sub> (50 mL). The mixture was stirred for 18 h at room temperature. The resulting solution was washed with water. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness, affording the titled compound as a purple solid (45 mg, 73% yield). TLC (silica gel, CHCl<sub>3</sub>/acetone = 10/1)  $R_f = 0.8$ ; MALDI-TOF-mass (dithranol) m/z [M+H]<sup>+</sup> 851.1542, calcd for [C<sub>42</sub>H<sub>40</sub>IN<sub>6</sub>O<sub>2</sub>Zn]<sup>+</sup> 851.1543; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 9.64 (d, J = 4.8 Hz, 2H,  $\beta$ -pyrrole), 9.01 (d, J = 4.8 Hz, 2H,  $\beta$ -pyrrole), 8.95 (d, J = 4.8 Hz, 2H,  $\beta$ -pyrrole), 8.41 (d, J = 7.9 Hz, 1H, phenylene), 8.27 (d, J = 7.9 Hz, 1H, phenylene), 8.09 (d, J = 7.9 Hz, 1H, phenylene), 7.87 (d, J = 7.9 Hz, 1H, phenylene), 6.18 (m, 2H, -CH=), 5.52 (dd, J = 17, 1.8 Hz, 2H, =CH<sub>2</sub>), 5.46 (d, J = 1.7 Hz, 1H, Im), 5.39 (d, J = 4.8 Hz, 2H,  $\beta$ -pyrrole), 5.34 (dd, J = 10, 1.8 Hz, 2H, =CH<sub>2</sub>), 5.22 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 4.22 (d, J = 5.5 Hz, 4H, -OCH<sub>2</sub>-), 3.91 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 3.03 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 2.05 (d, J = 1.7 Hz, 1H, Im), 1.61 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 151.24 (C), 150.11 (C), 148.80 (C), 148.15 (C), 146.18 (C), 143.91 (C), 136.59 (CH), 136.41 (CH), 135.61 (CH), 135.44 (CH), 135.42 (CH), 131.83 (CH), 129.53 (CH), 128.73 (CH), 127.28 (CH), 121.46 (CH), 119.78 (C), 119.47 (C), 117.98 (CH), 116.95 (CH<sub>2</sub>), 96.42 (C), 93.58 (C), 72.20 (CH<sub>2</sub>), 70.18 (CH<sub>2</sub>), 38.73 (CH<sub>2</sub>), 32.77 (CH<sub>3</sub>), 32.19 (CH<sub>2</sub>).





In a 20 mL Schlenk tube were placed  $[Im^{Me}-ZnP-PhI]_2$  (45 mg, 0.053 mmol), 5-(4,4,5,5tetramethyl-1,3,2-dioxaborolan-2-yl)-2,2'-bipyridine (45 mg, 0.16 mmol), Cs<sub>2</sub>CO<sub>3</sub> (140 mg, 0.43 mmol), toluene (4.0 mL), *N*,*N*-dimethylformamide (2.0 mL), and water (250 µL). The mixture degassed by freeze-thaw cycles and replaced with Ar gas was added by Pd(PPh<sub>3</sub>)<sub>4</sub> (12 mg, 0.010 mmol) and stirred at 90 °C for 18 h. CHCl<sub>3</sub> (ca. 50 mL) and water (ca. 25 mL) were added to the resulting solution, and the organic layer was washed with water and passed through Phase Separator paper (Whatman). The solvent was evaporated to dryness and the residue was purified with a flush silica gel column (eluent: CHCl<sub>3</sub>  $\rightarrow$  CHCl<sub>3</sub>/pyridine = 1/1). Further purification by precipitation with CHCl<sub>3</sub> and methanol afforded 39 mg (84% yield) of the titled compound as a dark purple solid. TLC (silica gel, CHCl<sub>3</sub>/pyridine = 10/1)  $R_f = 0.5$ ; MALDI-TOF-mass (dithranol) m/z [M+H]<sup>+</sup> 879.4359, calcd for [C<sub>52</sub>H<sub>47</sub>N<sub>8</sub>O<sub>2</sub>Zn]<sup>+</sup> 879.3108; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 9.68 (d, *J* = 4.6 Hz, 2H,  $\beta$ -pyrrole), 9.38 (d, *J* = 2.5 Hz, 1H, bpy 6), 9.12 (d, *J* = 4.6 Hz, 2H, β-pyrrole), 8.98 (d, J = 4.6 Hz, 2H, β-pyrrole), 8.83 (dd, J = 7.7 and 2.0 Hz, 1H, phenylene), 8.80 (d, J = 5.0 Hz, 1H, bpy 6'), 8.69 (d, J = 7.9 Hz, 1H, bpy 3), 8.59 (d, J = 7.6 Hz, 1H, bpy 3'), 8.45 (dd, J = 7.9, 2.5 Hz, 1H, bpy 4), 8.29 (dd, J = 7.8, 2.0 Hz, 1H, phenylene), 8.25 (dd, J = 7.7, 2.0 Hz, 1H, phenylene), 8.07 (dd, J = 7.8, 2.0 Hz, 1H, phenylene), 7.92 (td, J = 7.6, 2.0 Hz, 1H, bpy 4'), 7.39 (dd, J = 7.6, 5.0 Hz, 1H, bpy 5'), 6.19 (m, 2H, -CH=), 5.53 (d, J = 14 Hz, 2H, =CH<sub>2</sub>), 5.51 (1H, Im), 5.43 (d, J = 4.6 Hz, 2H, β-pyrrole), 5.34 (d, J = 10 Hz, 2H, =CH<sub>2</sub>), 5.25 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 4.23 (d, J = 5.0 Hz, 1H, Im), 1.66 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 156.18 (C), 155.25 (C), 151.25 (C), 150.09 (C), 149.52 (CH), 149.07 (C), 148.17 (C), 148.13 (CH), 146.24 (C), 144.48 (C), 137.23 (CH), 136.72 (C), 136.37 (C), 135.67 (CH), 135.51 (CH), 135.45 (CH), 132.03 (CH), 129.50 (CH), 128.66 (CH), 127.27 (CH), 125.19 (CH), 124.97 (CH), 123.96 (CH), 121.54 (CH), 121.41 (CH), 121.34 (CH), 120.57 (C), 119.42 (C), 117.98 (CH), 116.93 (CH<sub>2</sub>), 96.38 (C), 72.19 (CH<sub>2</sub>), 70.20 (CH<sub>2</sub>), 38.72 (CH<sub>2</sub>), 32.78 (CH<sub>3</sub>), 32.20 (CH<sub>2</sub>).

Dimer of Zn porphyrin=Re complex dyad ([Im<sup>Me</sup>-ZnP-Ph-5Bpy=Re]<sub>2</sub>).



In a 20 mL Schlenk tube were  $[Im^{Me}-ZnP-Ph-5Bpy]_2$  (11 mg, 0.013 mmol), Re(CO)<sub>5</sub>Br (5.4 mg, 0.013 mmol), and toluene (6.0 mL). The mixture was heated to 90 °C and stirred for 18 h. The resulting precipitate was collected by centrifugation and washed with toluene (ca. 5 mL×3). The solid was dried in vacuo, giving the titled compound as a purple solid (10 mg, 62% yield). <sup>1</sup>H NMR (500 MHz, DMF- $d_7$ )  $\delta$ /ppm = 9.86 (d, J = 4.0 Hz, 2H,  $\beta$ -pyrrole), 9.31 (d, J = 5.5 Hz, 1H, bpy), 9.20 (d, J = 4.6 Hz, 2H,  $\beta$ -pyrrole), 9.16 (m, 2H, bpy), 9.12 (d, J = 4.0 Hz, 2H,  $\beta$ -pyrrole), 9.06 (d, J = 8.0 Hz, 1H, bpy), 9.00 (dd, J = 7.5, 2.0 Hz, 1H, phenylene), 8.67 (dd, J = 7.5, 2.0 Hz, 1H, phenylene), 8.56–8.48 (m, 2H, phenylene and bpy), 8.46 (dd, J = 7.5, 2.0 Hz, 1H, phenylene), 7.94 (dd, J = 7.9, 5.5 Hz, 1H, bpy), 6.23 (m, 2H, -CH=), 6.07 (d, J = 2.0 Hz, 1H, Im), 5.57 (d, J = 17 Hz, 2H, =C $H_2$ ), 5.48 (d, J = 4.6 Hz, 2H,  $\beta$ -pyrrole), 5.27 (m, 4H, -C $H_2$ CH<sub>2</sub>CH<sub>2</sub>-), 5.33 (d, J = 11 Hz, 2H, =C $H_2$ ), 4.29 (d, J = 5.2 Hz, 4H, -OC $H_2$ -), 4.04 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 3.25–2.96

(m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 2.18 (d, J = 2.0 Hz, 1H, Im), 1.80 (s, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, DMF- $d_7$ )  $\delta$ /ppm = 198.09 (CO), 198.00 (CO), 189.90 (CO), 155.93 (C), 154.84 (C), 153.62 (CH), 151.27 (CH), 150.28 (C), 148.80 (C), 148.27 (C), 145.83 (C), 145.81 (C), 140.49 (CH), 139.79 (C), 138.40 (CH), 136.19 (CH), 135.90 (CH), 135.68 (CH), 133.80 (C), 131.77 (CH), 129.96 (CH), 129.14 (CH), 128.36 (C), 127.97 (CH), 127.34 (CH), 125.80 (CH), 125.68 (CH), 124.98 (CH), 124.82 (CH), 121.13 (CH), 120.14 (C), 119.99 (C), 119.14 (CH), 115.78 (CH<sub>2</sub>), 97.04 (C), 71.77 (CH<sub>2</sub>), 70.09 (CH<sub>2</sub>), 39.25 (CH<sub>2</sub>), 32.25 (CH<sub>3</sub>), 31.94 (CH<sub>2</sub>).

# 5-(4-Tolyl)-15-(1-methylimidazol-2-yl)-10,20-bis(3-allyloxypropy)porphyrin (Im<sup>Me</sup>-H<sub>2</sub>P-PhCH<sub>3</sub>).



Im<sup>Me</sup>-H<sub>2</sub>P-PhCH<sub>3</sub>

In a 500 mL three-necked flask were placed 1-methyl-imidazole-2-carbaldehyde (170 mg, 1.5 mmol), p-tolualdehyde (190 mg, 1.5 mmol), meso-(3-allyloxypropyl)dipyrromethane (740 mg, 3.0 mmol), and CHCl<sub>3</sub> (300 mL), and the mixture was degassed by bubbling with Ar gas for 15 min. Trifluoroacetic acid (TFA, 0.34 mL, 4.4 mmol) in CHCl<sub>3</sub> (ca. 2 mL) was slowly added, and the reaction mixture was stirred at room temperature in dark. After stirred for 3 h, the mixture was added by triethylamine (0.63 mL, 4.5 mmol) and p-chloranil (1.2 g, 4.7 mmol) and stirred at room temperature for overnight. The resulting mixture was evaporated to dryness and the residue was purified with an alumina column (eluent:  $CHCl_3/acetone = 10/1$ ) and silica gel columns (eluent:  $CHCl_3 \rightarrow CHCl_3/acetone = 10/1$ ). The collected solution was evaporated to dryness, giving a purple solid (120 mg, 12% yield). TLC (silica gel, CHCl<sub>3</sub>/acetone = 10/1)  $R_f = 0.3$ ; MALDI-TOFmass (dithranol) m/z  $[M+H]^+$  677.3547, calcd for  $[C_{43}H_{45}N_6O_2]^+$  677.3598; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 9.54 (d, J = 4.8 Hz, 2H,  $\beta$ -pyrrole), 9.47 (d, J = 4.8 Hz, 2H,  $\beta$ -pyrrole), 8.90 (d, J = 4.8 Hz, 2H,  $\beta$ -pyrrole), 8.79 (d, J = 4.8 Hz, 2H,  $\beta$ -pyrrole), 8.12 (d, J = 7.7 Hz, 1H, phenylene), 8.01 (d, J = 7.7 Hz, 1H, phenylene), 7.69 (d, J = 1.5 Hz, 1H, Im), 7.58 (d, J = 7.7 Hz, 1H, phenylene), 7.54 (d, J = 7.7 Hz, 1H, phenylene), 7.48 (d, J = 1.5 Hz, 1H, Im), 6.08 (m, 2H, -CH=), 5.41 (dd, J = 17, 1.7 Hz, 2H, =CH<sub>2</sub>), 5.26 (dd, J = 10, 1.7 Hz, 2H, =CH<sub>2</sub>), 5.11 (t, J = 7.4 Hz, 4H,  $-CH_2CH_2CH_2$ -), 4.07 (dd, J = 5.5, 1.7 Hz, 4H,  $-OCH_2$ -), 3.65 (t, J = 5.8 Hz, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 3.40 (s, 3H, CH<sub>3</sub>), 2.79 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>-), 2.73 (s, 3H, CH<sub>3</sub>), -2.66 (s, 2H, NH).

Zinc(II) 5-(4-tolyl)-15-(1-methylimidazol-2-yl)-10,20-bis(3-allyloxypropy)porphyrin ([Im<sup>Me</sup>-ZnP-PhCH<sub>3</sub>]<sub>2</sub>, D).



Zinc(II) acetate (120 mg, 0.64 mmol) in methanol (ca. 3 mL) was added to a solution of  $Im^{Me}$ -H<sub>2</sub>P-PhCH<sub>3</sub> (120 mg, 0.18 mmol) in CHCl<sub>3</sub> (100 mL). The mixture was stirred for 3 h at room temperature. The resulting solution was washed with water. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness, affording the titled compound as a purple solid (120 mg, 92% yield). TLC (silica gel, CHCl<sub>3</sub>/acetone = 10/1)  $R_f$  = 0.9; MALDI-TOF-mass (dithranol) m/z [M]<sup>+</sup> 738.2666, calcd for [C<sub>43</sub>H<sub>42</sub>N<sub>6</sub>O<sub>2</sub>Zn]<sup>+</sup> 738.2660; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 9.62 (d, *J* = 4.4 Hz, 2H,  $\beta$ -pyrrole), 9.05 (d, *J* = 4.4 Hz, 2H,  $\beta$ -pyrrole), 8.94 (d, J = 4.4 Hz, 2H,  $\beta$ -pyrrole), 8.55 (dd, *J* = 7.6, 2.0 Hz, 1H, phenylene), 8.04 (dd, *J* = 7.6, 2.0 Hz, 1H, phenylene), 7.74 (dd, *J* = 7.6, 2.0 Hz, 1H, phenylene), 7.57 (dd, *J* = 7.6, 2.0 Hz, 1H, phenylene), 6.18 (m, 2H, -CH=), 5.52 (m, 3H, =CH<sub>2</sub> and Im), 5.40 (d, *J* = 4.4 Hz, 2H,  $\beta$ -pyrrole), 5.33 (dd, *J* = 11, 1.7 Hz, 2H, =CH<sub>2</sub>), 5.21 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 4.22 (d, *J* = 5.4 Hz, 4H, -OCH<sub>2</sub>-), 3.93 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 3.04 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 2.81 (s, 3H, CH<sub>3</sub>), 2.12 (d, *J* = 1.8 Hz, 1H, Im), 1.65 (s, 3H, CH<sub>3</sub>).

### Covalent linked dimer of Zn porphyrin (C-[Im<sup>Me</sup>-ZnP-PhCH<sub>3</sub>]<sub>2</sub>, D').



In a 200 mL flask were placed  $[Im^{Me}-ZnP-PhCH_3]_2$  (9.7 mg,  $6.0 \times 10^{-6}$  mol), Grubbs catalyst (1<sup>st</sup> generation, 9.8 mg,  $1.2 \times 10^{-6}$  mol), and CHCl<sub>3</sub> (100 mL). The mixture was stirred at room temperature under Ar atmosphere. The reaction progress was monitored with UV–vis absorption

spectra in pyridine and MALDI-TOF mass spectra. After being stirred for 3.5 h, the resulting solution was washed with water and subsequently brine. The organic layer was dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> and evaporated to dryness. The residue was purified with a silica gel column (eluent: CHCl<sub>3</sub>). The collected solution was evaporated to dryness, giving a purple solid (6.3 mg, 74% yield). MALDI-TOF-mass (dithranol) m/z [M]<sup>+</sup> 1420.4938, calcd for [C<sub>82</sub>H<sub>76</sub>N<sub>12</sub>O<sub>4</sub>Zn<sub>2</sub>]<sup>+</sup> 1420.4695; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 9.57–9.49 (m, 2H,  $\beta$ -pyrrole), 9.06–8.87 (m, 4H,  $\beta$ -pyrrole), 8.62–8.51 (m, 1H, phenylene), 8.06–7.94 (m, 1H, phenylene), 7.77–7.69 (m, 1H, phenylene), 7.60–7.48 (m, 1H, phenylene), 6.43 (t, *J* = 2.8 Hz, 1.5H, -C*H*=), 6.09 (t, *J* = 2.8 Hz, 0.5H, -C*H*=), 5.03–5.32 (m, 7H,  $\beta$ -pyrrole, Im, -C*H*<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 4.66 (d, *J* = 2.8 Hz, 1H, -OC*H*<sub>2</sub>-), 4.41 (d, *J* = 2.8 Hz, 3H, -OC*H*<sub>2</sub>-), 4.29–4.09 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 3.34–2.90 (m, 4H, -CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>-), 2.80 (s, 3H, CH<sub>3</sub>), 2.10 (m, 1H, Im), 1.68–1.65 (m, 3H, CH<sub>3</sub>).

#### 2-(4,4-Dimethylpentan-2-yl)-5,7,7-trimethyloctyl chloride.



FINEOXOCOL180<sup>®</sup> (10 g, 39 mmol) and dry DMF (0.6 mL) were placed in a 50 mL flask, and SOCl<sub>2</sub> (5.0 mL, 69 mmol) was added to it. The mixture was heated to 80 °C and stirred for 6h. After SOCl<sub>2</sub> was removed in vacuo, DMF was completely removed by repeating addition of toluene (5 mL) and evaporation three times. The brown residue was purified with a flush silica gel column (eluent: hexane) to give the titled compound (11 g, 94% yield). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 3.71–3.27 (m, 2H, CH<sub>2</sub>), 1.96–1.74 (m, 1H, CH), 1.51–0.78 (m, 16H), 0.90 (s, 9H, <sup>t</sup>Bu), 0.89 (s, 9H, <sup>t</sup>Bu).

#### 1-{2-(4,4-Dimethylpentan-2-yl)-5,7,7-trimethyloctyl}imidazole.



Imidazole (3.7 g, 54 mmol) and NaH (60% in oil, 2.1 g, 54 mmol) were placed in a 1 L threenecked flask. After being purged with Ar gas, dry DMF (500 mL) was added to it at 0 °C and then 2-(4,4-dimethylpentan-2-yl)-5,7,7-trimethyloctyl chloride (11 g, 37 mmol) was added by

dissolving in dry DMF (200 mL). The reaction mixture was stirred for 4 h at 80 °C. The reaction was quenched by adding water (200 mL) and the product was extracted with diethyl ether (100 mL×3). The organic layer was washed with 3 M HCl aqueous solution (280 mL), K<sub>2</sub>CO<sub>3</sub> aqueous solution (pH 9, 280 mL) and brine (300 mL), and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated to dryness, and the residue was purified with a flush silica gel column (eluent: hexane  $\rightarrow$  CHCl<sub>3</sub>) to give the titled compound (9.5 g, 81% yield). TLC (silica gel, CHCl<sub>3</sub>/acetone = 10/1)  $R_f = 0.4$ ; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 7.44 (s, 1H, Im), 7.05 (s, 1H, Im), 6.88 (s, 1H, Im), 4.00–3.50 (m, 2H, CH<sub>2</sub>), 1.89–0.74 (m, 35H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 137.58 (CH), 129.52 (CH), 119.09 (CH), 51.39 (CH<sub>2</sub>), 51.34 (CH<sub>2</sub>), 51.17 (CH<sub>2</sub>), 51.01 (CH<sub>2</sub>), 48.84 (CH<sub>2</sub>), 48.61 (CH<sub>2</sub>), 48.55 (CH<sub>2</sub>), 48.50 (CH<sub>2</sub>), 48.42 (CH<sub>2</sub>), 47.48 (CH), 47.40 (CH), 47.34 (CH), 38.00 (C), 37.95 (C), 37.47 (C), 37.42 (C), 31.40 (C), 31.37 (C), 31.18 (C), 31.13 (C), 31.10 (C), 30.09 (CH or CH<sub>3</sub>), 29.05 (CH or CH<sub>3</sub>), 28.93 (CH or CH<sub>3</sub>), 28.45 (CH or CH<sub>3</sub>), 26.98 (CH<sub>2</sub>), 25.50 (CH<sub>2</sub>), 25.38 (CH<sub>2</sub>), 22.79 (CH<sub>3</sub>), 22.76 (CH<sub>3</sub>), 22.59 (CH<sub>3</sub>), 22.40 (CH<sub>3</sub>), 17.95 (CH<sub>3</sub>), 17.83 (CH<sub>3</sub>), 17.61 (CH<sub>3</sub>).

1-(2-(4,4-Dimethylpentan-2-yl)-5,7,7-trimethyloctyl)imidazole-2-carbaldehyde (Im<sup>IS</sup>-CHO).



In a 500 mL flask were placed 1-{2-(4,4-dimethylpentan-2-yl)-5,7,7-trimethyloctyl}imidazole (9.5 g, 30 mmol) and dry THF (100 mL), and then the solution was cooled to -40 °C. *n*-BuLi (1.59 M in hexane, 57 mL, 90 mmol) was added dropwise to the solution and the mixture was warmed to -20 °C. After being stirred for 3 h at -20 °C, dry DMF (35 mL, 46 mmol) was added to it. The reaction mixture was stirred for overnight at room temperature. The reaction was quenched by adding water (120 mL) and the product was extracted with diethyl ether (100 mL × 3). The organic layer was washed with 3M HCl aqueous solution (280 mL), K<sub>2</sub>CO<sub>3</sub> aqueous solution (pH 10, 280 mL), and brine (280 mL), and dried over anhydrous MgSO<sub>4</sub>. The solvent was evaporated to dryness, and the residue was purified with a flush silica gel column (eluent: CHCl<sub>3</sub>  $\rightarrow$  CHCl<sub>3</sub>/acetone = 10/1). The collected fraction was evaporated to dryness, giving pale-

brown oil (6.8 g, 66% yield). TLC (silica gel, CHCl<sub>3</sub>/acetone = 10/1)  $R_f$  = 0.7; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 9.815, 9.813, 9.812, 9.810, 9.808, 9.806 (s×6, 1H, CHO), 7.30–7.28 (m, 1H, Im), 7.15–7.13 (m, 1H, Im), 4.57–4.10 (m, 2H, CH<sub>2</sub>), 1.88–1.62 (m, 1H, CH), 1.89–0.62 (m, 34H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$ /ppm = 182.11 (CHO), 182.08 (CHO), 143.87 (C), 143.79 (C), 131.57 (CH), 126.93 (CH), 51.40 (CH<sub>2</sub>), 51.33 (CH<sub>2</sub>), 51.18 (CH<sub>2</sub>), 50.95 (CH<sub>2</sub>), 49.62 (CH<sub>2</sub>), 49.33 (CH<sub>2</sub>), 49.23 (CH<sub>2</sub>), 48.65 (CH<sub>2</sub>), 48.53 (CH<sub>2</sub>), 48.30 (CH<sub>2</sub>), 48.11 (CH<sub>2</sub>), 46.82 (CH), 46.73 (CH), 46.68 (CH), 37.78 (CH<sub>2</sub>), 37.72 (CH<sub>2</sub>), 37.37 (CH<sub>2</sub>), 31.41 (C), 31.19 (C), 31.15 (C), 31.08 (C), 30.13 (CH or CH<sub>3</sub>), 29.48 (CH or CH<sub>3</sub>), 29.96 (CH<sub>3</sub>), 29.77 (CH or CH<sub>3</sub>), 29.72 (CH<sub>3</sub>), 29.59 (CH or CH<sub>3</sub>), 29.48 (CH or CH<sub>3</sub>), 29.38 (CH or CH<sub>3</sub>), 29.30 (CH or CH<sub>3</sub>), 28.50 (CH or CH<sub>3</sub>), 26.87 (CH<sub>2</sub>), 26.74 (CH<sub>2</sub>), 25.31 (CH<sub>2</sub>), 22.85 (CH<sub>3</sub>), 22.75 (CH<sub>3</sub>), 22.58 (CH<sub>3</sub>), 22.39 (CH<sub>3</sub>), 17.83 (CH<sub>3</sub>), 17.74 (CH<sub>3</sub>), 17.61 (CH<sub>3</sub>), 17.40 (CH<sub>3</sub>).



**Figure S1.** MALDI-TOF mass (matrix: dithranol) of  $Im^{Me}-H_2P-PhI$ . Top: found, bottom: simulated by  $[C_{42}H_{42}IN_6O_2]^+$  ( $[M+H]^+$ ).



Figure S2. <sup>1</sup>H NMR spectrum of Im<sup>Me</sup>-H<sub>2</sub>P-PhI in CDCl<sub>3</sub> (300 MHz).



Figure S3. <sup>13</sup>C NMR spectrum of Im<sup>Me</sup>-H<sub>2</sub>P-PhI in CDCl<sub>3</sub> (75 MHz).



Figure S4. DEPT135 spectrum of Im<sup>Me</sup>-H<sub>2</sub>P-PhI in CDCl<sub>3</sub> (75 MHz).



**Figure S5.** MALDI-TOF mass (matrix: dithranol) of  $[Im^{Me}-ZnP-PhI]_2$ . Top: found, bottom: simulated by  $[C_{42}H_{40}IN_6O_2Zn]^+$  ( $[M+H]^+$ ).



Figure S6. <sup>1</sup>H NMR spectrum of [Im<sup>Me</sup>-ZnP-PhI]<sub>2</sub> in CDCl<sub>3</sub> (300 MHz).



Figure S7. <sup>13</sup>C NMR spectrum of [Im<sup>Me</sup>-ZnP-PhI]<sub>2</sub> in CDCl<sub>3</sub> (75 MHz).



Figure S8. DEPT135 spectrum of [Im<sup>Me</sup>-ZnP-PhI]<sub>2</sub> in CDCl<sub>3</sub> (75 MHz).



**Figure S9.** MALDI-TOF mass (matrix: dithranol) of  $[Im^{Me}-ZnP-Ph-5Bpy]_2$ . Top: found, bottom: simulated by  $[C_{52}H_{47}N_8O_2Zn]^+$  ( $[M+H]^+$ ).



Figure S10. <sup>1</sup>H NMR spectrum of [Im<sup>Me</sup>-ZnP-Ph-5Bpy]<sub>2</sub> in CDCl<sub>3</sub> (500 MHz).



Figure S11. <sup>13</sup>C NMR spectrum of [Im<sup>Me</sup>-ZnP-Ph-5Bpy]<sub>2</sub> in CDCl<sub>3</sub> (125 MHz).



Figure S12. DEPT135 spectrum of [Im<sup>Me</sup>-ZnP-Ph-5Bpy]<sub>2</sub> in CDCl<sub>3</sub> (125 MHz).



Figure S13.  $^{1}\text{H}^{-1}\text{H}$  COSY of  $[Im^{Me}-ZnP-Ph-5Bpy]_{2}$  in CDCl<sub>3</sub> (500 MHz).



Figure S14. <sup>1</sup>H NMR spectrum of [Im<sup>Me</sup>-ZnP-Ph-5Bpy=Re]<sub>2</sub> in DMF-*d*<sub>7</sub> (500 MHz).



Figure S15. <sup>13</sup>C NMR spectrum of [Im<sup>Me</sup>-ZnP-Ph-5Bpy=Re]<sub>2</sub> in DMF-d<sub>7</sub> (125 MHz).



Figure S16. DEPT135 spectrum of [Im<sup>Me</sup>-ZnP-Ph-5Bpy=Re]<sub>2</sub> in DMF-d<sub>7</sub> (125 MHz).



**Figure S17.** <sup>1</sup>H-<sup>1</sup>H COSY of **[Im<sup>Me</sup>-ZnP-Ph-5Bpy=Re]**<sub>2</sub> in DMF-*d*<sub>7</sub> (500 MHz).



Figure S18. HSQC of [Im<sup>Me</sup>-ZnP-Ph-5Bpy=Re]<sub>2</sub> in DMF-d<sub>7</sub>.



Figure S19. HMBC of [Im<sup>Me</sup>-ZnP-Ph-5Bpy=Re]<sub>2</sub> in DMF-d7.



**Figure S20.** MALDI-TOF mass (matrix: dithranol) of  $Im^{Me}-H_2P-PhCH_3$ . Top: found, bottom: simulated by  $[C_{43}H_{45}N_6O_2]^+$  ( $[M+H]^+$ ).



Figure S21. <sup>1</sup>H NMR spectrum of Im<sup>Me</sup>-H<sub>2</sub>P-PhCH<sub>3</sub> in CDCl<sub>3</sub> (300 MHz).



**Figure S22.** MALDI-TOF mass (matrix: dithranol) of  $[Im^{Me}-ZnP-PhCH_3]_2$  (**D**). Top: found, bottom: simulated by  $[C_{43}H_{42}N_6O_2Zn]^+$  ( $[M]^+$ ) and  $[C_{43}H_{43}N_6O_2Zn]^+$  ( $[M+H]^+$ ).



Figure S23. <sup>1</sup>H NMR spectrum of [Im<sup>Me</sup>-ZnP-PhCH<sub>3</sub>]<sub>2</sub> (D) in CDCl<sub>3</sub> (400 MHz).



**Figure S24.** MALDI-TOF mass (matrix: dithranol) of *C*-[Im<sup>Me</sup>-ZnP-PhCH<sub>3</sub>]<sub>2</sub> (D'). Top: found, bottom: simulated by  $[C_{82}H_{76}N_{12}O_4Zn_2]^+$  ([M]<sup>+</sup>) and  $[C_{82}H_{77}N_{12}O_4Zn_2]^+$  ([M+H]<sup>+</sup>).



Figure S25. <sup>1</sup>H NMR spectrum of *C*-[Im<sup>Me</sup>-ZnP-PhCH<sub>3</sub>]<sub>2</sub> (D') in CDCl<sub>3</sub> (400 MHz).



**Figure S26.** <sup>1</sup>H NMR spectrum of 2-(4,4-dimethylpentan-2-yl)-5,7,7-trimethyloctyl chloride in CDCl<sub>3</sub> (400 MHz).



**Figure S27.** <sup>1</sup>H NMR spectrum of 1-{2-(4,4-dimethylpentan-2-yl)-5,7,7-trimethyloctyl}imidazole in CDCl<sub>3</sub> (300 MHz).



**Figure S28.** <sup>13</sup>C NMR spectrum of 1-{2-(4,4-dimethylpentan-2-yl)-5,7,7-trimethyloctyl}imidazole in CDCl<sub>3</sub> (75 MHz).



**Figure S29.** DEPT135 spectrum of 1-{2-(4,4-dimethylpentan-2-yl)-5,7,7-trimethyloctyl}-imidazole in CDCl<sub>3</sub> (75 MHz).



**Figure S30.** <sup>1</sup>H NMR spectrum of 1-(2-(4,4-dimethylpentan-2-yl)-5,7,7-trimethyloctyl)imidazole-2-carbaldehyde in CDCl<sub>3</sub> (400 MHz).



**Figure S31.** <sup>13</sup>C NMR spectrum of 1-(2-(4,4-dimethylpentan-2-yl)-5,7,7-trimethyloctyl)imidazole-2-carbaldehyde in CDCl<sub>3</sub> (75 MHz).



**Figure S32.** DEPT135 spectrum of 1-(2-(4,4-dimethylpentan-2-yl)-5,7,7-trimethyloctyl)-imidazole-2-carbaldehyde in CDCl<sub>3</sub> (75 MHz).



**Figure S33.** <sup>1</sup>H-<sup>1</sup>H COSY of 1-(2-(4,4-dimethylpentan-2-yl)-5,7,7-trimethyloctyl)-imidazole-2-carbaldehyde in CDCl<sub>3</sub> (400 MHz).



**Figure S34.** MALDI-TOF mass (matrix: dithranol) of  $Im^{IS}-H_2P-PhI$ . Top: found, bottom: simulated by  $[C_{59}H_{76}IN_6O_2]^+$  ( $[M+H]^+$ ).



Figure S35. <sup>1</sup>H NMR spectrum of Im<sup>IS</sup>-H<sub>2</sub>P-PhI in CDCl<sub>3</sub> (400 MHz).



**Figure S36.** Comparison of <sup>1</sup>H NMR spectra between Im<sup>Me</sup>-H<sub>2</sub>P-PhI (top) and Im<sup>IS</sup>-H<sub>2</sub>P-PhI (bottom) in CDCl<sub>3</sub>.



Figure S37.  $^{13}$ C NMR spectrum of Im<sup>IS</sup>-H<sub>2</sub>P-PhI in CDCl<sub>3</sub> (100 MHz).



Figure S38. DEPT135 spectrum of Im<sup>IS</sup>-H<sub>2</sub>P-PhI in CDCl<sub>3</sub> (100 MHz).



Figure S39. <sup>1</sup>H-<sup>1</sup>H COSY of Im<sup>IS</sup>-H<sub>2</sub>P-PhI in CDCl<sub>3</sub> (400 MHz).

![](_page_34_Figure_0.jpeg)

**Figure S40.** MALDI-TOF mass (matrix: dithranol) of  $[Im^{IS}-ZnP-PhI]_2$ . Top: found, bottom: simulated by  $[C_{59}H_{74}IN_6O_2Zn]^+$  ( $[M+H]^+$ ).

![](_page_34_Figure_2.jpeg)

Figure S41. <sup>1</sup>H NMR spectrum of [Im<sup>IS</sup>-ZnP-PhI]<sub>2</sub> in CDCl<sub>3</sub> (400 MHz).

![](_page_35_Figure_0.jpeg)

Figure S42. Comparison of <sup>1</sup>H NMR spectra between [Im<sup>Me</sup>-ZnP-PhI]<sub>2</sub> (top) and [Im<sup>IS</sup>-ZnP-PhI]<sub>2</sub> (bottom) in CDCl<sub>3</sub>.


Figure S43. <sup>13</sup>C NMR spectrum of [Im<sup>IS</sup>-ZnP-PhI]<sub>2</sub> in CDCl<sub>3</sub> (100 MHz).



Figure S44. DEPT135 spectrum of [Im<sup>IS</sup>-ZnP-PhI]<sub>2</sub> in CDCl<sub>3</sub> (100 MHz).



Figure S45. <sup>1</sup>H-<sup>1</sup>H COSY of [Im<sup>IS</sup>-ZnP-PhI]<sub>2</sub> in CDCl<sub>3</sub> (400 MHz).



Figure S46. Comparison of UV-vis absorption spectra between  $Im^{IS}-H_2P-PhI$  (blue) and  $[Im^{IS}-ZnP-PhI]_2$  (red) in CHCl<sub>3</sub>.



**Figure S47.** MALDI-TOF mass (matrix: dithranol) of  $[Im^{IS}-ZnP-Ph-5Bpy]_2$ . Top: found, bottom: simulated by  $[C_{69}H_{81}N_8O_2Zn]^+$  ( $[M+H]^+$ ).



Figure S48. <sup>1</sup>H NMR spectrum of [Im<sup>IS</sup>-ZnP-Ph-5Bpy]<sub>2</sub> in CDCl<sub>3</sub> (500 MHz).



Figure S49. Comparison of <sup>1</sup>H NMR spectra between [Im<sup>Me</sup>-ZnP-Ph-5Bpy]<sub>2</sub> (top) and [Im<sup>IS</sup>-ZnP-Ph-5Bpy]<sub>2</sub> (bottom) in CDCl<sub>3</sub>.



Figure S50. <sup>13</sup>C NMR spectrum of [Im<sup>IS</sup>-ZnP-Ph-5Bpy]<sub>2</sub> in CDCl<sub>3</sub> (125 MHz).



Figure S51. DEPT135 spectrum of [Im<sup>IS</sup>-ZnP-Ph-5Bpy]<sub>2</sub> in CDCl<sub>3</sub> (125 MHz).



Figure S52. <sup>1</sup>H-<sup>1</sup>H COSY of [Im<sup>IS</sup>-ZnP-Ph-5Bpy]<sub>2</sub> in CDCl<sub>3</sub> (500 MHz).



Figure S53. HSQC of [Im<sup>IS</sup>-ZnP-Ph-5Bpy]<sub>2</sub> in CDCl<sub>3</sub>.



Figure S54. HMQC of [Im<sup>IS</sup>-ZnP-Ph-5Bpy]<sub>2</sub> in CDCl<sub>3</sub>.



**Figure S55.** UV-vis absorption spectra in CHCl<sub>3</sub> of the products using **[Im<sup>IS</sup>-ZnP-Ph-5Bpy]**<sub>2</sub> and 1.5 equiv of Re(CO)<sub>5</sub>Br against the bpy group before (blue solid line) and after (green broken line) refluxing with pyridine, and using **[Im<sup>IS</sup>-ZnP-Ph-5Bpy]**<sub>2</sub> and 0.97 equiv of Re(CO)<sub>5</sub>Br (red solid line).



**Figure S56.** IR spectra (KBr) of the product using **[Im<sup>IS</sup>-ZnP-Ph-5Bpy]**<sub>2</sub> and 1.5 equiv of Re(CO)<sub>5</sub>Br against the bpy group before (blue solid line) and after (green broken line) refluxing with pyridine.



**Figure S57.** MALDI-TOF mass (matrix: dithranol) of **[Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re]**<sub>2</sub> (**ReDRe**). Top: found, bottom: simulated by [C<sub>72</sub>H<sub>81</sub>BrN<sub>8</sub>O<sub>5</sub>ReZn]<sup>+</sup> ([M+H]<sup>+</sup>).



Figure S58. <sup>1</sup>H NMR spectrum of [Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re]<sub>2</sub> (ReDRe) in CDCl<sub>3</sub> (500 MHz).



Figure S59. <sup>13</sup>C NMR spectrum of [Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re]<sub>2</sub> (ReDRe) in CDCl<sub>3</sub> (125 MHz).



Figure S60. DEPT135 spectrum of [Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re]<sub>2</sub> (ReDRe) in CDCl<sub>3</sub> (125 MHz).



Figure S61. <sup>1</sup>H-<sup>1</sup>H COSY of [Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re]<sub>2</sub> (ReDRe) in CDCl<sub>3</sub> (500 MHz).



Figure S62. HMQC of [Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re]<sub>2</sub> (ReDRe) in CDCl<sub>3</sub>.



Figure S63. IR spectrum of [Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re]<sub>2</sub> (ReDRe) in KBr pellet. Inset: magnification of the CO stretching region.



**Figure S64.** UV-vis absorption spectra in pyridine of **ReDRe** before (blue broken line) and after (red solid line) reaction with the Grubbs catalyst (overnight, at rt).



**Figure S65.** GPC-HPLC charts (column: TSK gel G2500H<sub>HR</sub>  $\times$  2+G2000H<sub>HR</sub>  $\times$  1, eluent: pyridine, flow rate: 1.0 mL/min, detection: 567 nm) of **ReDRe** before (blue broken line) and after (red solid line) reaction with the Grubbs catalyst.



Figure S66. MALDI-TOF mass (matrix: DCTB) of  $C-[Im^{IS}-ZnP-Ph-5Bpy=Re]_2$  (ReD'Re). Top: found, bottom: simulated by  $[C_{140}H_{153}Br_2N_{16}O_{10}Re_2Zn_2]^+$  ([M+H]<sup>+</sup>).



Figure S67. <sup>1</sup>H NMR spectrum of *C*-[Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re]<sub>2</sub> (ReD'Re) in CDCl<sub>3</sub> (500 MHz).



**Figure S68.** <sup>1</sup>H NMR spectra of (a) **ReDRe** and (b) **ReD'Re** in CDCl<sub>3</sub> (500 MHz). Magnifications for the olefin groups at 6.1~6.7 ppm for (c) **ReDRe** and (d) **ReD'Re**.



**Figure S69.** Three isomers of the porphyrin dimer parts in **ReD'Re** caused by the *E*- and *Z*- isomers. The molar ratio was calculated assuming that the metathesis reaction independently proceeded without being affected by the other reaction sites.



Figure S70. <sup>13</sup>C NMR spectrum of *C*-[Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re]<sub>2</sub> (ReD'Re) in CDCl<sub>3</sub> (125 MHz).



Figure S71. DEPT135 spectrum of C-[Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re]<sub>2</sub> (ReD'Re) in CDCl<sub>3</sub> (125 MHz).



Figure S72. <sup>1</sup>H-<sup>1</sup>H COSY of *C*-[Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re]<sub>2</sub> (ReD'Re) in CDCl<sub>3</sub> (500 MHz).



Figure S73. HSQC of C-[Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re]<sub>2</sub> (ReD'Re) in CDCl<sub>3</sub>.



**Figure S74.** IR spectrum of *C*-[Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re]<sub>2</sub> (ReD'Re) in KBr pellet. Inset: magnification of the CO stretching region.



**Figure S75.** GPC-HPLC charts (column: TSK gel G2500H<sub>HR</sub>  $\times$  2+G2000H<sub>HR</sub>  $\times$  1, eluent: pyridine, flow rate: 1.0 mL/min, detection: 440 nm) of the crude product obtained after the metathesis reaction using **ReDRe** and **D** (molar ratio 1:4), and the isolated samples by preparative GPC-HPLC.



Figure S76. MALDI-TOF mass (matrix: DCTB) of  $C-[Im^{Me}-ZnP-PhCH_3][Im^{IS}-ZnP-Ph-5Bpy=Re]$  (ReD'). Top: found, bottom: simulated by  $[C_{111}H_{114}BrN_{14}O_7ReZn_2]^+$  ([M]<sup>+</sup>).



Figure S77. <sup>1</sup>H NMR spectrum of *C*-[Im<sup>Me</sup>-ZnP-PhCH<sub>3</sub>][Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re] (ReD') in CDCl<sub>3</sub> (500 MHz).



Figure S78. <sup>13</sup>C NMR spectrum of *C*-[Im<sup>Me</sup>-ZnP-PhCH<sub>3</sub>][Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re] (ReD') in CDCl<sub>3</sub> (125 MHz).



Figure S79. DEPT135 spectrum of *C*-[Im<sup>Me</sup>-ZnP-PhCH<sub>3</sub>][Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re] (ReD') in CDCl<sub>3</sub> (125 MHz).



**Figure S80.** <sup>1</sup>H-<sup>1</sup>H COSY of *C*-[Im<sup>Me</sup>-ZnP-PhCH<sub>3</sub>][Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re] (ReD') in CDCl<sub>3</sub> (500 MHz).



Figure S81. HMQC of C-[Im<sup>Me</sup>-ZnP-PhCH<sub>3</sub>][Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re] (ReD') in CDCl<sub>3</sub>.



**Figure S82.** IR spectrum of *C*-[Im<sup>Me</sup>-ZnP-PhCH<sub>3</sub>][Im<sup>IS</sup>-ZnP-Ph-5Bpy=Re] (ReD') in KBr pellet. Inset: magnification of the CO stretching region.



Figure S83. Comparison of UV-vis absorption spectra between  $[Im^{Me}-ZnP-Ph-5Bpy]_2$  (blue broken line) and  $[Im^{IS}-ZnP-Ph-5Bpy]_2$  (red solid line) in CHCl<sub>3</sub>.



**Figure S84.** (a) UV-vis absorption and (b) fluorescence spectra ( $\lambda_{ex} = 568$  nm) of **ReDRe** (blue broken line) and **ReD'Re** (red solid line) in CHCl<sub>3</sub>.



**Figure S85.** Energy diagram of **ReD'Re** and **ReD'** in DMA ( $\varepsilon_s = 38.3$ ). The energy levels of the excited singlet (S<sub>1</sub>) and triplet (T<sub>1</sub>) states of the dimer were respectively estimated from the intersection between normalized absorption and fluorescence bands (Y. Kuramochi, Y. Kawakami, A. Satake, *Inorg. Chem.* 2017, **56**, 11008), and from the phosphorescence spectrum at 77 K (Y. Kuramochi, S. Hashimoto, Y. Kawakami, M. S. Asano, A. Satake, *Photochem. Photobiol. Sci.* 2018, **17**, 883). The energy level of the CS state was estimated using the first oxidation potential of **D'**,  $E(ZnP^+/ZnP) = +0.22$  V, and the first reduction potential of *fac*-Re(bpy)(CO)<sub>3</sub>Br,  $E(Re/Re^-) = -1.72$  V v.s. Fc\Fc<sup>+</sup> in DMA.

## Fluorescence quenching efficiency of ReD'Re estimated from that of ReD'.

The fluorescence quantum yields of **D**'  $(\Phi_f^0)$ , **ReD**'  $(\Phi_f^1)$ , and **ReD'Re**  $(\Phi_f^2)$  are expressed below using the radiative  $(k_r)$  and nonradiative  $(k_{nr})$  rate constants and the CS rate constant  $(k_{CS})$ (Figure S85).

$$\Phi_{\rm f}^0 = \frac{k_r}{k_r + k_{nr}} \tag{S1}$$

$$\Phi_{\rm f}^1 = \frac{k_T}{k_r + k_{nr} + k_{CS}} \tag{S2}$$

$$\Phi_{\rm f}^2 = \frac{k_r}{k_r + k_{nr} + 2k_{CS}} \tag{S3}$$

Combing equations (S1) and (S2) gives:

$$\frac{\Phi_{\rm f}^1}{\Phi_{\rm f}^0} = \frac{k_r + k_{nr}}{k_r + k_{nr} + k_{CS}} = \frac{1}{1 + k_{CS} \tau_{\rm f}^0}$$
(S4)

where  $\tau_{\rm f}^0$  is the fluorescence decay of **D**'. By using the ratio of the fluorescence quantum yields of **ReD'** to **D'** ( $\Phi_{\rm f}^{1}/\Phi_{\rm f}^{0} = 0.12$ ), the value of  $k_{\rm CS} \pi^0$  is estimated to be 7.3. As  $\pi^0$  is estimated from the time-resolved fluorescence decay to be 2.0 ns (H. Nakagawa, K. Ogawa, A. Satake, Y. Kobuke, *Chem. Commun.* 2006, 1560), the value of  $k_{\rm CS}$  was calculated to be  $3.7 \times 10^9 \, {\rm s}^{-1}$ . The ratio of the fluorescence quantum yields of **ReD'Re** to **D'** is expressed as the following equation:

$$\frac{\Phi_{\rm f}^2}{\Phi_{\rm f}^0} = \frac{k_r + k_{nr}}{k_r + k_{nr} + 2k_{CS}} = \frac{1}{1 + 2k_{CS}\tau_{\rm f}^0}$$
(S5)

By using  $k_{\rm CS} \tau_{\rm f}^0 = 7.3$  estimated from **ReD'**, the value of  $\Phi_{\rm f}^2/\Phi_{\rm f}^0$  was calculated to be 0.064.

## Fluorescence lifetime of ReD' and ReD'Re estimated from the quenching efficiencies.

The reciprocals of the fluorescence lifetimes were expressed as the equations S6–S8 using the lifetime of **D'** ( $\tau_{\rm f}^0 = 2.0 \text{ ns}$ ) and  $k_{\rm CS}$  ( $3.7 \times 10^9 \text{ s}^{-1}$ ):

$$1/\tau_{\rm f}^{0} = k_{r} + k_{nr} = 5.0 \times 10^{8} \,{\rm s}^{-1}$$
(S6)  

$$1/\tau_{\rm f}^{1} = k_{r} + k_{nr} + k_{CS} = 4.2 \times 10^{9} \,{\rm s}^{-1}$$
(S7)  

$$1/\tau_{\rm f}^{2} = k_{r} + k_{nr} + 2 \,k_{CS} = 7.9 \times 10^{9} \,{\rm s}^{-1}$$
(S8)

Thus, the lifetimes for **ReD'** and **ReD'Re** were estimated to be  $\tau_{f}^{1} = 0.24$  ns and  $\tau_{f}^{2} = 0.13$  ns, respectively.



**Figure S86.** Stern–Volmer plots for fluorescence quenching by BIH in DMA of **D'** (green triangle), **ReD'** (red circle), and **ReD'Re** (blue diamond) at 298 K. From the slope of the plots ( $K_{SV} = 3.5 \text{ M}^{-1}$ , 0.65 M<sup>-1</sup>, and 0.32 M<sup>-1</sup> for **D'**, **ReD'**, and **ReD'Re**, respectively) and the fluorescence lifetime ( $\tau_f^0 = 2.0 \text{ ns}$ ), the quenching rate constant ( $k_q$ ) of **D'** was estimated to be 1.8  $\times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  ( $k_q = K_{SV} / \tau_i^0$ ). Judging from the value in the order of 10<sup>9</sup> M<sup>-1</sup> s<sup>-1</sup>, the electron transfer from BIH to the excited singlet state of the dimer is a diffusion-controlled process. Assuming  $k_q = 1.8 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ , the fluorescence lifetimes were calculated be 0.37 ns and 0.18 ns for **ReD'** and **ReD'Re**, respectively.



**Figure S87.** (a) CO formation with time during irradiation at 560 nm from LED lamps with a merry-go-round apparatus for CO<sub>2</sub>-saturated DMA solutions (total 1.0 mL) containing **ZnP-phen=Re** (0.05 mM) and BIH (0.1 M) in the absence (green) and presence of additives ([PhOH] = 0.1 M (blue), DMA:TEOA = 5:1 v/v (red)). (b) Comparison with Figure S87a over time for **ReD'** (0.025 mM) and BIH (0.1 M) in CO<sub>2</sub>-saturated DMA-TEOA (5:1 v/v) (black circles).

Entry	Photocatalyst	Additive	$CO / \mu mol (TON)^b$
1	<b>ReD'</b> (0.025 mM)	BIH (0.1 M)	0.38 (15)
2	<b>ReD'</b> (0.025 mM)	BIH (0.1 M) + PhOH (0.1 M)	19.4 (777)
3	<b>ReD'</b> (0.025 mM)	BIH (0.1 M) + TEOA (17 vol%)	70.5 (2820)
4	<b>ReD'Re</b> (0.025 mM)	BIH (0.1 M) + TEOA (17 vol%)	62.0 (1250)
5	<b>ReD'Re</b> (0.025 mM)	TEOA (17 vol%)	0.70 (14) <sup>e</sup>
6	<b>D'</b> (0.025 mM) + <b>Re</b> (0.025 mM) <sup>c</sup>	BIH (0.1 M) + TEOA (17 vol%)	1.84 (74)
7	<b>D'</b> (0.025 mM) + <b>Re</b> (0.05 mM) <sup>d</sup>	BIH (0.1 M) + TEOA (17 vol%)	14.1 (283)
8	<b>ZnP-phen=Re</b> (0.05 mM)	BIH (0.1 M)	2.80 (56)
9	<b>ZnP-phen=Re</b> (0.05 mM)	BIH (0.1 M) + TEOA (17 vol%)	2.65 (53)
10	<b>ZnP-phen=Re</b> (0.05 mM)	BIH (0.1 M) + PhOH (0.1 M)	8.62 (172)

**Table S1.** Results of CO<sub>2</sub> reduction in DMA ( $\lambda_{ex} = 560$  nm, 18 h)<sup>a</sup>

<sup>*a*</sup> Photocatalytic reactions performed in CO<sub>2</sub>-saturated DMA solutions (total volume of the solution: 1.0 mL) under irradiation by 560 nm for 18 h using a merry-go-round apparatus equipped with LED lamps. <sup>*b*</sup> TON based on the Re complex unit. <sup>*c*, *d*</sup> **Re**: *fac*-Re(bpy)(CO)<sub>3</sub>Br. <sup>*e*</sup> Irradiation for 48 h.



**Figure S88.** Formation of CO during irradiation at  $\lambda_{ex} = 560$  nm (Xe lamp,  $3.7 \times 10^{-8}$  einstein s<sup>-1</sup>) using BIH (0.1 M) and PhOH (0.1 M) in CO<sub>2</sub>-saturated DMA containing **ReD'** (0.1 mM) or **ReD'Re** (0.1 mM).


**Figure S89.** Formation of CO during irradiation at  $\lambda_{ex} = (a) 420 \text{ nm} (2.6 \times 10^{-8} \text{ einstein s}^{-1})$ , (b) 450 nm (2.9 × 10<sup>-8</sup> einstein s<sup>-1</sup>), and (c) 560 nm (3.6 × 10<sup>-8</sup> einstein s<sup>-1</sup>) from a Xe lamp using BIH (0.1 M) in CO<sub>2</sub>-saturated DMA-TEOA (5:1 v/v) containing **ReD'** (left, red squares; 0.025 mM for 420 and 450 nm and 0.1 mM for 560 nm) or **ReD'Re** (right, blue triangles; 0.025 mM for 420 and 450 nm and 0.1 mM for 560 nm).



**Figure S90.** Formation of CO during irradiation at  $\lambda_{ex} = 560$  nm from a Xe lamp with different light intensities  $(3.6 \times 10^{-8}, 7.5 \times 10^{-8}, 8.9 \times 10^{-8}, \text{ and } 1.2 \times 10^{-7} \text{ einstein s}^{-1})$  using BIH (0.1 M) in CO<sub>2</sub>-saturated DMA-TEOA (5:1 v/v) containing **ReD'** (0.1 mM).



**Figure S91.** (a) CO formation (TON<sub>CO</sub>) with time in CO<sub>2</sub>-saturated DMA-TEOA (5:1 v/v) solution containing **ReD'** (0.025 mM) and BIH (0.1 M) using a merry-go-round apparatus equipped with LED lamps at 560 nm (Input power: 2 or 10 mW). (b) Plots of CO formation versus product of input power and irradiation time.



**Figure S92.** Formation of CO during irradiation at  $\lambda_{ex} = 560$  nm (Xe lamp,  $5.2 \times 10^{-9}$  einstein s<sup>-1</sup>) using BIH (red circles: 0.05 M, blue diamonds: 0.01 M) and PhOH (0.1 M) in CO<sub>2</sub>-saturated DMA solutions containing **ZnP-phen=Re** (0.3 mM).



**Figure S93.** (a) Formation of CO (TON<sub>CO</sub>) during irradiation at 560 nm (Input power: 10 mW) from LED lamps with a merry-go-round apparatus using BIH (red circle, 0.1 M; green diamond. 0.05 M; blue triangle, 0.01 M) and **ReD'** (0.025 mM) in CO<sub>2</sub>-saturated DMA-TEOA (5:1 v/v). (b) Plot of TOF against concentration of BIH. The quenching efficiency relative to  $\eta_q$  at [BIH] = 0.1 M was calculated using  $\eta_q = [BIH] K_{SV} / (1 + [BIH] K_{SV})$  assuming  $K_{SV} = 15 \text{ M}^{-1}$ .



**Figure S94.** Energy diagram of **ReD'Re** and **ReD'** in the presence of BIH in DMA at 298 K. The energy levels of the charge-separated (CS) states from the ground state were calculated using  $E(\text{ZnP}^+/\text{ZnP}) = +0.22 \text{ V}, E(\text{ZnP}/\text{ZnP}^-) = -1.91 \text{ V}, E(\text{Re}/\text{Re}^-) = -1.72 \text{ V}, \text{ and } E(\text{BIH}^+/\text{BIH}) = -0.10 \text{ V} \text{ vs. Fc/Fc}^+ \text{ in DMA}.$ 



**Figure S95.** (a) DPVs of **D** (0.05 mM) and **D**' (0.5 mM) in Ar-saturated DMSO with 0.1 M  $^{n}$ Bu<sub>4</sub>NPF<sub>6</sub> as a supporting electrolyte. (b) UV-vis absorption spectra of **D** (0.05 mM) in DMSO containing 0.1 M  $^{n}$ Bu<sub>4</sub>NPF<sub>6</sub> using a 1 mm quartz cell.



**Figure S96.** Fluorescence spectra of **D** (blue line) and **ReDRe** (red line) (the corresponding monomers) in DMSO at 298 K. The fluorescence spectra were normalized with the absorbance at the excitation wavelength ( $\lambda_{ex} = 568$  nm). The inset shows UV-vis absorption spectra of **D** (blue line) and **ReDRe** (red line) in DMSO.



**Figure S97.** UV-vis absorption spectra (1 mm cell) of a CO<sub>2</sub>-saturated DMSO-TEOA (5:1 v/v) solution containing BIH (0.05 M) and **ReDRe** (10  $\mu$ M) before (blue line) and after (red line) irradiation at 560 nm from LED lamps with a merry-go-round apparatus for 7 h. Inset shows magnification of the Q band region.



Figure S98. A plausible mechanism of the formation of two-electron reduced species in (a) the monomer (**ReDRe** in DMSO) and (b) the dimer (**ReD'Re**).