Supplementary Information for

Visible Light-Driven Water Oxidation by Covalently-Linked Molecular Catalyst−Sensitizer Dyad Assembled on TiO_2 Electrode

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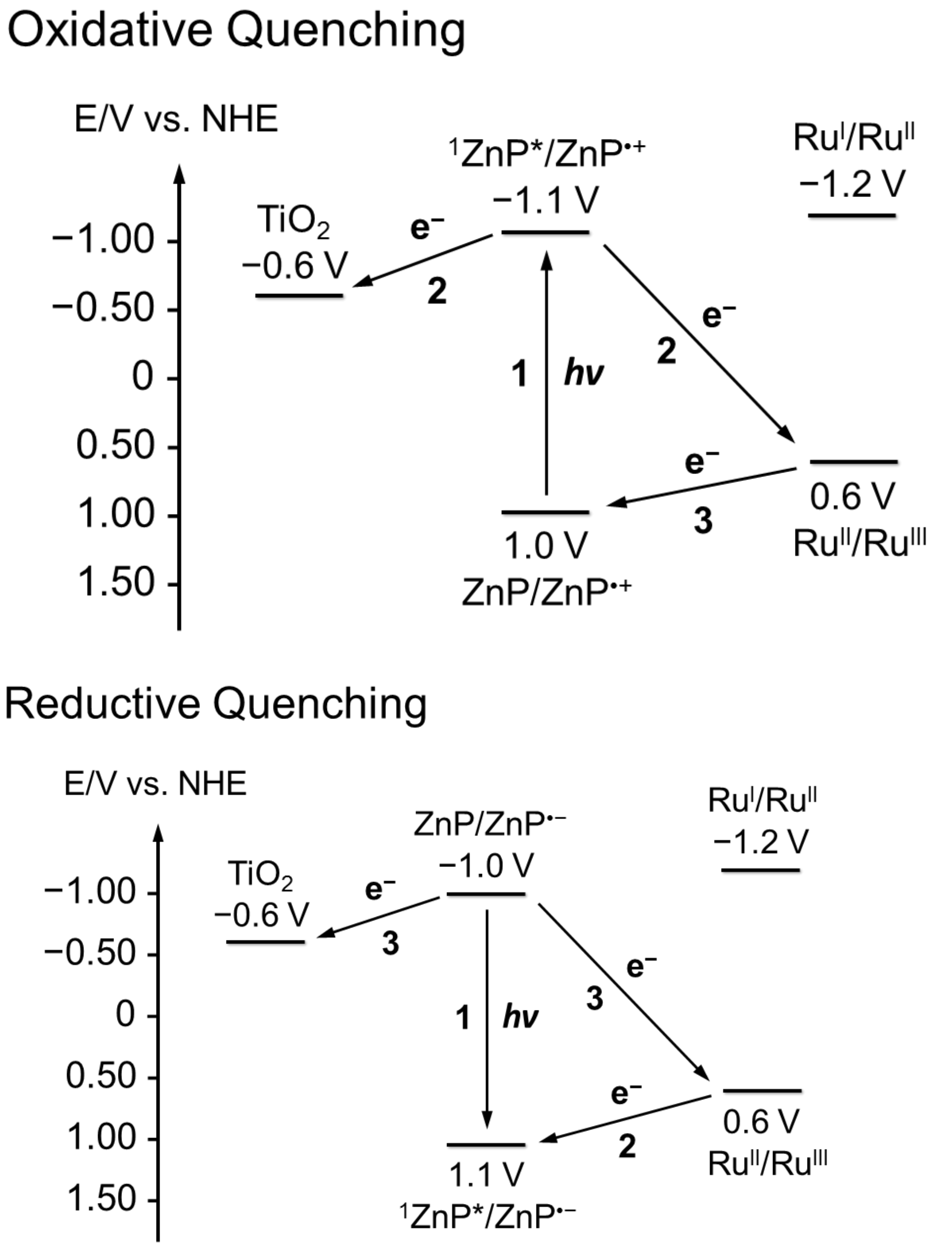
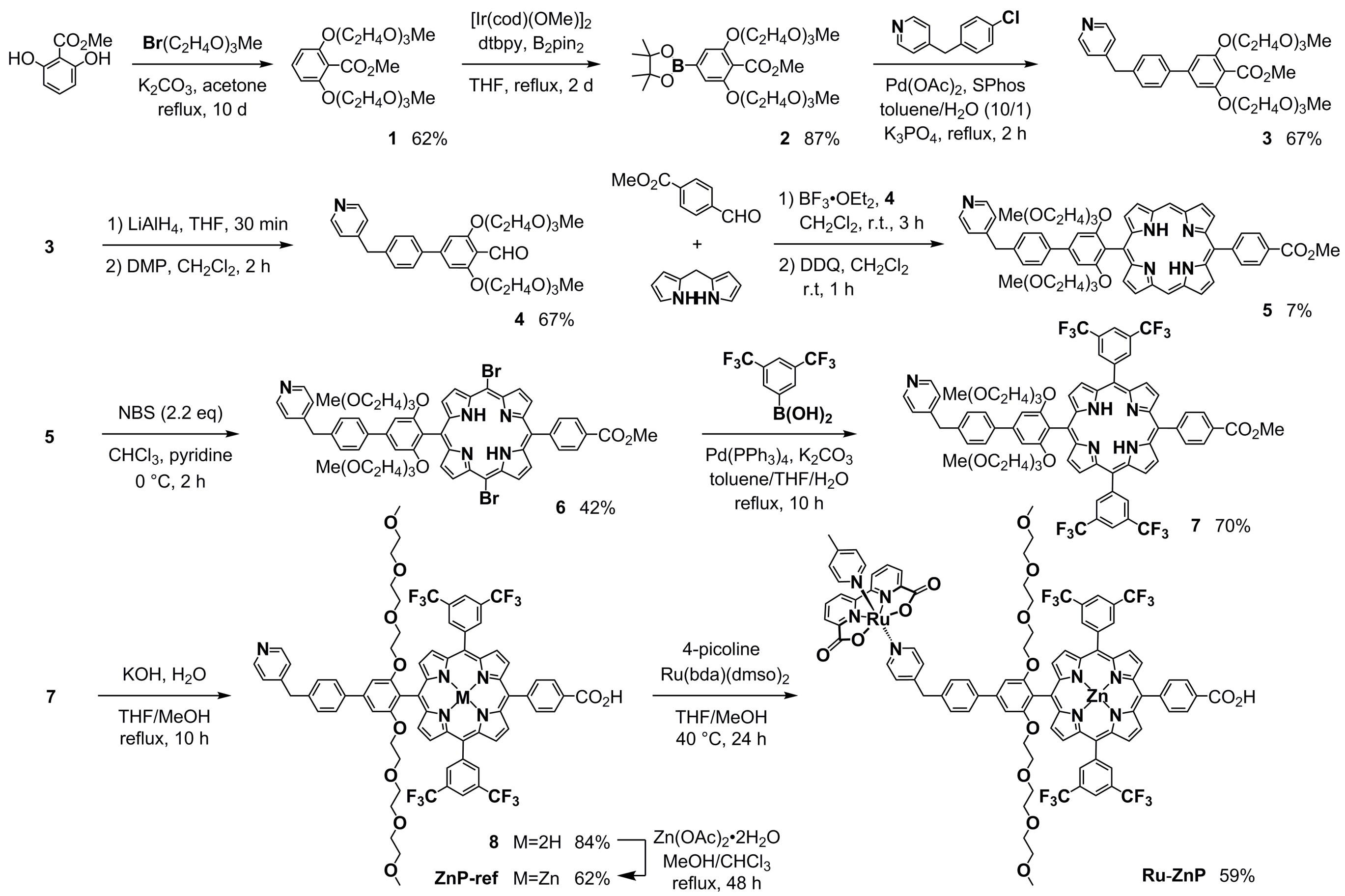


Figure S1. Energy level diagrams of **Ru**-**ZnP** on TiO_2/FTO at neutral pH. (a) Oxidative quenching (top) and (b) reductive quenching (bottom) of $^1ZnP^*$. Oxidative quenching of $^1ZnP^*$ by WOC (path 2 (right arrow) in a) would compete with ET to TiO_2 (path 2 (left arrow) in a), reducing anodic photocurrent, while reductive quenching of $^1ZnP^*$ by WOC (path 2 in b) and subsequent ET from $ZnP^{•-}$ to TiO_2 (path 3 in b), contributing anodic photocurrent. EnT quenching of $^1ZnP^*$ by the adjacent WOC and formation of the WOC excited-state (WOC*) may lead to rapid thermal relaxation of WOC* to the ground state without photocurrent generation. Such intramolecular quenching would not influence the PEC properties significantly because the electron injection process from $^1ZnP^*$ to the CB of TiO_2 (path 2 (left arrow) in a and path 3 (left arrow) in b) is much faster than the above quenching processes. The redox values of the porphyrin unit for reductive quenching are obtained in solution. The potential of Ru^I/Ru^{II} was obtained from the literature.[14b]

Synthesis



Scheme S1 Synthesis of the dyad **Ru**-**ZnP**.

1: To a round-bottomed two necked flask equipped with reflux condenser were added potassium carbonate (9.420 g, 68.16 mmol), methyl 2,6-dihydroxybenzonate (4.15 g, 24.7 mmol), 2-[2-[2-(2-methoxyethoxy)ethoxy]ethoxy]ethyl bromide (15.00 g, 66.05 mmol), and acetone (200 mL). The mixture was refluxed for 10 d. After cooling, the mixture was filtered, concentrated, and the residue was purified by silica gel column chromatography with dichloromethane/ethyl acetate = 1/2, then 1/3 as an eluent to afford **1** as a colorless liquid (7.02 g, 15.2 mmol, 62%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 7.31 (t, *J* = 8.4 Hz, 1H), 6.69 (d, *J* = 8.4 Hz, 2H), 4.14 (t, *J* = 4.8 Hz, 4H), 3.83 (s, 3H), 3.79 (t, *J* = 4.8 Hz, 4H), 3.68-3.66 (m, 4H), 3.63-3.60 (m, 8H), 3.53-3.51 (m, 4H), 3.34 (s, 6H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 166.6, 156.6, 131.0, 105.6, 71.9, 70.9, 70.7, 70.5, 69.4, 68.8, 59.0, 52.1; HRMS (ESI): m/z calcd for $C_{22}H_{36}O_{10}Na$: 483.2201 $[M+Na]^+$; found: 483.2189; IR (neat): 2920, 2874, 1733, 1597, 1453, 1468, 1299, 1257, 1106, 633, 543, 535, 523 cm^{-1}.

2: To a round-bottomed flask equipped with reflux condenser were added **1** (6.464 g, 14.04 mmol), 4,4’-di-*tert*-butyl-2,2’-dipyridyl (0.411 g, 1.53 mmol), bis(pinacolato)diboron (5.733 g, 22.58 mmol), and THF (50 mL), and degassed with argon for 90 min. (1,5-Cyclooctadiene)(methoxy)iridium(I) dimer (0.290 g, 0.437

mmol) was added to the reactor, and refluxed for 2 d in the dark. The reaction mixture was then evaporated, and purified with silica gel column chromatography with dichloromethane/ethyl acetate = 1/2 as an eluent to afford **2** as a colorless viscous liquid (7.152 g, 12.19 mmol, 87%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 6.96 (s, 2H), 4.17 (t, *J* = 5.1 Hz, 4H), 3.83 (s, 3H), 3.79 (t, *J* = 5.1 Hz, 4H), 3.70-3.67 (m, 4H), 3.64-3.61 (m, 8H), 3.55-3.51 (m, 4H), 3.35 (s, 6H), 1.32 (s, 12H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 166.8, 156.3, 117.1, 111.5, 84.5, 72.3, 71.3, 70.9, 70.8, 69.9, 69.3, 59.0, 52.4, 25.0; HRMS (ESI): m/z calcd for $C_{28}H_{51}BNO_{12}$ 604.3499 $[M+NH_4]^+$; found: 604.3479; IR (neat): 2977, 2918, 2875, 1736, 1565, 1495, 1453, 1409, 1355, 1257, 1107, 969, 851, 697, 663, 627, 534 cm^{-1}.

3: A Schlenk tube containing **2** (5.250 g, 8.952 mmol), 4-(4-chlorobenzyl)pyridine (2.190 g, 10.75 mmol), potassium phosphate (3.874 g, 18.25 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxybiphenyl (Sphos, 75.6 mg, 0.184 mmol), toluene (14 mL), and water (1.4 mL) was degassed with argon for 75 min, and then palladium(II) acetate (20.1 mg, 89.5 µmol) was added. After stirring at 100 °C for 2 h, the solvents were evaporated, and the residue was purified with silica gel column chromatography with dichloromethane/ethyl acetate = 2/1, then 1/1 as an eluent to afford **3** as a yellowish liquid (3.793 g, 6.042 mmol, 67%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 8.39 (d, *J* = 5.9 Hz, 2H), 7.45 (d, *J* = 8.2 Hz, 2H), 7.19 (d, *J* = 8.2 Hz, 2H), 7.06 (d, *J* = 5.9 Hz, 2H), 6.70 (s, 2H), 4.18 (t, *J* = 5.1 Hz, 4H), 4.01 (s, 2H), 3.86 (s, 3H), 3.81 (t, *J* = 5.1 Hz, 4H), 3.70-3.68 (m, 4H), 3.64-3.60 (m, 8H), 3.53-3.51 (m, 4H), 3.34 (s, 6H); ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ 166.7, 157.1, 150.3, 150.1, 144.4, 139.6, 139.4, 129.8, 127.8, 124.4, 113.4, 105.0, 72.3, 71.3, 70.9, 70.8, 69.9, 69.4, 59.0, 52.4, 41.1; HRMS (ESI): m/z calcd for $C_{34}H_{46}NO_{10}$ 628.3116 $[M+H]^+$; found: 628.3100; IR (neat): 2876, 1730, 1601, 1562, 1431, 1400, 1336, 1270, 1197, 1102, 942, 848, 813, 783, 636, 580 cm^{-1}.

4: To a round-bottomed flask containing **3** (3.781 g, 6.023 mmol) and THF (50 mL) was added lithium aluminium hydride (0.949 g, 25.0 mmol) at 0 °C. After stirring at room temperature for 30 min, the mixture was cooled at 0 °C, and several clumps of ice were carefully added to quench the reaction. The solution was filtered with Celite, thoroughly washed with methanol and THF, and concentrated. The residue was then dissolved in dichloromethane (10 mL), and Dess-Martin periodinane (DMP, 3.181 g, 7.500 mmol) was added to the reaction. After stirring at room temperature for 2 h, the mixture was directly subjected to alumina column chromatography with acetone/ethyl acetate = 1/1 and then acetone as an eluent to afford **4** as a slightly yellowish liquid (2.413 g, 4.037 mmol, 67%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 10.50 (s, 2H), 8.48 (d, *J* = 5.9 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.4 Hz, 2H), 7.14 (d, *J* = 5.9 Hz, 2H), 6.80 (s, 2H), 4.25 (t, *J* = 4.8 Hz, 4H), 4.01 (s, 2H), 3.87 (t, *J* = 4.7 Hz, 4H), 3.71-3.68 (m, 4H), 3.61-3.54 (m, 8H), 3.49-3.47 (m, 4H), 3.30 (s, 6H); ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ 188.5, 161.9, 150.1, 148.4, 140.3, 138.9, 129.9, 127.8, 124.5, 114.2, 104.8, 72.2, 71.3, 70.9, 69.8, 69.3, 58.9, 41.1; HRMS (ESI): m/z calcd for $C_{33}H_{43}NO_9Na$ 620.2830 $[M+Na]^+$; found: 620.2809; IR (neat): 2873, 1681, 1598, 1553, 1517, 1400, 1286, 1240, 1189, 1098, 938, 848, 637, 605 cm^{-1}.

5: A round-bottomed two-necked flask containing **4** (1.196 g, 2.001 mmol), methyl 4-formylbenzoate (0.327 g, 1.99 mmol), dipyrromethane (0.584 g, 3.99 mmol), and dichloromethane (1 L) was degassed with argon for 30 min, and trifluoroacetic acid (0.1 mL) was added to the reactor. After stirring at room temperature for 3 h, 2,3-dichloro-5,6-dicyano-*p*-benzoquinone (1.368 g, 6.026 mmol) was then added, and further stirred for 1 h. 6

mL of triethylamine was added to quench the reaction, and the mixture was directly subjected to alumina column chromatography with dichloromethane/ethyl acetate = 1/1, then ethyl acetate as an eluent to afford **5** as a red powder (0.139 g, 0.137 mmol, 7%). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 10.19 (s, 2H), 9.32 (d, *J* = 4.7 Hz, 2H), 9.27 (d, *J* = 4.4 Hz, 2H), 9.01 (d, *J* = 4.7 Hz, 2H), 8.94 (d, *J* = 4.8 Hz, 2H), 8.52 (d, *J* = 5.5 Hz, 2H), 8.43 (d, *J* = 8.0 Hz, 2H), 8.29 (d, *J* = 8.0 Hz, 2H), 7.79 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 7.7 Hz, 2H), 7.20-7.17 (m, 4H), 4.07 (*pseudo* s, 5H), 4.01 (t, *J* = 4.8 Hz, 4H), 2.87 (t, *J* = 4.4 Hz, 4H), 2.76 (s, 6H), 2.40 (t, *J* = 5.1 Hz, 4H), 2.11 (t, *J* = 4.7 Hz, 4H), 2.01 (t, *J* = 4.8 Hz, 4H), 1.78 (t, *J* = 4.5 Hz, 4H), −3.18 (br, 2H); ^{13}C{^{1}H} NMR ($CDCl_3$, 75.5 MHz): δ 167.4, 159.9, 149.4, 146.4, 146.1, 143.4, 140.0, 138.5, 134.8, 131.7, 131.5, 130.4, 129.7, 129.5, 128.1, 127.8, 124.4, 117.6, 111.5, 104.9, 70.8, 69.5, 69.1, 68.7, 58.4, 52.4, 41.0; HRMS (ESI): m/z calcd for $C_{60}H_{62}O_{10}N_5$ 1012.4491 [M+H]$^+$; found: 1012.4467; IR (neat): 2904, 2878, 2863, 1710, 1596, 1580, 1555, 1427, 1400, 1347, 1277, 1238, 1194, 1136, 1099, 1062, 987, 971, 917, 820 cm^{-1}; mp 106-108 °C.

6: To a flask containing chloroform solution (10 mL) of **5** (138.9 mg, 137.2 µmol) were added pyridine (0.1 mL) and *N*-bromosuccinimide (52.7 mg, 296 µmol) at 0 °C. After stirring for 2 h, acetone was added to quench the reaction, and the mixture was evaporated to dryness. The residue was then purified by silica gel column chromatography with dichloromethane/ethyl acetate = 3/2 as an eluent and subsequent reprecipitation from methanol at −78 °C to afford **6** as a reddish purple solid (68.1 mg, 58.2 µmol, 42%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 9.64 (d, *J* = 5.1 Hz, 2H), 9.61 (d, *J* = 5.1 Hz, 2H), 8.95 (d, *J* = 4.8 Hz, 2H), 8.82 (d, *J* = 4.4 Hz, 2H), 8.55 (d, *J* = 5.9 Hz, 2H), 8.45 (d, *J* = 8.1 Hz, 2H), 8.28 (d, *J* = 8.1 Hz, 2H), 7.90 (d, *J* = 8.1 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.29 (s, 2H), 7.25 (d, *J* = 5.5 Hz, 2H), 4.13-4.10 (m, 9H), 3.01 (t, *J* = 4.6 Hz, 4H), 2.91 (s, 6H), 2.72 (t, *J* = 4.6 Hz, 4H), 2.47 (t, *J* = 4.8 Hz, 4H), 2.25 (t, *J* = 4.4 Hz, 4H), 2.10 (t, *J* = 4.6 Hz, 4H), −2.70 (s, 2H); ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ 167.4, 160.1, 150.3, 146.5, 144.2, 140.1, 139.6, 134.9, 134.0-131.9 (m, ^{13}C^{79}Br and ^{13}C^{81}Br), 130.4, 130.1, 128.3, 128.0, 124.5, 120.5, 118.7, 114.7, 105.0, 103.5, 71.5, 70.1, 69.7, 69.6, 69.4, 69.1, 58.5, 52.7, 41.3; HRMS (ESI): m/z calcd for $C_{60}H_{60}Br_2O_{10}N_5$ 1168.2701 [M+H]$^+$; found: 1168.2673; IR (neat): 2873, 1713, 1599, 1556, 1463, 1430, 1399, 1274, 1258, 1240, 1193, 1096, 1033, 992, 960, 911, 847, 791, 783, 762, 747, 725, 715, 666, 649 cm^{-1}; mp 111-113 °C.

7: A Schlenk tube containing **6** (160.0 mg, 136.8 µmol), 3,5-bis(trifluoromethyl)phenylboronic acid (548 mg, 141 µmol), potassium carbonate (246.1 mg, 1.781 mmol), THF (7 mL), toluene (3 mL), and water (3 mL) was degassed with argon for 20 min, and tetrakis(triphenylphosphine)palladium(0) (15.8 mg, 13.7 µmol) was added to the reactor. After stirring at 80 °C for 10 h, the reaction was evaporated, and the residue was purified by silica gel column chromatography with dichloromethane/ethyl acetate = 10/2, then 10/3 as an eluent. Recrystallization from ethanol afforded **7** as a reddish purple crystal (138.4 mg, 96.4 µmol, 70%). ^{1}H NMR (CD_2Cl_2, 300 MHz): δ 9.03 (d, *J* = 5.1 Hz, 2H), 8.91 (d, *J* = 4.7 Hz, 2H), 8.76-8.73 (m, 8H), 8.53 (d, *J* = 5.9 Hz, 2H), 8.46 (d, *J* = 8.4 Hz, 2H), 8.39 (s, 2H), 8.32 (d, *J* = 8.4 Hz, 2H), 7.88 (d, *J* = 8.0 Hz, 2H), 7.45 (d, *J* = 8.0 Hz, 2H), 7.30 (s, 2H), 7.24 (d, *J* = 5.9 Hz, 2H), 4.12 (s, 2H), 4.11-4.08 (m, 7H), 3.01 (t, *J* = 4.8 Hz, 4H), 2.86 (s, 6H), 2.68-2.65 (m, 4H), 2.43-2.40 (m, 4H), 2.33-2.29 (m, 4H), 2.14-2.11 (m, 4H), −2.78 (s, 2H); ^{13}C{^{1}H} NMR (CD_2Cl_2, 75.5 MHz): δ 167.4, 160.2, 150.4, 150.3, 146.8, 144.6, 144.1, 140.0, 139.6, 135.0, 134.1, 130.8, 130.4, 130.1, 128.3, 128.0, 125.9, 124.5, 122.3, 120.3, 119.1, 116.5, 114.4, 105.3, 71.5, 70.1, 69.8, 69.7, 69.4, 69.2, 58.5, 52.7, 41.3; HRMS (ESI): m/z calcd for $C_{76}H_{66}F_{12}O_{10}N_5$ 1436.4613 [M+H]$^+$; found: 1436.4616; IR (neat): 2873, 1718, 1600, 1555, 1431, 1384, 1340, 1274, 1173, 1103, 1019, 971, 906, 846, 764, 729, 709, 681 cm^{-1}; mp 127-128 °C.

8: A round-bottomed flask equipped with reflux condenser containing **7** (136.7 mg, 95.2 µmol), THF (50 mL), and aqueous sodium hydroxide (1.4 M, 10 mL) was heated to 90 °C, and stirred at the temperature for 10 h. The solvent was then evaporated to dryness, and CH_2Cl_2 was added to dissolve the residue. The mixture was washed with pH 2 of HCl solution, then with distilled water three times. The organic phase was concentrated and the residue was reprecipitated from CH_2Cl_2/hexane to afford **8** as a reddish purple solid (113.2 mg, 79.6 µmol, 84%). ^1H NMR (CD_2Cl_2, 300 MHz): δ 8.95 (d, J = 4.8 Hz, 2H), 8.81 (d, J = 4.8 Hz, 2H), 8.68-8.64 (m, 8H), 8.47 (d, J = 5.9 Hz, 2H), 8.39 (d, J = 8.0 Hz, 2H), 8.30 (s, 2H), 8.25 (d, J = 8.1 Hz, 2H), 7.80 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.21 (s, 2H), 7.17 (d, J = 5.5 Hz, 2H), 4.05 (s, 2H), 4.01 (t, J = 5.1 Hz, 4H), 2.92 (t, J = 4.7 Hz, 4H), 2.78 (s, 6H), 2.59 (t, J = 4.7 Hz, 4H), 2.33 (t, J = 4.7 Hz, 4H), 2.22 (t, J = 4.7 Hz, 4H), 2.04 (t, J = 4.7 Hz, 4H), –2.87 (s, 2H); $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 75.5 MHz): δ 181.4, 160.2, 150.8, 150.0, 147.1, 144.5, 144.1, 140.1, 139.5, 135.0, 134.1, 132.0, 130.8, 130.3, 130.1, 128.7, 128.0, 125.9, 124.7, 123.9, 122.3, 120.2, 119.1, 116.6, 105.3, 71.5, 70.1, 69.7, 69.4, 69.2, 58.5; HRMS (ESI): m/z calcd for $C_{75}H_{64}F_{12}O_{10}N_5$ 1422.4456 $[M+H]^+$; found: 1422.4418; IR (neat): 2921, 2893, 2873, 1708, 1602, 1558, 1384, 1339, 1276, 1174, 1123, 1018, 971, 906, 870, 847, 798, 767, 731, 708, 680, 621, 575 cm^{-1}; mp 227-228 °C.

ZnP-ref: A flask containing dichloromethane solution (30 mL) of **8** (57.1 mg, 39.8 µmol) was added methanol solution (5 mL) of zinc acetate dihydrate (56.9 mg, 259 µmol). After stirring at reflux temperature for 48 h, the mixture was washed with sat. sodium hydrogen carbonate and distilled water, and the organic phase was concentrated. The residue was reprecipitated from methanol/chloroform to afford **ZnP-ref** as a purple solid (36.8 mg, 24.5 µmol, 62%). ^1H NMR (CD_3OD, 300 MHz): δ 9.00 (d, J = 4.7 Hz, 2H), 8.92 (d, J = 4.7 Hz, 2H), 8.77 (s, 4H), 8.73 (d, J = 4.7 Hz, 2H), 8.69 (d, J = 4.8 Hz, 2H), 8.45-8.40 (m, 6H), 8.30 (d, J = 8.4 Hz, 2H), 7.94 (d, J = 8.1 Hz, 2H), 7.46 (d, J = 8.1 Hz, 2H), 7.38 (d, J = 6.2 Hz, 2H), 7.36 (s, 2H), 4.16 (s, 2H), 4.09 (t, J = 4.2 Hz, 4H), 2.99 (t, J = 5.1 Hz, 4H), 2.67 (s, 6H), 2.39-2.36 (m, 4H), 2.14-2.11 (m, 4H), 2.03-2.00 (m, 4H), 1.84-1.81 (m, 4H) (Figure S2); $^{13}C\{^1H\}$ NMR (thf-d_8, 75.5 MHz): δ 160.9, 152.5, 150.4, 150.3, 150.1, 150.0, 146.8, 143.8, 150.1, 134.5, 131.5, 130.2, 128.4, 128.2, 124.5, 117.2, 104.9, 72.2, 70.6, 70.5, 69.6, 69.1, 68.3, 58.3; HRMS (ESI): m/z calcd for $C_{75}H_{61}F_{12}O_{10}N_5ClZn$ 1518.3212 $[M+Cl]^-$; found: 1518.3212; IR (neat): 2907, 2867, 1714, 1691, 1605, 1556, 1520, 1426, 1379, 1327, 1277, 1223, 1176, 1127, 993, 922, 901, 875, 848, 823, 793, 770, 711, 690 cm^{-1}; mp > 300 °C. UV/Vis (methanol): λ_{max} (ε) = 404 (46 400), 424 (551 000), 517 (3 500), 556 (21 000), 598 nm (5 200 M^{-1} cm^{-1}).

Ru-ZnP: A flask containing Ru(bda)$(dmso)_2$ (16.3 mg, 32.6 µmol), THF (10 mL), and methanol (10 mL) was degassed with argon for 30 min, and then picoline (3.0 mg, 32 µmol) was added to the reactor in the dark. After stirring for 5 min at 40 °C, **ZnP-ref** (5.5 mg, 3.7 µmol) was added to the reaction mixture. After stirring for 24 h in the dark at the temperature, the solvent was removed, and the residue was purified by silica gel column chromatography with acetone/methanol = 3/1 as an eluent to afford **Ru-ZnP** as a red solid (4.2 mg, 2.2 µmol, 59%). When the crude mixture was subjected to the chromatography, a trace amount of ascorbic acid was added to the mixture to reduce an air oxidized Ru^{III} center. ^1H NMR (CD_3OD, 300 MHz): δ 8.98 (d, J = 4.7 Hz, 2H), 8.92 (d, J = 4.4 Hz, 2H), 8.76 (s, 4H), 8.73 (d, J = 4.7 Hz, 2H), 8.68 (d, J = 4.7 Hz, 2H), 8.56 (dd, J = 8.0, 1.1 Hz, 2H), 8.45 (s, 2H), 8.42 (d, *J* = 7.7 Hz, 2H), 8.28 (d, *J* = 8.4 Hz, 2H), 8.03 (dd, *J* = 7.7, 1.1 Hz, 2H), 7.87 (t, *J* = 7.7 Hz, 2H), 7.83 (d, *J* = 6.6 Hz, 2H), 7.73 (d, *J* = 6.6 Hz, 2H), 7.65 (d, *J* = 6.6 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 2H), 7.29 (s, 2H), 7.13 (d, *J* = 6.1 Hz, 2H), 7.05 (dd, *J* = 6.6, 0.8 Hz, 2H), 4.06 (t, *J* = 4.0 Hz, 4H), 4.00 (s, 2H), 2.97-2.93 (m, 4H), 2.66 (s, 6H), 2.38-2.35 (m, 4H), 2.26 (s, 3H), 2.13-2.10 (m, 4H), 2.01-1.98 (m, 4H), 1.83-1.80 (m, 4H) (Figure S3); HRMS (ESI): m/z calcd for $C_{93}H_{74}F_{12}O_{14}N_8ClZnRu$ 1955.3162 $[M+Cl]^-$; found: 1955.3155; IR (neat): 2921, 2873, 1712, 1601, 1553, 1481, 1428, 1377, 1327, 1276, 1222, 1171, 1126, 1103, 992, 921, 847, 822, 794, 767, 709, 680 cm^{-1}; m.p. > 300 °C; UV/Vis (methanol): λ_{max} (ε) = 404 (51 000), 425 (550 000), 519 (7 100), 556 (22 000), 597 nm (5 400 M^{-1} cm^{-1}).

ZnP-ref (300 MHz, thf-d_8)

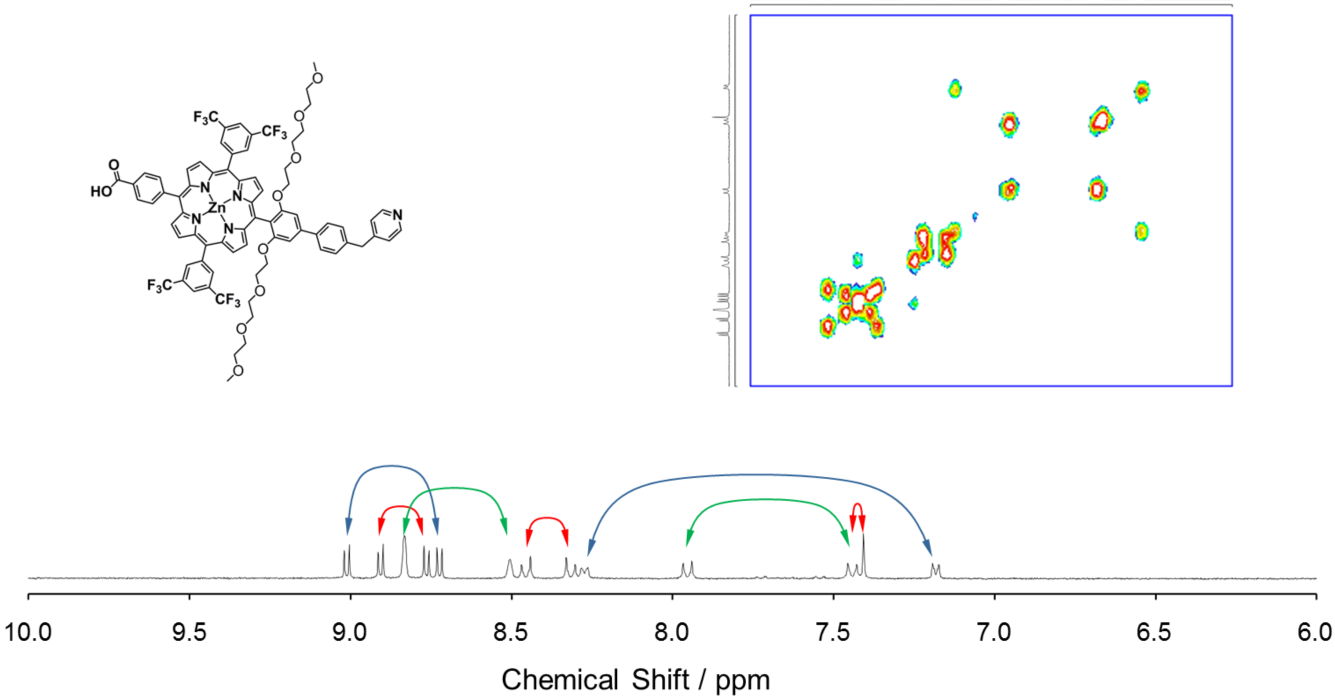


Figure S2. ^{1}H NMR spectrum of **ZnP-ref** in THF-d_8 at r.t. Inset depicts ^{1}H-^{1}H COSY spectrum of **ZnP-ref** under the same condition.

Ru-ZnP (300 MHz, CD_3OD)

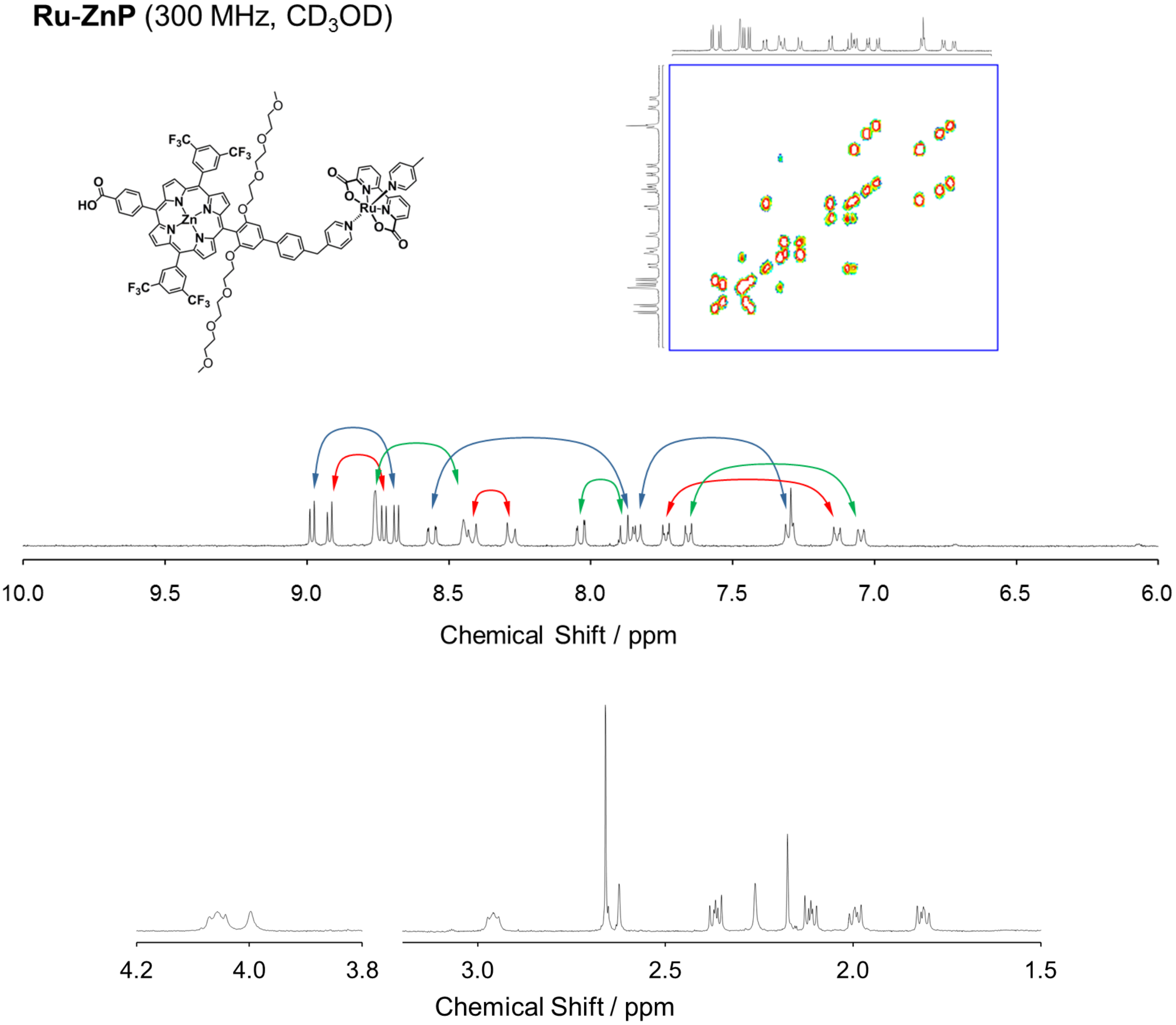
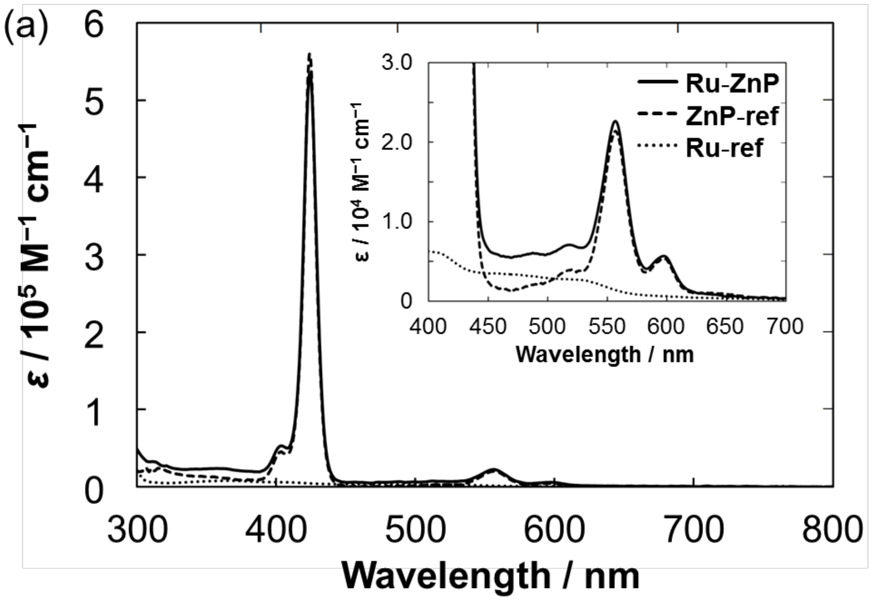


Figure S3. ^1H NMR spectrum of **Ru-ZnP** in CD_3OD with a trace amount of ascorbic acid at r.t. Inset depicts ^1H-^1H COSY spectrum of **Ru-ZnP** under the same condition.



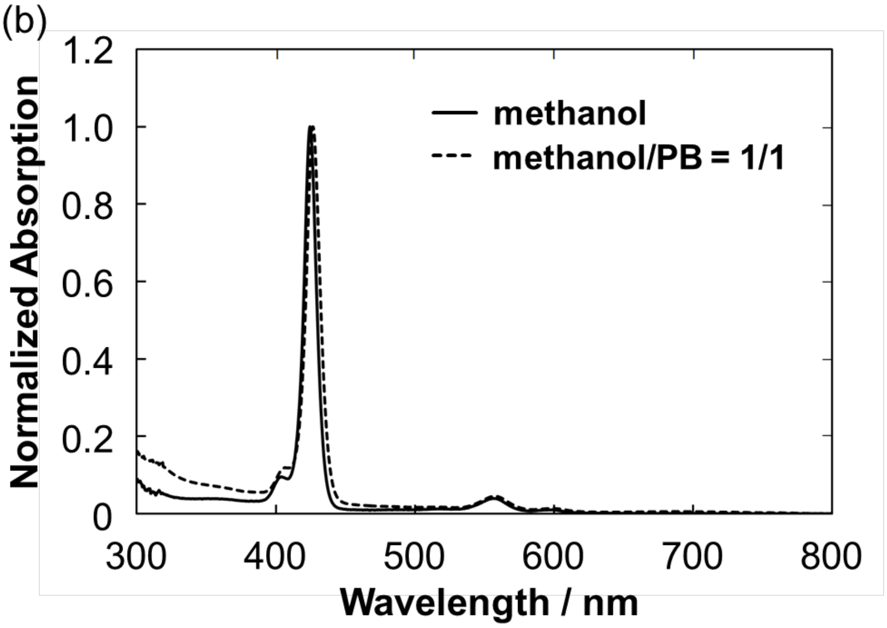


Figure S4. (a) UV-visible absorption spectra of **Ru**-**ZnP** (solid line), **ZnP**-**ref** (dashed line) and **Ru**-**ref** (dotted line) in methanol. (b) UV-visible absorption spectra of **Ru**-**ZnP** in methanol (solid line, [**Ru**-**ZnP**] = 4 µM) and in PB/methanol = 1/1 (dashed line).

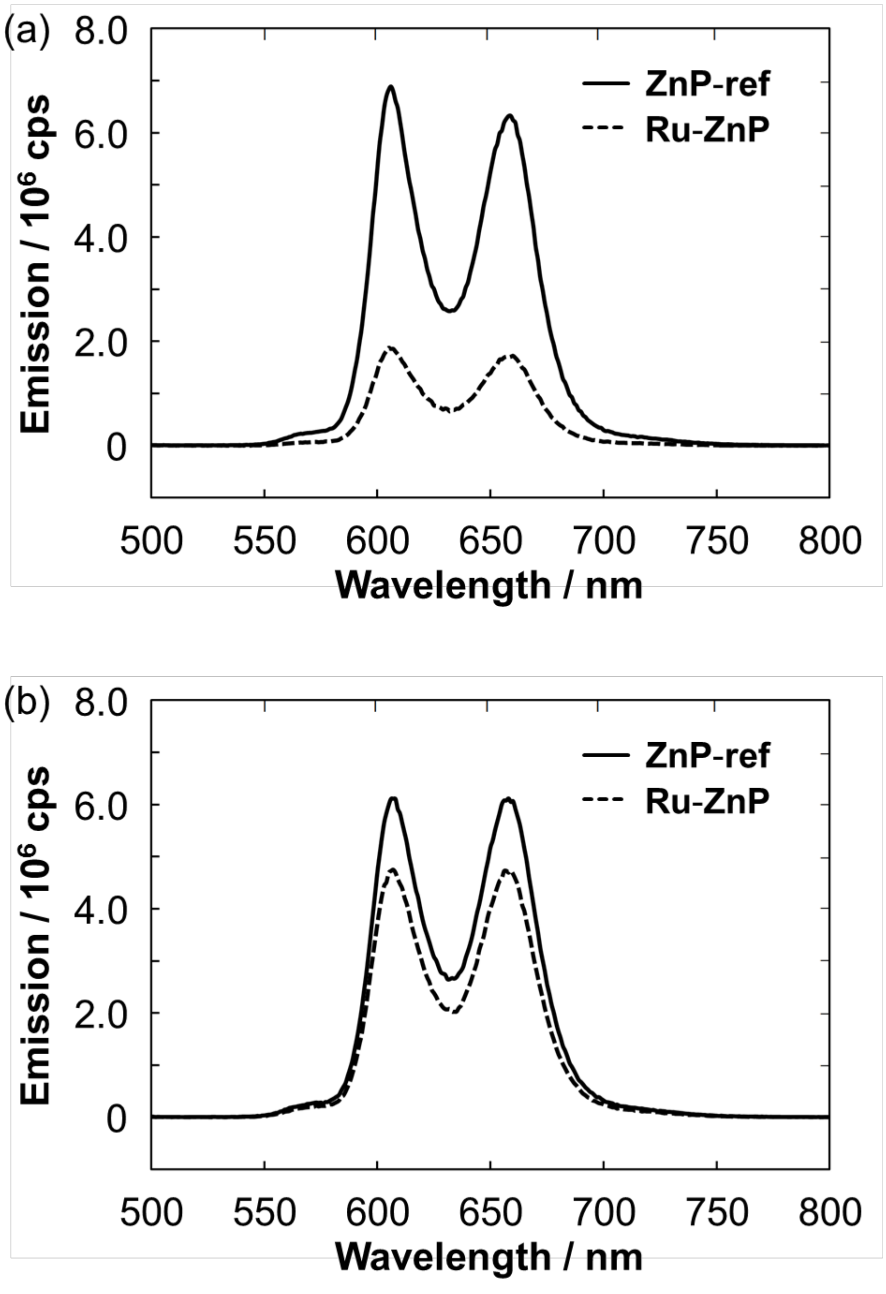


Figure S5. Steady-state fluorescence spectra of **Ru-ZnP** (dashed line) and **ZnP-ref** (solid line) in (a) methanol and (b) THF. The absorbances at the excitation wavelengths of 425 nm in methanol and 427 nm in THF were adjusted to be identical for comparison.

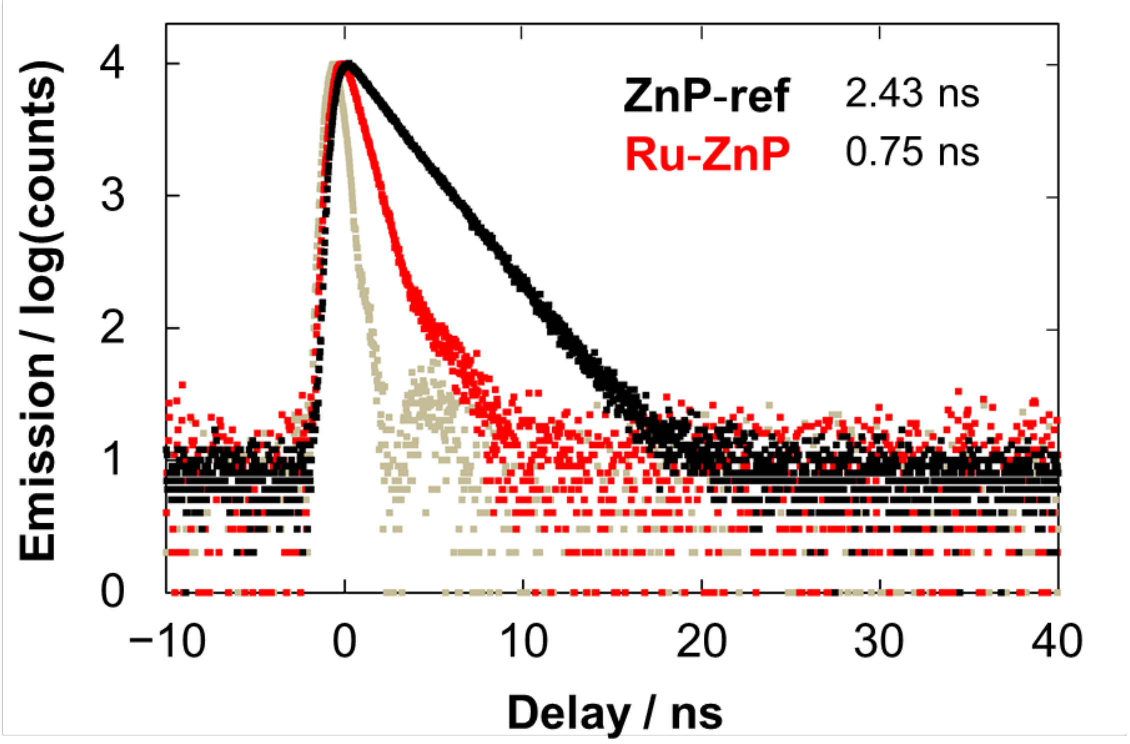


Figure S6. Fluorescence decays of **Ru**-**ZnP** (red) and **ZnP**-**ref** (black) in methanol. Trace with brown square is the instrument response function (IRF): λ_{ex} = 416 nm, λ_{obs} = 606 nm.

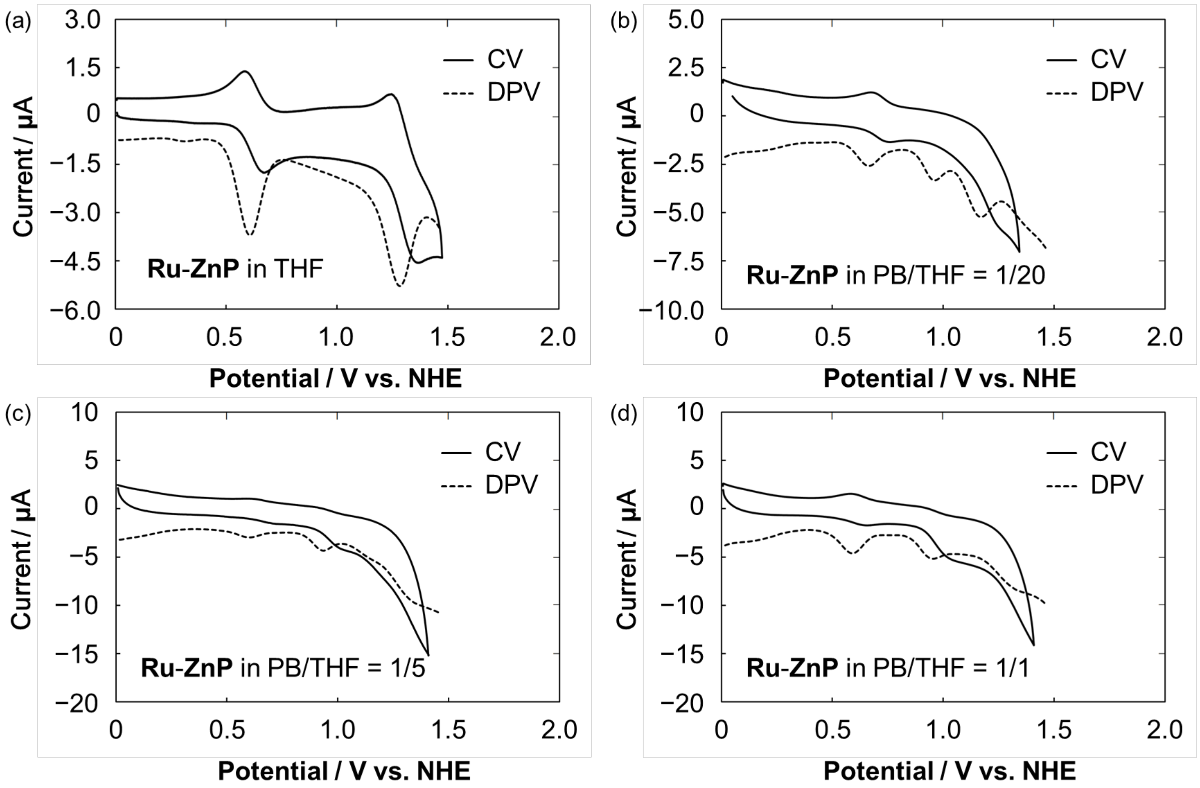


Figure S7. Cyclic voltammograms (solid line) and differential pulse voltammograms (dashed line) of **Ru-ZnP** in mixtures of sodium phosphate buffered aqueous solution (PB, 20 mM, pH 7.5) and THF. PB/THF = v/v: (a) 0/1, (b) 1/20, (c) 1/5 and (d) 1/1.

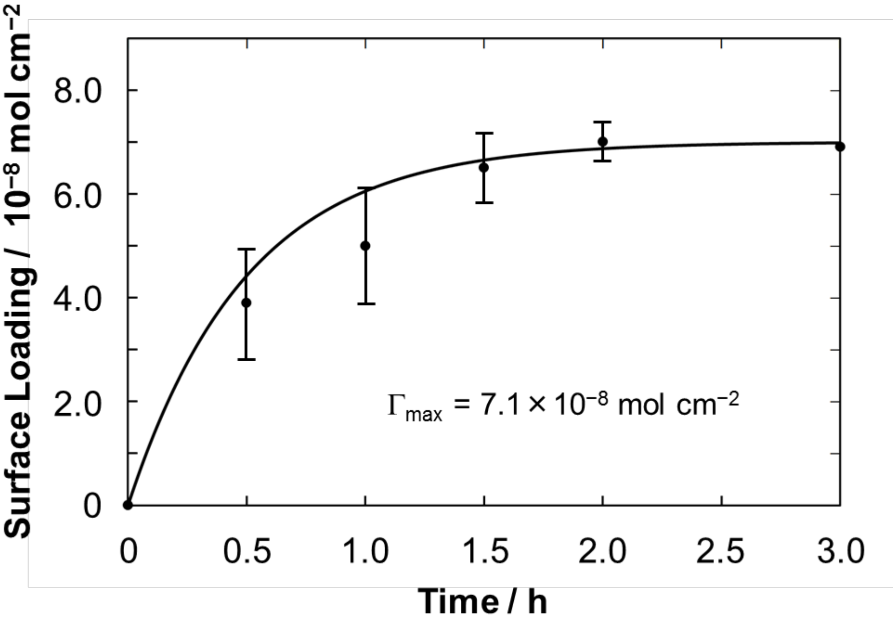


Figure S8. Plot of surface coverage of **Ru**-**ZnP** on TiO_2/FTO as a function of immersion time. The surface loading was determined by using Meyer's method.[39] The thickness of TiO_2 was 12 µm.

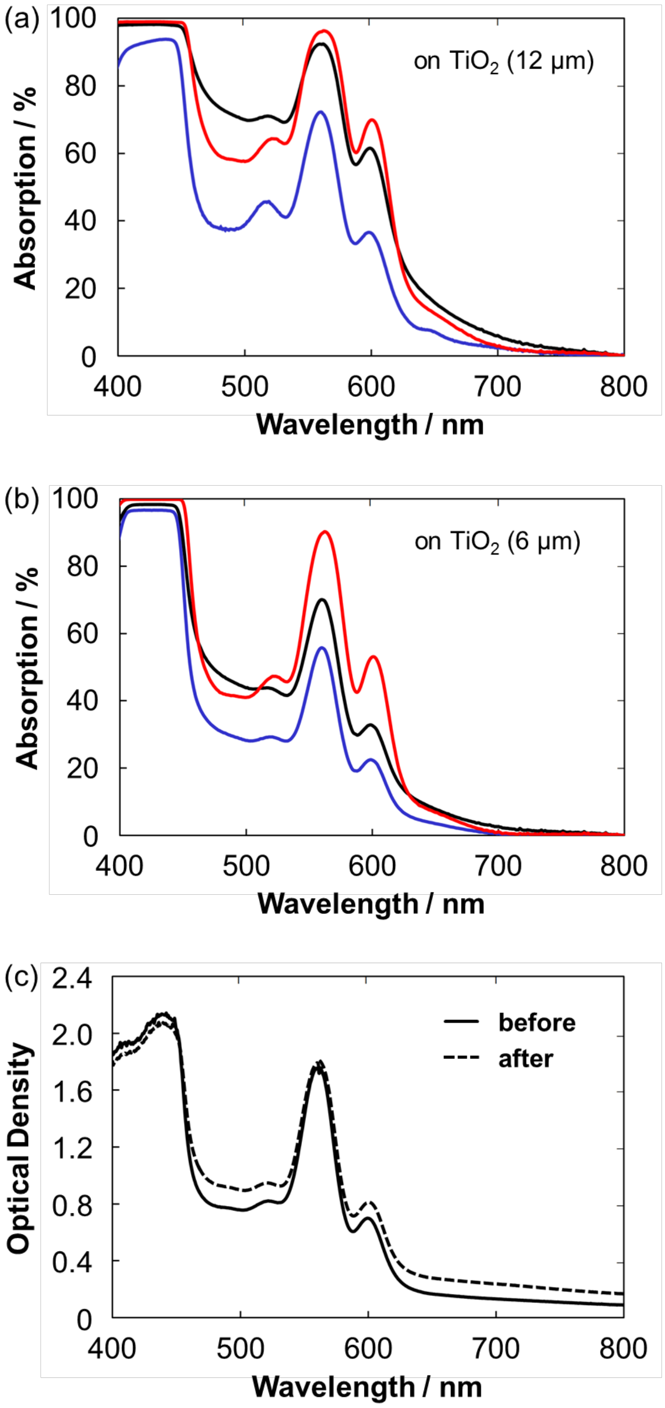


Figure S9. Light-harvesting efficiency (LHE) of (a) **Ru**-**ZnP**/TiO_2/FTO (black), **Ru**-**ref**+**ZnP**-**ref**/TiO_2/FTO (blue) and **ZnP**-**ref**/TiO_2/FTO (red) with TiO_2 thicknesses of (a) 12 µm and (b) 6 µm. (c) Optical density of **Ru**-**ZnP**/TiO_2/FTO films (12 µm) before and after the long-term PEC operation. LHE was calculated according to the following equation (S1):

$$\mathrm{LHE} = 100 \times (1 - 10^{-\mathrm{Absorbance}}) \qquad \text{(S1)}$$

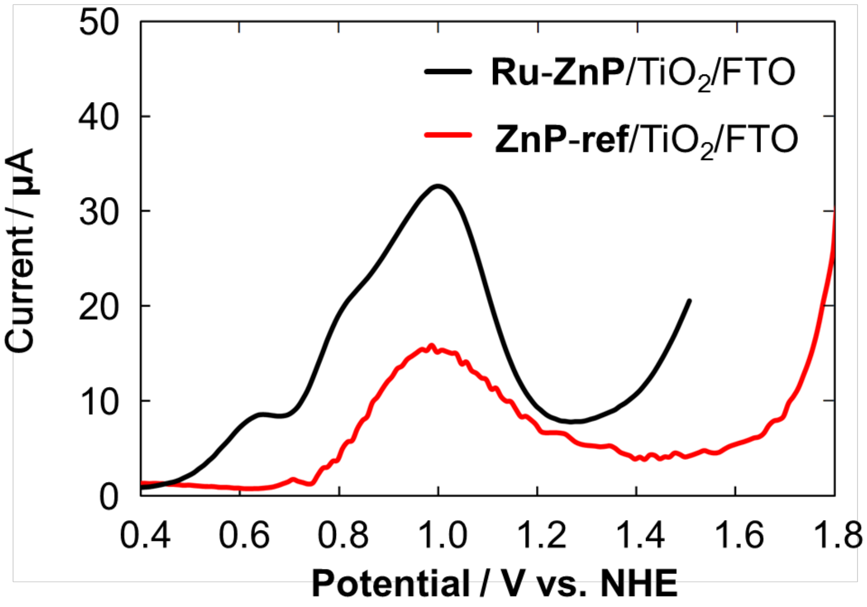


Figure S10. Differential pulse voltammograms of **Ru**-**ZnP**/TiO_2/FTO (black) and **ZnP**-**ref**/TiO_2/FTO (red). The TiO_2/FTO electrodes with a TiO_2 thickness of 10 μm were prepared by doctor blade technique. All the electrochemical measurements were carried out in PB (0.1 M, pH 7.3). The active area was 1 cm^2 for the measurements.

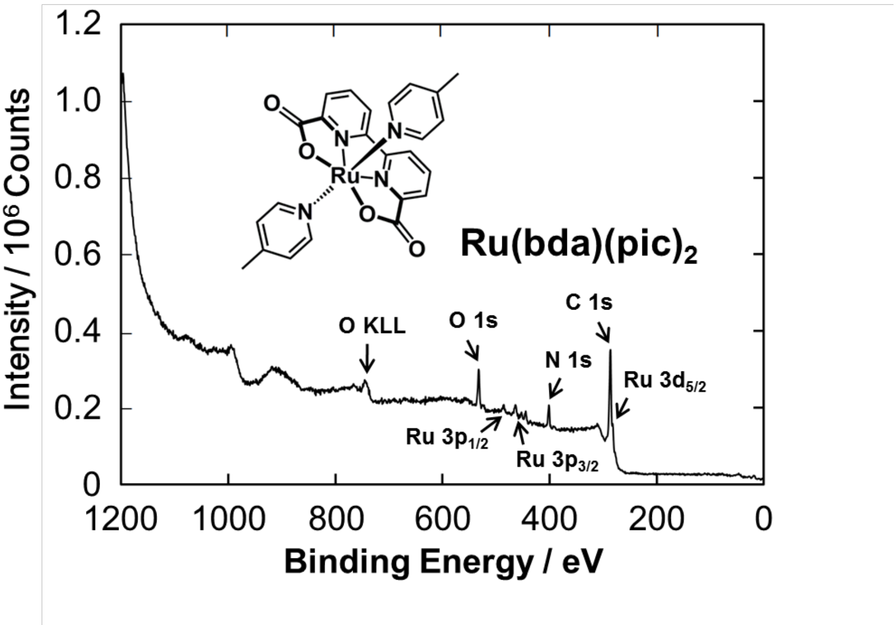


Figure S11. XPS spectrum of **Ru(bda)(pic)$_2$**.

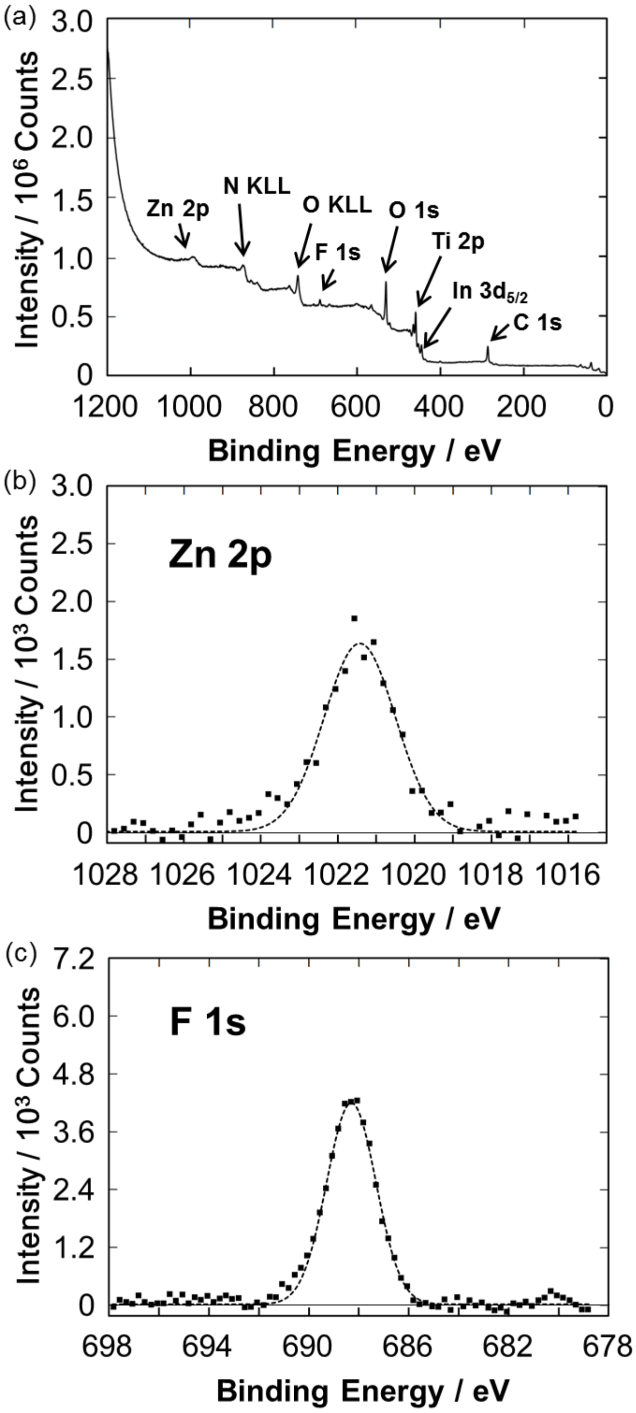


Figure S12. XPS spectra of **Ru**-**ZnP**/TiO_2/FTO. (a) whole region, (b) Zn2p region and (c) F1s region. The Zn2p and F1s XPS spectra exhibit single distinct zinc and fluorine peaks at 1021.2 and 688.3 eV, respectively, supporting the immobilization of **Ru**-**ZnP** on TiO_2/FTO.

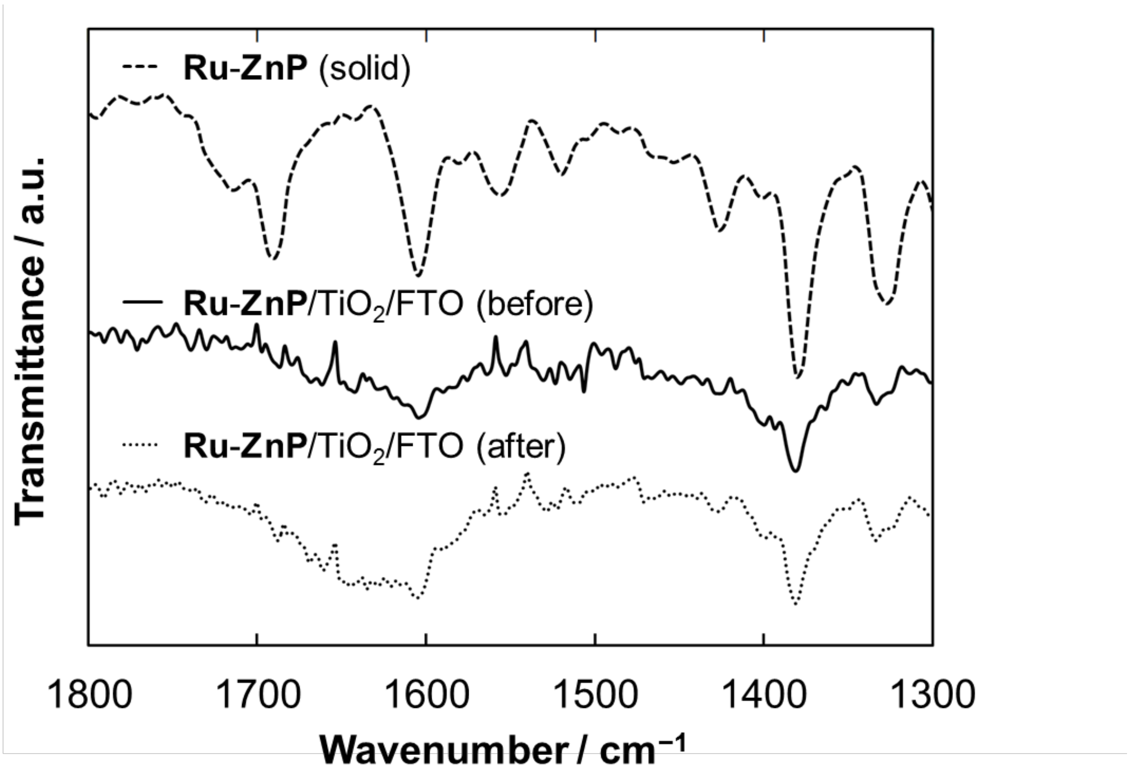


Figure S13. ATR-IR specrtra of **Ru**-**ZnP** (solid, dashed line) and **Ru**-**ZnP**/TiO_2/FTO before (solid line) and after the PEC operation (dotted line).

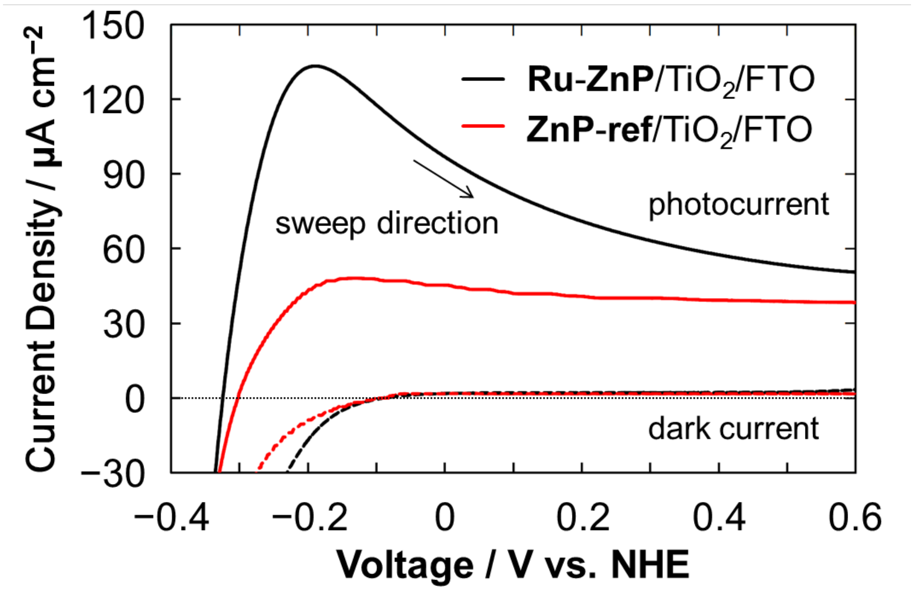


Figure S14. I-V curves for the **Ru-ZnP**/TiO_2/FTO (black) and **ZnP-ref**/TiO_2/FTO electrodes (red). Solid line: under white light illumination (W_{in} = 35 mW cm^{-2}, $\lambda > 380$ nm), dashed line: under dark. Electrolyte: PB (0.1 M, initial pH 7.3). The electrodes were prepared by immersing the TiO_2/FTO electrode into the **Ru-ZnP** and **ZnP-ref** solution for 2 h.

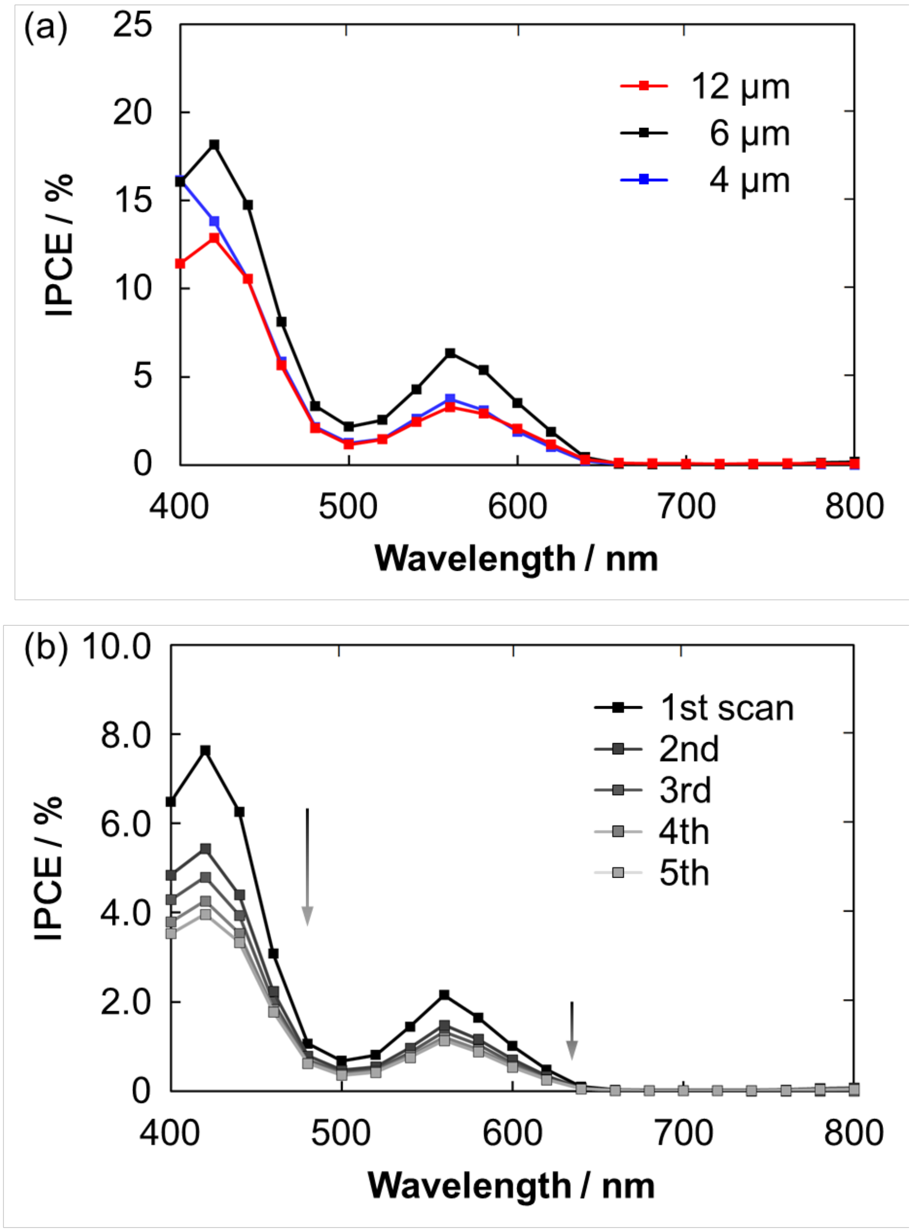


Figure S15. Photocurrent action spectra of the **Ru-ZnP**/TiO_2/FTO electrode under various conditions. (a) the TiO_2 thicknesses of 12 μm (red), 6 μm (black) and 4 μm (blue). (c) Durability test for the **Ru-ZnP**/TiO_2/FTO electrode with a TiO_2 thickness of 4 μm. The external bias was –0.2 V vs. NHE. The wavelength was scanned from 400 nm to 800 with a rate of 2 nm s^{-1}.

Table S1. Photophysical and electrochemical properties of molecules used in this study.

compound	solvent	$E_{1/2}$ / V vs. NHE		$E_{0\text{-}0}$ / eV		τ_f / ns[a]
		ZnP/ZnP$^{\bullet+}$	Ru^{II}/Ru^{III}	ZnP unit	Ru unit	
Ru-ZnP	MeOH			2.06		0.75
	THF	1.29	0.61	2.06		
ZnP-ref	MeOH			2.06		2.43
	THF	1.29		2.06		
Ru(bda)(pic)$_2$	CH_2Cl_2		0.60[b]		1.75[c]	

[a] The lifetime of the porphyrin fluorescence monitoring at 606 nm. [b] The value from ref 27d. [c] The value from ref 14b at 77 K.