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Syntheses, Properties, and Photoreactions of the Hybrid Molecules Consisting of a Co^{II} Mononuclear Complex and Porphyrins

Hiroki Kon and Toshi Nagata*[a]

Abstract: New hybrid molecules consisting of mononuclear Co^{II} complexes and porphyrin moieties were synthesized and their new photoreactions were examined. Three porphyrins with different *meso*-substituents (2,6-dimethoxyphenyl, 3,5-di-*tert*-butylphenyl, and 2,6-difluorophenyl groups) were used to change the redox potentials of the hybrid compounds. The hybrid molecules were prepared by the stepwise condensation of amide bonds. The cyclic voltammograms of these hybrid molecules showed the redox processes of both the cobalt and porphyrin moieties. The redox potentials of the porphyrins showed a systematic change that was consistent with the electronic effects of the *meso*-substituents. The emission spectra only showed fluorescence of the porphyrins with slightly decreased intensities. When a solution of the hybrid molecule, durohydroquinone, and *N*,*N*-diisopropylethylamine in $CHCl_3$/MeCN was irradiated with visible light (>580 nm), durohydroquinone was converted into duroquinone with the concurrent formation of the reduced product of $CHCl_3$. The hydroquinone was employed as an electron donor capable of reversible redox reactions, which is in contrast to conventional sacrificial reagents such as EDTA. The course of the photoreaction was followed by ^1H NMR spectroscopy and the amount of produced duroquinone was between 50–60 % after 600 min. We propose that the photoreaction involves a photoinduced electron transfer from the hydroquinone to the excited porphyrin, followed by the formation of a Co^I intermediate by charge shift, thus leading to the reaction with $CHCl_3$.

Keywords: cobalt • photochemistry • porphyrins • quinones • redox chemistry

Introduction

The combination of photoinduced electron transfer and the redox chemistry of transition-metal complexes is an attractive way to achieving useful photochemical energy conversion and synthetic transformations. For instance, plant photosynthesis shows us two important examples: an oxygen-evolving center (Mn_4Ca cluster) coupled with the P680 pigment in photosystem II,[1] and $F_X/F_A/F_B$ electron acceptors (iron–sulfur clusters) coupled with the P700 pigment in photosystem I.[2] Artificial systems have also been reported; representative examples include the classical photoinduced hydrogen production using metal polypyridine complexes[3] and the photochemical reduction of carbon dioxide by Ru/Re polypyridine complexes and by Co^{II} complexes,[4] as well as the more-recent heterodinuclear systems by the groups of Artero,[5] Brewer,[6] Ishitani,[7] and Sakai.[8] Although these works are wonderful achievements, they share one potentially disturbing drawback: they all use precious metals such as Ru, Rh, and Re. Owing to the low abundance of these elements in the earth's crust,[9] these systems may suffer from problems with availability in the near future. Therefore, it is desirable to substitute these elements with more-common ones; for example, ruthenium-based photosensitizers can be replaced with organic dyes.[10] The metal complexes for redox chemistry can be chosen from many varieties, among which cobalt,[5,11] nickel,[12–14] and iron complexes[15–17] seem to be reasonable candidates.

We chose Zn porphyrins as photosensitizers and a Co^{II} complex as a redox-active metal center. Zinc porphyrins are not strictly organic compounds, but zinc is a very common element and thus presents no problem with sustainability. Cobalt is classified as a "rare metal" by the Japanese government,[18] yet its abundance and annual production are about 10^3–10^4 times larger than those of Ru, Rh, or Re.[9,19] Moreover, the redox chemistry of Co^{II} is particularly interesting because it can be converted into a supernucleophilic Co^I species by single-electron reduction processes, which is well-matched with photoinduced electron transfer.

Herein, we report the syntheses of zinc-porphyrin/cobalt(II)-complex hybrid molecules. We have two objectives: 1) to utilize our terpyridine–bipyridine binary ligand[20] in the Co^{II} complex and to combine this complex with the porphyrin part using organic synthesis, and 2) to develop new photochemical reactions that involve the electron transfer of photoexcited porphyrins and Co^{II} complexes.

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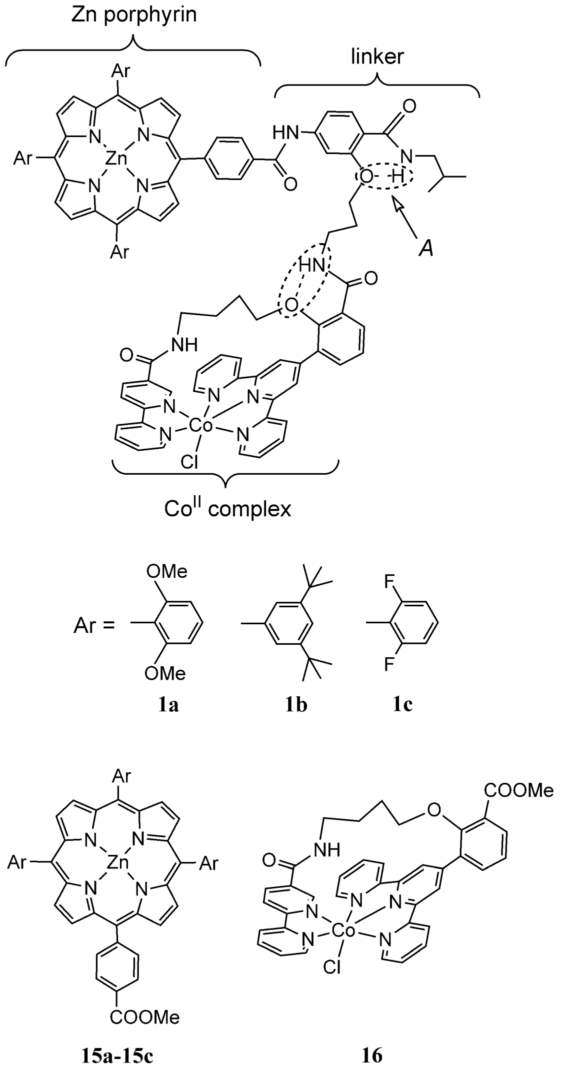
Results and Discussion

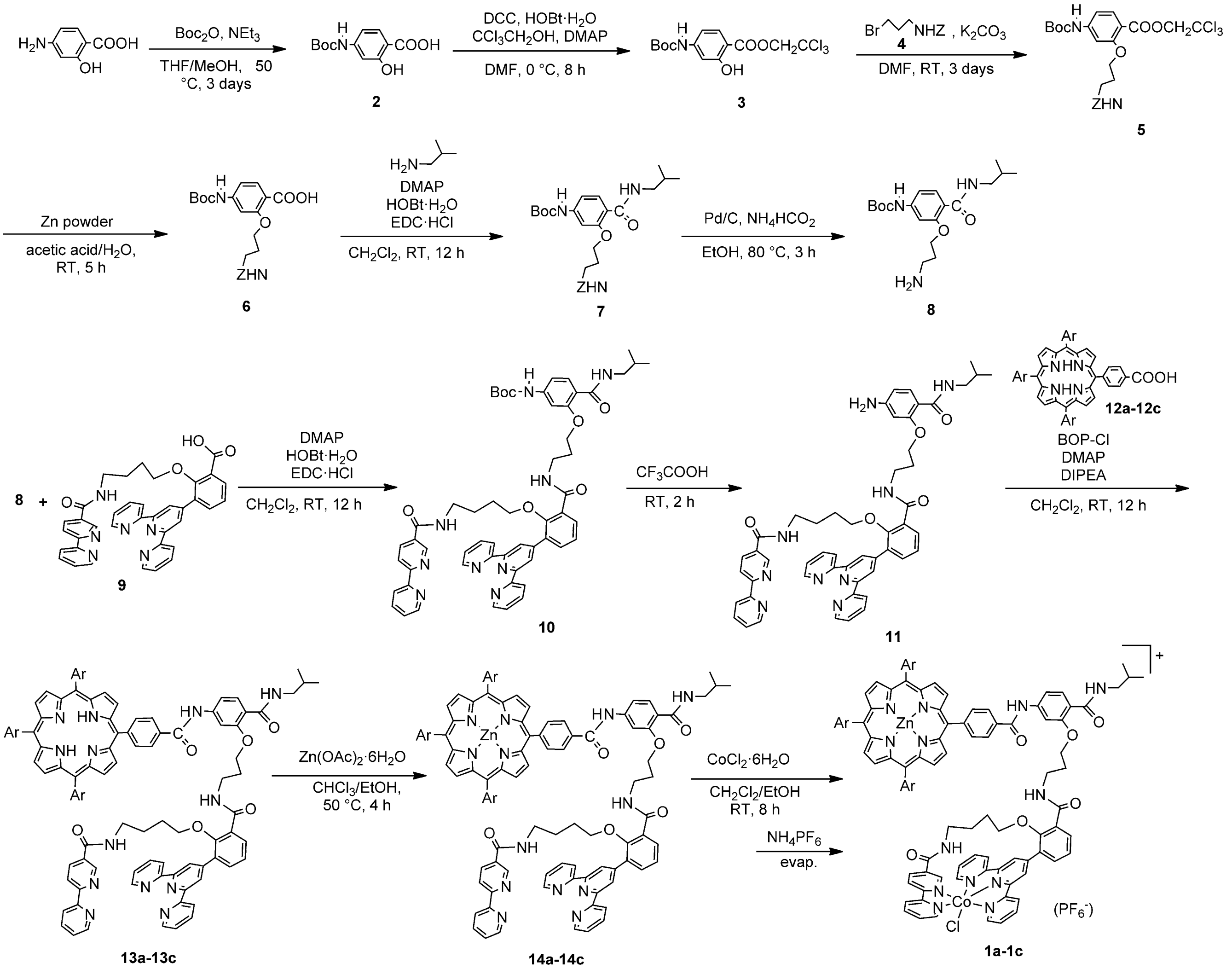
Design and synthesis: Scheme 1 shows the structure of the hybrid molecules ($ZnP–Co^{II}$, **1a**–**1c**) that each consist of a Zn^{II} porphyrin (ZnP) and a Co^{II} complex. As shown in Scheme 1, two amide NH groups are expected to form intramolecular hydrogen bonds with the adjacent ether oxygen atoms, thereby restricting the conformation of the polymethyleneoxy ($(CH_2)_nO$) group. In particular, the hydrogen bond marked *A* should prevent the cobalt complex from swinging away from the porphyrin moiety, by forcing the $O{-}CH_2$ bond to point in the direction of porphyrin. The syntheses of hybrid molecules **1a**–**1c** are shown in Scheme 2. The first key compound is the linker unit (**7**), which contains two orthogonally protected amino groups. The Z (Z = benzyloxycarbonyl) protecting group was removed and the resulting amine **8** was condensed with the carboxylic acid group of binary ligand **9**.[20] Then the Boc (Boc = *tert*-butoxycarbonyl) protecting group was removed and the resulting amine (**11**) was condensed with the porphyrin carboxylic acid. We used three different porphyrins (**12a**–**12c**), which contained different *meso* substituents, with the aim of influencing the redox potentials. The target $ZnP–Co^{II}$ hybrid molecules **1a**–**1c** were obtained by the introduction of a Zn^{II} ion into the porphyrin ring followed by a Co^{II} ion to the binary ligand. The order in which we introduced the metal ions was significant. Prior introduction of the Zn^{II} ion effectively protected the porphyrin ring from the formation of the Co^{II} porphyrin, and the excess Zn^{II} ion bound to the binary ligand could be easily removed by treatment with aqueous disodium dihydrogen ethylenediaminetetraacetate. The hybrid molecules **1a**–**1c** were obtained as the fine powder by exchanging the counter anion for PF_6.



Scheme 1. The zinc-porphyrin/cobalt(II)-complex hybrid molecules (**1a**–**1c**) and their related compounds (**15a**–**15c** and **16**) used in this study.

Cyclic voltammograms: The cyclic voltammograms (CVs) of compounds **1a**–**1c** are shown in Figure 1. The measurements were performed in DMF/THF (1:1 v/v) because this mixed solvent system dissolved all of the compounds to a reasonable concentration. For compound **1a**, reversible waves at −2.11, −1.81, and 0.20 V, and quasi-reversible waves at −1.46 and −0.27 V were observed. From comparison with the CVs of the reference compounds (see the Supporting Information, Table S1), the peaks at −1.81, −1.46, and −0.27 V were assigned to the redox couples of the Co^{II} moiety, and other peaks at −2.11 V and 0.20 V were assigned to the redox couples of the ZnP moiety. The assignments of each redox waves are $trpy/trpy^{-\bullet}$ (−1.81 V), Co^{II}/Co^{I} (−1.46 V), Co^{III}/Co^{II} (−0.27 V), $ZnP/ZnP^{-\bullet}$ (−2.11 V), and $ZnP^{+\bullet}/ZnP$ (0.20 V). These redox processes were observed at almost the same potentials as those of the reference compounds. The redox waves of the Co^{II} moiety were broadened, thereby indicating slow electron transfer in these redox processes. This observation can be ascribed to the structural change around the cobalt coordination environment.[20] In spite of the broadened waves, these redox processes are chemically reversible, as indicated by the unchanged voltammograms after repeated scans. Comparison of the integrated current values also suggested that these were all one-electron processes. For compounds **1b** and **1c**, the redox peaks from the Co^{II} moieties were observed at same potentials as for compound **1a**. On the other hand, the redox waves of porphyrin moieties were systematically shifted. This shift is ascribed to the influence of the *meso* substitutions, namely the electron-donating 2,6-dimethoxyphenyl group and the electron-withdrawing 2,6-difluorophenyl group in compounds **1b** and **1c**, respectively.

Absorption and emission spectra: The UV/Vis absorption spectra of compounds **1a**–**1c** showed bands that could be attributed to the porphyrin moieties (Soret bands at around 425 nm and Q-bands at around 550 nm) and cobalt(II)–polypyridine moieties (π–π* transition at around 270 nm; see the Supporting Information, Figure S-29 and Table S-2). By comparison with the spectra of the reference compounds,



Scheme 2. Synthetic routes to compounds **1a**–**1c**.

the spectra of compounds **1a**–**1c** were well-described as sums of the spectra of the individual components. The emission spectra of the ZnP–Co^{II} hybrid molecules **1a**–**1c** showed the characteristic porphyrin fluorescence signals, although the emission intensities were weaker than those of the individual porphyrin components (**15a**–**15c**; see the Supporting Information, Figure S-30). These weaker emissions are attributed to the electron transfer involving the Co^{II} moiety and the singlet excited states of the porphyrin ring. The Co^{III} moiety can act either as an oxidative quencher or as a reductive quencher, and the contribution of each process should depend on the ΔG values of the electron transfer ($ZnP^*–Co^{II} \rightarrow ZnP^{+\bullet}–Co^{I}$: −0.42 eV, −0.29 eV, and −0.09 eV; $ZnP^*–Co^{II} \rightarrow ZnP^{-\bullet}–Co^{III}$: −0.24 eV, −0.42 eV, and −0.57 eV).

Concept of the photochemistry: Our compounds (**1a**–**1c**) contain a photoactive porphyrin group and a Co^{II} complex in one combined system. Consequently, we wanted to look for a new photochemical process, in which a strongly reducing Co^{I} center is generated by photoinduced electron transfer (PET) and then reacts with an organic substrate to give reduced products. We chose $CHCl_3$ ($CDCl_3$) as the substrate because it is well-known that Co^{I} species readily react with polychlorinated organic compounds.[21] To balance the redox reactions, we also needed a reductant that donates electrons to the photoexcited porphyrin group before or after photoinduced electron transfer. Although sacrificial electron donors such as ethylenediaminetetraacetic acid (EDTA) or triethanolamine have been commonly used, these are not very attractive because the reaction involved is actually the degradation, rather than production, of high-energy substances. On the other hand, the direct oxidative production of high-energy substances (such as O_2 from water) is not always straightforward, although it is the most preferable. In that case, the second-best approach is to use a reduced form of a reversible redox pair as the electron source, which is exactly what happens in natural photosynthesis.[22] In photosystem II, the terminal electron accepter is a quinone, which is reduced to a hydroquinone. Then the hydroquinone is oxi-

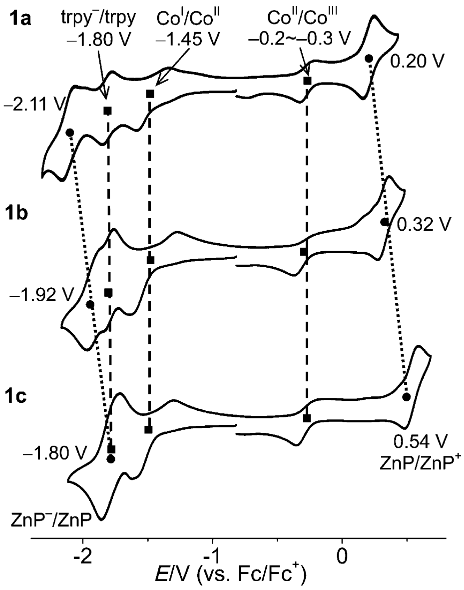


Figure 1. Cyclic voltammograms for compounds **1a**–**1c** in DMF/THF. DMF = *N*,*N*-dimethylformamide.

dized back to a quinone by cytochrome b_6f, which gives electrons to photosystem I. In a similar fashion, we use a hydroquinone as the terminal donor in our photoreaction.

Description of the photochemistry: When a solution of the hybrid molecules **1a**–**1c** (0.8–0.9 μmol), durohydroquinone (14 μmol), *N*,*N*-diisopropylethylamine (DIPEA, 23 μmol), and $CDCl_3$ (or $CHCl_3$, 0.4 mL) in CD_3CN (0.4 mL) was irradiated with visible light (>580 nm), durohydroquinone was gradually converted into duroquinone. Figure 2 shows the time-dependent changes in the ^{1}H NMR spectra of the reaction with compound **1a** and $CDCl_3$. As the reaction proceeds, the signal at 1.98 ppm (duroquinone) grows larger at the expense of the signal at 2.11 ppm (durohydroquinone). At the same time, the signals of DIPEA shifted to lower field, thus indicating the formation of the protonated from. The ^{1}H NMR spectra and GC-MS analyses also showed the formation of other products originating from $CDCl_3$ ($CHCl_3$), namely $CDHCl_2$ (CH_2Cl_2), $CDCl_2CDCl_2$ ($CHCl_2CHCl_2$), and *cis*-CDCl=CDCl (*cis*-CHCl=CHCl). A trace amount of H_2 was detected by GC. In addition, an unidentified product with the formula $C_{11}H_{13}O_2Cl$ (corresponding to duroquinone+"CHCl") was detected in the GC-MS spectra. When compounds **1b** or **1c** were used in the place of compound **1a**, the photoreaction profile was very similar to that of compound **1a**. The progress of the photoreaction is shown in Figure 3. We examined four systems: compounds **1a**–**1c** and an equimolar mixture of zinc porphyrin **15a** and cobalt(II) complex **16**. The systems containing compounds **1a**–**1c** reacted at almost identical rates, whereas the system containing compounds **15a**/**16** reacted slightly faster. As control experiments, we also examined the reactions of the mixed **15a**/**16** system with the omission of each of the individual components. (**15a**, **16**, DIPEA, $CDCl_3$, and light). The systems lacking compound **15a** or light reacted very slowly, and the systems lacking any other components did not react at all. The relative quantities of the significant materials after 600 min irradiation are listed in Table 1, together with the turnover numbers and quantum yields of the quinones. These numbers were obtained from the integration of the ^{1}H NMR spectra. Although the mass balance is not complete, because there are yet unidentified products, it is clear

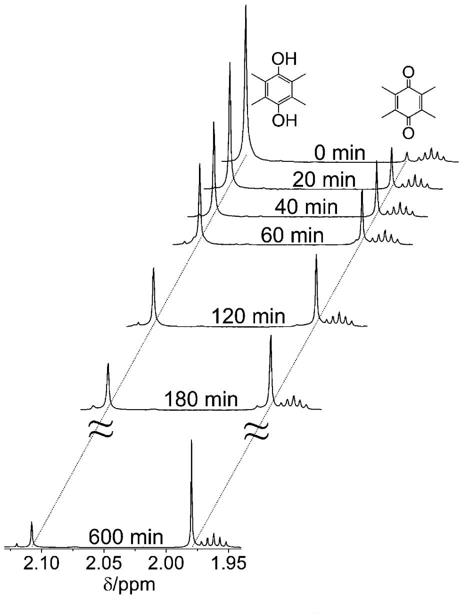


Figure 2. The time-dependent changes in the ^{1}H NMR spectrum of compound **1a** during the photoreaction.

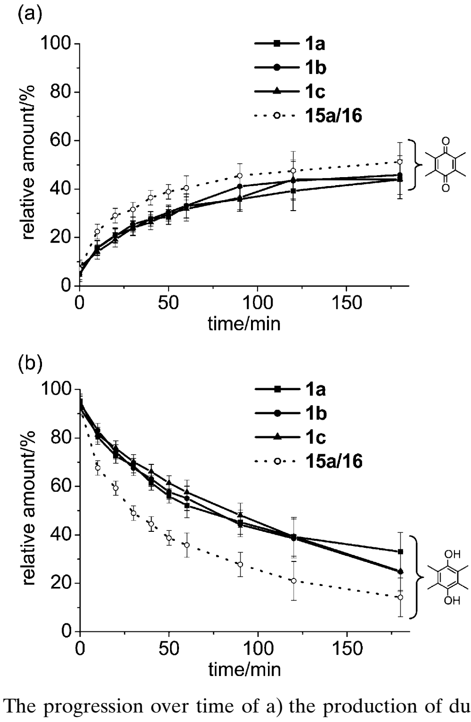


Figure 3. The progression over time of a) the production of duroquinone, and b) the consumption of durohydroquinone in the photoreaction.

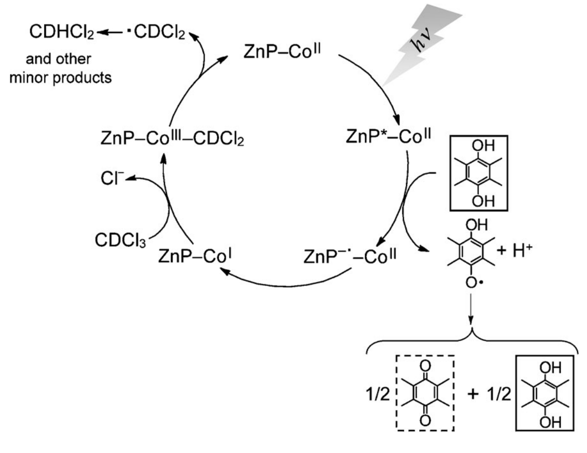
Table 1. Yields of the products and TON of duroquinone for the photoreaction with $CHCl_3$ after irradiation for 600 min.

Compound	Duroquinone [%]	CH_2Cl_2 [%]	CH_2ClCH_2Cl [%]	*cis*-CHClCHCl [%]	Quantum yield[a]	TON[a]
1a	51.8	17.9	4.1	0.8	0.0084	8.9
1b	60.2	16.3	5.1	1.6	0.0091	9.6
1c	58.1	21.7	3.8	1.2	–[b]	9.0
15a/16b	69.9	17.7	3.7	0.8	0.0087	9.8

[a] Values for duroquinone. [b] Not determined because of technical problems (the deposition of insoluble materials during the photoreaction).

that the main products are duroquinone and chlorocarbon compounds that are derived from $CDCl_3$. In all cases, the turnover numbers based on the porphyrin exceeded unity, which indicates that this reaction involves photocatalysis, rather than a one-shot photoreaction. The quantum yields of the photoreaction were estimated to be 0.8–0.9%: these low numbers indicate that these are many non-productive pathways (see discussion below). Thus, the overall reaction can be summarized as follows: durohydroquinone+DIPEA+$CDCl_3$ ($CHCl_3$) →duroquinone+DIPEA•HCl+$CDHCl_2$ (CH_2Cl_2), etc.

Plausible reaction mechanism: The above results show that both the Co^{II} complex and the porphyrin moiety are necessary for this reaction to proceed. On the other hand, the excited state of the Co^{II} moiety must not be involved because the Co^{II} complex has almost no absorption band above 580 nm. The most-likely role of the Co^{II} complex is to generate a Co^{I} intermediate, which will easily react with $CHCl_3$ to produce active species. A plausible reaction mechanism is shown in Scheme 3. The mechanism involves reductive quenching of the excited porphyrin by hydroquinone (or its anionic form), followed by a charge-shift reaction to generate the Co^{I} species.[23] Alternatively, it is also possible that oxidative quenching by Co^{II} occurs to generate the Co^{I} species directly. However, we prefer the mechanism shown in Scheme 3 because the porphyrin–cobalt(II) hybrid molecules were not more active than the porphyrin/cobalt(II) intermolecular system. It was disappointing that connecting the porphyrin and the Co^{II} complex retarded, rather than accelerated, the photoreaction. Part of this retardation is caused by intramolecular fluorescence quenching (see the Supporting Information, Figure S-30), which can compete with the intermolecular electron transfer (to give the porphyrin anion radical directly) and the intersystem crossing (to give the triplet excited state which then can take part in the electron transfer and subsequent reactions). It is also possible that the charge shift from $ZnP^{-\bullet}$ to Co^{II} is not the rate-determining step. There are many other potential bottlenecks in this system, for example reductive quenching by hydroquinone, reduction of the chlorocarbons by Co^{I}, and so on. It would appear that this bottleneck is the cause of the low quantum yields. To improve this reaction, we will need kinetic parameters for individual steps, which is currently under investigation.



Scheme 3. The proposed mechanism of the photoreaction.

Conclusion

We prepared a series of zinc-porphyrin/cobalt(II)-complex hybrid molecules by using the "binary" ligand we have previously reported. The hybrid molecules showed modest fluorescence quenching, which was attributed to intramolecular electron transfer between the photoexcited porphyrin and the Co^{II} moiety. A new photoreaction was developed, in which these hybrid molecules act as photocatalysts and a hydroquinone was converted into a quinone with the concurrent reduction of $CHCl_3$. This reaction opens the door to the utilization of a regeneratable electron donor in photochemical materials, and to the construction of a Z-scheme mimic using artificial quinone pools.

Experimental Section

General: Reagents were purchased from Wako, Nacalai, and Aldrich, and used as received unless otherwise noted. $CHCl_3$ for the photoreaction was used after distillation from K_2CO_3. Compound **4** was prepared according to the literature procedure.[24] ^1H, ^{13}C, and ^{19}F NMR spectra were measured at RT on JEOL LA400 and LA500 spectrometers. For compounds **13a–13c**, HH-COSY, HSQC, and HMBC spectra were measured with a JEOL JMN-ECA920 spectrometer. For ^1H and ^{13}C NMR spectroscopy, tetramethylsilane was used as the internal reference. For ^{19}F NMR, C_6F_6 was used as the internal reference ($\delta = -164.9$ ppm vs. $CFCl_3$). ESI-MS spectra were recorded on a Waters Micromass LCT. UV/Vis absorption and emission spectra were recorded on a Shimadzu UV-2500PC spectrometer and a Shimadzu RE-5300PC spectrofluorometer, respectively. GC-MS spectra were recorded on an Agilent 6890 Series GC system equipped with a JMS-GC mate II GCMS SYSTEM. An ADB-WAX(122–7032, Agilent Technologies) capillary column was used at 40–250 °C. The synthesis of compounds **9**, **12a–12c**, and **15a–15c**, the ^1H NMR, ^{13}C NMR spectra, ESI-MS (**1a–1c**) data, ^{19}F NMR spectroscopic characterization (**12c** and **13c**), and HR-FAB-MS data (**10** and **13a**–**13c**) are compiled in the Supporting Information.

Electrochemical methods: Cyclic voltammograms were measured with an ALS/CHI Model 660 voltammetric analyzer at a scan rate of $100\,\mathrm{mV\,s^{-1}}$. The working and counter electrodes were a platinum disk and a platinum wire, respectively. The sample solutions (ca. 0.001 M) in DMF/THF (1:1 v/v) with 0.1 M $n\mathrm{Bu_4NClO_4}$ were deoxygenated with a stream of nitrogen gas. All values of redox potentials are reported in reference to $\mathrm{Fc/Fc^+}$ (Fc = ferrocene); in practice, a $\mathrm{Ag/Ag^+}$ electrode was used as a reference (-0.32 V vs. $\mathrm{Fc/Fc^+}$).

Photoreaction: The photoreactions were performed using a standard "merry-go-round" type apparatus. The sample solutions were prepared in the glove box under a nitrogen atmosphere and placed in NMR sample tubes (5 mm outer diameter) with J-Young valves. The sample solutions typically contained the hybrid molecule (ca. 1.0 μmol), DIPEA (0.023 mmol), and durohydroquinone (ca. 0.013 mmol) in $\mathrm{CDCl_3}$ (or $\mathrm{CHCl_3}$)/$\mathrm{CD_3CN}$ (1:1 v/v, 0.8 mL). A 65 W halogen lamp (Toshiba JDR11^0 V65WN/K5S) was used with a colored glass filter (Asahi Techno Glass O-58, 50×50×2.5 mm) that cuts off wavelength shorter than 580 nm. The temperature was kept at 30(±1) °C by circulating water. The course of the reaction was followed by ^{1}H NMR spectroscopy and the products were analyzed by GC-MS. The measurement of quantum yield was performed by the following setup: A solid-state green laser (532 nm, 10 mW, Shimadzu Beammate) was introduced into a 10×10 mm quartz cuvette with a J-Young stopcock. Behind the cuvette was placed a power meter (Sanwa LP1) to monitor the light intensity. The sample solution (3 mL) was placed in the cuvette under a $\mathrm{N_2}$ atmosphere and irradiated with vigorous stirring. After irradiation for 10 h, the solution was examined by ^{1}H NMR spectroscopy.

Synthesis

4-(*tert*-Butoxycarbonylamino)-2-hydroxybenzoic acid (2): To a mixture of 4-aminosalicylic acid (24.7 g, 0.16 mol), MeOH (85 mL) and triethylamine (23 mL, 0.16 mol), a solution of di-*tert*-butyl dicarbonate (42.3 g, 0.19 mol) in THF (100 mL) was added, and the mixture was heated at 50 °C for 3 days. A solution of $\mathrm{KHSO_4}$ (44 g, 0.32 mol) in water (150 mL) was added, and the mixture was concentrated using a rotary evaporator. The oily material was extracted with EtOAc, and the organic phase was washed with brine, dried over $\mathrm{Na_2SO_4}$, and evaporated. The pale-brown solid was recrystallized from MeOH/$\mathrm{H_2O}$, and dried under vacuum at 50 °C . Yield: 37.1 g (0.15 mol, 91 %); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): $\delta = 11.32$ (br s, 1H; COO*H*), 9.71 (s, 1H; amide N*H*), 7.64 (d, ^3J(H,H) = 8.4 Hz, 1H; Ar C6−*H*), 7.11 (d, ^4J(H,H) = 2.0 Hz, 1H; Ar C5−*H*), 6.97 (dd, ^3J(H,H) = 8.8 Hz, ^4J(H,H) = 2.0 Hz, 1H; Ar C3−*H*), 1.46 ppm (s, 9H; Boc).

2,2,2-Trichloroethyl 4-(*tert*-butoxycarbonylamino)-2-hydroxybenzoate (3): A solution of compound **2** (5.06 g, 20 mmol) and 1-hydroxybenzotriazole monohydrate (HOBt·$\mathrm{H_2O}$, 3.36 g, 22 mmol) in DMF (20 mL) was cooled to 0 °C, and a solution of dicyclohexylcarbodiimide (DCC, 4.54 g, 22 mmol) in DMF (20 mL) was added dropwise over 15 min. After stirring for 1.5 h at 0 °C, 2,2,2-trichloroethanol (14.9 g, 100 mmol) and 4-dimethylaminopyridine (DMAP, 122 mg, 1 mmol) were added. The mixture was stirred overnight with gradual warming to RT. The white solid (dicyclohexylurea) was removed by filtration, and washed with a small amount of DMF. Acetic acid (0.12 mL, 2 mmol) was added to the filtrate, which was concentrated under vacuum (ca. 1 torr) at 50–70 °C. The residue (dark-brown oil or brown solid) was taken up in water (100 mL) and extracted with EtOAc (150 mL). The organic phase was washed three times with saturated aqueous $\mathrm{NaHCO_3}$, dried over $\mathrm{Na_2SO_4}$, and evaporated. The residual solid was recrystallized from EtOAc/*n*-hexane to give 4.04 g (10.5 mmol) of the product. The filtrate was concentrated, and purified by column chromatography on silica gel (*n*-hexane/EtOAc = 100:0 to 70:30), to give 1.14 g (3.0 mmol) of the product. Yield: 5.18 g (13.5 mmol, 68 %); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta = 10.36$ (s, 1H; O*H*), 7.83 (d, ^3J(H,H) = 8.8 Hz, 1H; Ar C6−*H*), 7.11 (d, ^4J(H,H) = 2.0 Hz, 1H; Ar C4−*H*), 6.86 (dd, ^3J(H,H) = 9.2 Hz, ^4J(H,H) = 2.0 Hz, 1H; Ar C3−*H*), 6.64 (s, 1H; Boc N*H*), 4.93 (s, 2H; OC*H*$_2$CCl$_3$), 1.51 ppm (s, 9H; Boc).

2,2,2-Trichloroethyl 2-(3-(benzyloxycarbonylamino)propyloxy)-4-(*tert*-butoxycarbonylamino)benzoate (5): A mixture of compound **3** (1.62 g, 4.2 mmol), compound **4** (1.44 g, 5.3 mmol), and $\mathrm{K_2CO_3}$ (1.16 g, 8.4 mmol) in DMF (10 mL) was stirred at RT for 3 days. Water (80 mL) was added and the mixture was extracted with EtOAc. The organic phase was washed twice with 5 % $\mathrm{KHSO_4}$, dried over $\mathrm{Na_2SO_4}$, and evaporated. The residual solid was recrystallized from EtOAc/*n*-hexane. Yield: 1.91 g (3.32 mmol, 79 %); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta = 7.96$ (d, ^3J(H,H) = 8.4 Hz, 1H; Ar C6−*H*), 7.52 (s, 1H; Boc N*H*), 7.26–7.40 (m, 5H; Z), 6.71 (s, 1H; Ar C3−*H*), 6.65 (dd, ^3J(H,H) = 8.8 Hz, ^4J(H,H) = 2.0 Hz, 1H; Ar C5−*H*), 6.58 (br s, 1H; Z−N*H*), 5.12 (s, 2H; OC*H*$_2$Ph), 4.78 (s, 2H; OC*H*$_2$CCl$_3$), 4.19 (t, ^3J(H,H) = 5.6 Hz, 2H; OC*H*$_2$CH$_2$CH$_2$NH), 3.49 (m, 2H; OCH$_2$CH$_2$C*H*$_2$NH), 2.08 (m, 2H; OCH$_2$C*H*$_2$CH$_2$NH), 1.53 ppm (s, 9H; Boc).

2-(3-(Benzyloxycarbonylamino)propyloxy)-4-(*tert*-butoxycarbonylamino) benzoic acid (6): A mixture of compound **5** (244.1 mg, 0.425 mmol) and zinc powder (240.0 mg) in acetic acid (3 mL) and $\mathrm{H_2O}$ (0.3 mL) was stirred at RT for 5 h. The grayish powder was removed by filtration and the filtrate was extracted with EtOAc and $\mathrm{H_2O}$. The separated organic phase was dried over $\mathrm{Na_2SO_4}$ and evaporated. The residual solid was recrystallized from MeOH/$\mathrm{H_2O}$. Yield: 187.2 mg (0.422 mmol, 99 %); ^{1}H NMR (400 MHz, [D$_6$]DMSO, 25 °C): $\delta = 12.09$ (br s, 1H; COO*H*), 9.64 (s, 1H; Ar C3−*H*), 7.62 (d, ^3J(H,H) = 8.0 Hz, 2H; Ar C6−*H*), 7.28–7.38 (m, 7H; Z, Boc N*H*, Z−N*H*), 7.01 (d, ^3J(H,H) = 8.0 Hz, 2H; Ar C5−*H*), 5.00 (s, 2H; C(O)OC*H*$_2$Ph), 3.97 (t, ^3J(H,H) = 6.0 Hz, 2H; OC*H*$_2$CH$_2$), 3.21 (m, 2H; CH$_2$C*H*$_2$NH), 1.88 (m, 2H; OCH$_2$C*H*$_2$CH$_2$), 1.47 ppm (s, 9H; Boc).

2-(3-(Benzyloxycarbonylamino)propyloxy)-4-(*tert*-butoxycarbonylamino)-*N*-isobutylbenzamide (7): Compound **6** (201.5 mg, 0.454 mmol), isobutylamine (50 μL, 0.50 mmol), DMAP (7.1 mg, 0.058 mmol), HOBt·$\mathrm{H_2O}$ (121.2 mg, 0.90 mmol), and 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride (EDC·HCl, 158.6 mg, 0.83 mmol) were dissolved in $\mathrm{CH_2Cl_2}$ (8 mL) and the mixture was stirred for 12 h at RT. The reaction mixture was diluted with $\mathrm{CH_2Cl_2}$ and the solution was washed with saturated aqueous $\mathrm{NaHCO_3}$. The organic phase was separated, dried over $\mathrm{Na_2SO_4}$, and evaporated. Purification was performed by column chromatography on alumina ($\mathrm{CH_2Cl_2}$/MeOH = 98:2), and recrystallized from $\mathrm{CH_2Cl_2}$/*n*-hexane. Yield: 197.3 mg (0.395 mmol, 87 %); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): $\delta = 7.99$ (d, ^3J(H,H) = 8.4 Hz, 1H; Ar C6−*H*), 7.76 (br s, 1H; amide N*H*−*i*Bu), 7.42 (s, 1H; Ar C3−*H*), 7.20–7.30 (m, 5H; Z), 6.85 (s, 1H; Boc N*H*), 6.62 (dd, ^3J(H,H) = 8.4 Hz, ^4J(H,H) = 2.0 Hz, 1H; Ar C5−*H*), 5.11 (br s, 1H; Z−N*H*), 5.02 (s, 2H; C(O)OC*H*$_2$Ph), 4.11 (t, ^3J(H,H) = 6.0 Hz, 2H; OC*H*$_2$CH$_2$CH$_2$), 3.31 (q, ^3J(H,H) = 6.4 Hz, 2H; OCH$_2$CH$_2$C*H*$_2$NHZ), 3.20 (t, ^3J(H,H) = 6.0 Hz, 2H; NHC*H*$_2$CH(CH$_3$)$_2$), 2.00 (m, 2H; OCH$_2$C*H*$_2$CH$_2$), 1.79 (m, 1H; NHCH$_2$C*H*(CH$_3$)$_2$), 1.43 (s, 9H; Boc), 0.87 ppm (d, ^3J(H,H) = 6.8 Hz, 6H; NHCH$_2$CH(C*H*$_3$)$_2$).

Compound 10: Compound **7** (60.6 mg, 0.120 mmol), palladium on carbon (10.2 mg), and ammonium formate (40.0 mg, 0.63 mmol) were suspended in EtOH (4 mL) and the mixture was heated to reflux at 80 °C. After 3 h, the solid was removed by filtration, and the filtrate was extracted with $\mathrm{CH_2Cl_2}$ and $\mathrm{H_2O}$. The separated organic phase was dried under vacuum to give a pale yellow oil (**8**). This oil was dissolved in $\mathrm{CH_2Cl_2}$ (5 mL), and compound **9** (67.6 mg, 0.109 mmol), DMAP (27.1 mg, 0.222 mmol), HOBt·$\mathrm{H_2O}$ (31.2 mg, 0.231 mmol), and EDC·HCl (45.3 mg, 0.237 mmol) were added to the solution. After stirring for 12 h, $\mathrm{CH_2Cl_2}$ and aqueous $\mathrm{NaHCO_3}$ were added to the mixture and the organic phase was washed with aqueous $\mathrm{NaHCO_3}$ and then $\mathrm{H_2O}$. The organic phase was dried over $\mathrm{Na_2SO_4}$, evaporated, and dried under vacuum. Purification was performed by column chromatography on alumina ($\mathrm{CH_2Cl_2}$/MeOH 98:2) followed by recrystallization from $\mathrm{CH_2Cl_2}$/*n*-hexane. Yield: 101.1 mg (0.104 mmol, 87 %); ^{1}H NMR (400 MHz, $\mathrm{CDCl_3}$, 25 °C, TMS): *linker (BocNHC$_6$H$_3$(CONHiBu)O(CH$_2$)$_3$NH)*: $\delta = 8.00$ (d, $^3J_{\mathrm{H,H}} = 8.4$ Hz, Ar C6−*H*), 7.98 (t, ^3J(H,H) = 6.0 Hz, 1H; CON*H*iBu), 7.51 (s, 1H; Ar C3−*H*), 7.48 (s, 1H; Boc N*H*), 7.46 (t, ^3J(H,H) = 6.4 Hz, 1H; CH$_2$CH$_2$CH$_2$N*H*CO), 6.77 (dd, ^3J(H,H) = 6.0 Hz, ^4J(H,H) = 2.0 Hz, 1H; Ar C5−*H*), 4.30 (t, ^3J(H,H) = 6.0 Hz, 2H; OC*H*$_2$CH$_2$CH$_2$NH), 3.65 (q, ^3J(H,H) = 6.0 Hz, 2H; OCH$_2$CH$_2$C*H*$_2$NH), 3.55 (t, ^3J(H,H) = 5.6 Hz, 2H;

$\mathrm{NHC}H_2\mathrm{CH(CH_3)_2}$), 2.24 (m, 2H; $\mathrm{OCH_2C}H_2\mathrm{CH_2NH}$), 1.89 (m, 1H; $\mathrm{NHCH_2C}H\mathrm{(CH_3)_2}$), 1.40 (s, 9H; Boc), 0.95, 0.97 (two singlets, 6H; $\mathrm{NHCH_2CH(C}H_3)_2$); *bpy (bpy−CO)*: 9.06 (d, ^4J(H,H) = 1.6 Hz, 1H; bpy C6−*H*), 8.67–8.70 (overlapping multiplet (om), 1H; bpy C6′−*H*), 8.43 (d, ^3J(H,H) = 8.0 Hz, 1H; bpy C3′−*H*), 8.40 (d, ^3J(H,H) = 8.0 Hz, 1H; bpy C3−*H*), 8.18 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 2.8 Hz, 1H; bpy C4−*H*), 7.90–7.85 (om, 1H; bpy C4′−*H*), 7.36–7.33 (om, 1H; bpy C5′−*H*); *trpy (trpy−*$C_6H_3C(O)O(CH_2)_4NH$*)*: 8.67–8.70 (om, 4H; trpy C3−*H*, trpy C3“−*H*, trpy C6−*H*, trpy C6”−*H*), 8.63 (s, 2H; trpy C3′−*H*, trpy C5′−*H*), 8.12 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 2.0 Hz, 1H; Ar C4−*H*), 7.90–7.85 (om, 2H; trpy C4−*H*, trpy C4“−*H*), 7.82 (dd, ^3J(H,H) = 8.0 Hz, ^4J(H,H) = 2.0 Hz, 1H; Ar C6−*H*), 7.62 (dd, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.6 Hz, 1H; Ar C5−*H*), 7.36–7.33 (om, 2H; trpy C5−*H*, trpy C5”−*H*), 3.29 (t, ^3J(H,H) = 6.4 Hz, 2H; $\mathrm{NHCH_2CH_2CH_2C}H_2\mathrm{O}$), 3.12 (q, ^3J(H,H) = 6.4 Hz, 2H; $\mathrm{NHC}H_2\mathrm{CH_2CH_2CH_2O}$), 1.35–1.46 ppm (m, ^3J(H,H) = 6.4 Hz, 4H; $\mathrm{NHCH_2C}H_2\mathrm{C}H_2\mathrm{CH_2O}$).

Compound 13a: Compound **10** (30.4 mg, 0.031 mmol) was dissolved in trifluoroacetic acid (TFA, 2 mL) and the solution was stirred at RT. After stirring for 2 h, the resulting solution was neutralized by the addition of saturated aqueous $NaHCO_3$. The mixture was extracted with CH_2Cl_2 and the organic phase was separated, evaporated, and dried under vacuum. The deprotected compound **11** was obtained as a colorless oil. The oil was dissolved in CH_2Cl_2 and compound **12a** (24.9 mg, 0.030 mmol), DMAP (2.0 mg, 0.016 mmol), bis(2-oxo-3-oxazolidinyl)-phosphinic chloride (BOP-Cl, 17.6 mg, 0.069 mmol), and *N*,*N*-diisopropylethylamine (DIPEA, 30 µL, 0.17 mmol) were added to the solution, and the mixture was stirred at RT. After 12 h, CH_2Cl_2 and saturated aqueous $NaHCO_3$ were added to the solution and the organic phase was separated and the solvent was evaporated. Purification was performed by olumn chromatography on alumina (CH_2Cl_2/MeOH 99:1), followed by recrystallization from CH_2Cl_2/*n*-hexane. Yield: 29.7 mg (0.0176 mmol, 57%); ^{1}H NMR (920 MHz, CD_2Cl_2, 25 °C): *linker (*$NHC_6H_3(CONHiBu)O(CH_2)_3NH$*)*: δ = 9.61 (s, 1H; $\mathrm{N}H\mathrm{C_6H_3}$), 8.12 (d, ^3J(H,H) = 7.9 Hz, 1H; Ar C6−*H*), 8.03 (d, ^4J(H,H) = 1.6 Hz, 1H; Ar C3−*H*), 7.97 (t, ^3J(H,H) = 5.5 Hz, 1H; CON*Hi*Bu), 7.92 (t, ^3J(H,H) = 5.7 Hz, 1H; $\mathrm{N}H\mathrm{(CH_2)_3O}$), 7.41 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 1.6 Hz, 1H; Ar C5−*H*), 4.40 (t, ^3J(H,H) = 6.3 Hz, 2H; $\mathrm{NHCH_2CH_2C}H_2\mathrm{O}$), 3.66 (q, ^3J(H,H) = 6.2 Hz, 2H; $\mathrm{NHC}H_2\mathrm{CH_2CH_2O}$), 3.29 (t, ^3J(H,H) = 6.4 Hz, 2H; $\mathrm{NHC}H_2\mathrm{CH(CH_3)_2}$), 2.26 (quintet, ^3J(H,H) = 6.4 Hz, 2H; $\mathrm{NHCH_2C}H_2\mathrm{CH_2O}$), 1.90 (nonet, ^3J(H,H) = 6.8 Hz, 1H; $\mathrm{NHCH_2C}H\mathrm{(CH_3)_2}$), 0.97 (d, ^3J(H,H) = 6.6 Hz, 6H; $\mathrm{NHCH_2CH(C}H_3)_2$); *bpy (bpy−CO)*: 9.01 (d, ^4J(H,H) = 2.1 Hz, 1H; bpy C6−*H*), 8.55 (m, 1H; bpy C6′−*H*), 8.40 (d, ^3J(H,H) = 8.1 Hz, 1H; bpy C3−*H*), 8.36 (d, ^3J(H,H) = 7.9 Hz, 1H; bpy C3′−*H*), 8.15 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 2.3 Hz, 1H; bpy C4−*H*), 7.68 (td, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.6 Hz, 1H; bpy C4′−*H*), 7.19 (td, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.8 Hz, 1H; bpy C4′−*H*); *trpy (trpy−*$C_6H_3(CO)O(CH_2)_4NH$*)*: 8.67 (s, 2H; trpy C3′−*H*, trpy 5′−*H*), 8.62–8.65 (overlapping multiplet, 4H; trpy C3−*H*, trpy C3“−*H*, trpy C6−*H*, trpy C6”−*H*), 8.04 (dd, ^3J(H,H) = 7.6 Hz, ^3J(H,H) = 1.6 Hz, 1H; Ar C6−*H*), 7.76 (td, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.6 Hz, 2H; trpy C4−*H*, trpy C4“−*H*), 7.62 (dd, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.6 Hz, 1H; Ar C4−*H*), 7.38 (t, ^3J(H,H) = 5.8 Hz, 1H; $\mathrm{N}H\mathrm{(CH_2)_4O}$), 7.33 (t, ^3J(H,H) = 7.5 Hz, 1H; Ar C5−*H*), 7.23 (td, ^3J(H,H) = 6.7 Hz, ^4J(H,H) = 1.8 Hz, 2H; trpy C5−*H*, trpy C5”−*H*), 3.60 (t, ^3J(H,H) = 5.9 Hz, 2H; $\mathrm{NHCH_2CH_2CH_2C}H_2\mathrm{O}$), 3.13 (q, ^3J(H,H) = 6.4 Hz, 2H; $\mathrm{NHC}H_2\mathrm{CH_2CH_2CH_2O}$), 1.49 (quintet, ^3J(H,H) = 6.1 Hz, 2H; $\mathrm{NHCH_2CH_2C}H_2\mathrm{CH_2O}$), 1.35 (quintet, ^3J(H,H) = 7.5 Hz, 2H; $\mathrm{NHCH_2C}H_2\mathrm{CH_2CH_2O}$); *porphyrin*: 8.68 (br s, 4H; β*H*), 8.62–8.65 (om, 2H; β*H*), 8.52 (br s, 2H; β*H*), 8.12 (d, ^3J(H,H) = 7.9 Hz, 2H; Ar C2−*H*, Ar C6−*H*), 8.08 (d, ^3J(H,H) = 7.6 Hz, 2H; Ar C3−*H*, Ar 5−*H*), 7.74 and 7.73 (2 × t, ^3J(H,H) = 8.9 Hz, 3H; $\mathrm{C_6}H_3\mathrm{(OMe)_2}$ C4−*H*), 7.02 and 7.00 (2 × br s, 6H; $\mathrm{C_6}H_3\mathrm{(OMe)_2}$ C3−*H* and C5−*H*), −2.80 ppm (s, 2H; inner N*H*).

Compound 13b: This compound was synthesized according to the same procedure as compound **13a** using compound **9** (42.5 mg, 0.0438 mmol) and TFA (3 mL); then compound **12b** (40.1 mg, 0.0403 mmol), BOP-Cl (22.2 mg, 0.0871 mmol), DMAP (5.2 mg, 0.0426 mmol), and DIPEA (35 µL, 0.200 mmol) in CH_2Cl_2 (5 mL). Yield: 51.5 mg (0.0279 mmol, 64%); ^{1}H NMR (920 MHz, CD_2Cl_2, 25 °C): *linker (*$NHC_6H_3(CONHiBu)O(CH_2)_3NH$*)*: δ = 9.53 (s, 1H; $\mathrm{N}H\mathrm{C_6H_3}$), 8.13 (d, ^3J(H,H) = 8.2 Hz, 1H; Ar C6−*H*), 7.99 (d, ^4J(H,H) = 1.6 Hz, 1H; Ar C3−*H*), 7.98 (t, ^3J(H,H) = 5.8 Hz, 1H; CON*Hi*Bu), 7.97 (t, ^3J(H,H) = 6.0 Hz, 1H; $\mathrm{N}H\mathrm{CH_2CH_2CH_2O}$), 7.43 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 1.8 Hz, 1H; Ar C5−*H*), 4.39 (t, ^3J(H,H) = 6.3 Hz, 2H; $\mathrm{NHCH_2CH_2C}H_2\mathrm{O}$), 3.69 (q, ^3J(H,H) = 6.3 Hz, 2H; $\mathrm{NHC}H_2\mathrm{CH_2CH_2O}$), 3.30 (t, ^3J(H,H) = 6.4 Hz, 2H; $\mathrm{NHC}H_2\mathrm{CH(CH_3)_2}$), 2.28 (quintet, ^3J(H,H) = 6.4 Hz, 2H; $\mathrm{NHCH_2C}H_2\mathrm{CH_2O}$), 1.92 (nonet, ^3J(H,H) = 6.7 Hz, 1H; $\mathrm{NHCH_2C}H\mathrm{(CH_3)_2}$), 0.99 (d, ^3J(H,H) = 6.8 Hz, 6H; $\mathrm{NHCH_2CH(C}H_3)_2$); *bpy (bpy−CO)*: 9.01 (d, ^4J(H,H) = 1.9 Hz, 1H; bpy C6−*H*), 8.51 (m, 1H; bpy C6′−*H*), 8.37 (d, ^3J(H,H) = 8.2 Hz, 1H; bpy C3−*H*), 8.30 (d, ^3J(H,H) = 7.9 Hz, 1H; bpy C3′−*H*), 8.14 (dd, ^3J(H,H) = 8.1 Hz, ^4J(H,H) = 2.3 Hz, 1H; bpy C4−*H*), 7.62 (td, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.8 Hz, 1H; bpy C4′−*H*), 7.16 (ddd, ^3J(H,H) = 7.4 Hz, ^3J(H,H) = 4.6 Hz, ^4J(H,H) = 1.2 Hz, 1H; bpy C5′−*H*); *trpy (trpy−*$C_6H_3(CO)O(CH_2)_4NH$*)*: 8.66 (s, 2H; trpy C3′−*H*, trpy C5′−*H*), 8.62 (d, ^3J(H,H) = 7.8 Hz, 2H; trpy C3−*H* and trpy C3“−*H*), 8.60 (m, 2H; trpy C6−*H* and trpy C6”−*H*), 8.06 (dd, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.9 Hz, 1H; Ar C6−*H*), 7.74 (td, ^3J(H,H) = 7.8 Hz, ^4J(H,H) = 1.7 Hz, 2H; trpy C4−*H*, trpy C4“−*H*), 7.62 (dd, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.8 Hz, 1H; Ar C4−*H*), 7.39 (t, ^3J(H,H) = 5.7 Hz, 1H; $\mathrm{N}H\mathrm{(CH_2)_4O}$), 7.33 (t, ^3J(H,H) = 7.5 Hz, 1H; Ar C5−*H*), 7.19 (ddd, ^3J(H,H) = 7.4 Hz, ^3J(H,H) = 4.6 Hz, ^4J(H,H) = 1.2 Hz, 2H; trpy C5−*H*, trpy C5”−*H*), 3.61 (t, ^3J(H,H) = 5.8 Hz, 2H; $\mathrm{NHCH_2CH_2CH_2C}H_2\mathrm{O}$), 3.15 (q, ^3J(H,H) = 6.6 Hz, 2H; $\mathrm{NHC}H_2\mathrm{CH_2CH_2CH_2O}$), 1.51 (overlapping multiplets, 2H; $\mathrm{NHCH_2CH_2C}H_2\mathrm{CH_2O}$), 1.39 (quintet, 2H; $\mathrm{NHCH_2C}H_2\mathrm{CH_2CH_2O}$); *porphyrin*: 8.89 (br s, 4H; β*H*), 8.84 (br s, 2H; β*H*), 8.67 (br s, 2H; β*H*), 8.20 (AA′BB′ system, 4H; $\mathrm{C_6}H_4\mathrm{CO}$), 8.08 (d, ^4J(H,H) = 1.8 Hz, 2H; di-*tert*-butylphenyl C2−*H* and C6−*H*), 8.07 (d, ^4J(H,H) = 1.8 Hz, 4H; di-*tert*-butylphenyl C2−*H* and C6−*H*), 7.84 (m, 3H; di-*tert*-butylphenyl C4−*H*), 1.52 (s, 54H; $\mathrm{C(C}H_3)_3$), −2.81 ppm (s, 2H, inner N*H*).

Compound 13c: This compound was synthesized according to the same procedure as compound **13a** using compound **9** (46.3 mg, 0.0477 mmol) and TFA (3 mL); then compound **12c** (34.5 mg, 0.0450 mmol), BOP-Cl (26.5 mg, 0.104 mmol), DMAP (6.1 mg, 0.050 mmol), and DIPEA (35 µL, 0.200 mmol) in CH_2Cl_2 (5 mL). Yield: 59.6 mg (0.0368 mmol, 77%). ^{1}H NMR (920 MHz, CD_2Cl_2, 25 °C): *linker (*$NHC_6H_3(CONHiBu)O(CH_2)_3NH$*)*: δ 9.76 (s, 1H; $\mathrm{N}H\mathrm{C_6H_3}$), 8.14 (d, ^3J(H,H) = 8.2 Hz, 1H; Ar C6−*H*), 8.06 (d, ^4J(H,H) = 1.8 Hz, 1H; Ar C3−*H*), 7.97 (t, ^3J(H,H) = 5.6 Hz, 1H; CON*Hi*Bu), 7.89 (t, ^3J(H,H) = 5.8 Hz, 1H; $\mathrm{N}H\mathrm{CH_2CH_2CH_2O}$), 7.44 (dd, ^3J(H,H) = 8.2 Hz, ^4J(H,H) = 1.6 Hz, 1H; Ar C5−*H*), 4.42 (t, ^3J(H,H) = 6.0 Hz, 2H; $\mathrm{NHCH_2CH_2C}H_2\mathrm{O}$), 3.65 (q, ^3J(H,H) = 6.3 Hz, 2H; $\mathrm{NHC}H_2\mathrm{CH_2CH_2O}$), 3.29 (t, ^3J(H,H) = 6.4 Hz, 2H; $\mathrm{NHC}H_2\mathrm{CH(CH_3)_2}$), 2.26 (quintet, ^3J(H,H) = 6.4 Hz, 2H; $\mathrm{NHCH_2C}H_2\mathrm{CH_2O}$), 1.90 (nonet, ^3J(H,H) = 6.7 Hz, 1H; $\mathrm{NHCH_2C}H\mathrm{(CH_3)_2}$), 0.97 (d, ^3J(H,H) = 6.5 Hz, 6H; $\mathrm{NHCH_2CH(C}H_3)_2$); *bpy (bpy−CO)*: 9.00 (d, ^4J(H,H) = 1.8 Hz, 1H; bpy C6−*H*), 8.46 (m, 1H; bpy C6′−*H*), 8.35 (d, ^3J(H,H) = 8.2 Hz, 1H; bpy C3−*H*), 8.28 (d, ^3J(H,H) = 7.8 Hz, 1H; bpy C3′−*H*), 8.13 (d, ^3J(H,H) = 8.2 Hz, 1H; bpy C4−*H*), 7.58 (t, ^3J(H,H) = 7.1 Hz, 1H; bpy C4′−*H*), 7.09 (t, ^3J(H,H) = 5.9 Hz, 1H; bpy C5′−*H*); *trpy (trpy−*$C_6H_3(CO)O(CH_2)_4NH$*)*: 8.66 (s, 2H; trpy C3′−*H*, trpy C5′−*H*), 8.62 (d, ^3J(H,H) = 7.6 Hz, 2H; trpy C3−*H*, trpy C3“−*H*), 8.61 (m, 2H; trpy C6−*H*, trpy C6”−*H*), 8.04 (dd, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.8 Hz, 1H; Ar C6−*H*), 7.74 (td, ^3J(H,H) = 7.6 Hz, ^4J(H,H) = 1.8 Hz, 2H; trpy C4−*H* and trpy C4“−*H*), 7.61 (dd, ^3J(H,H) = 7.4 Hz, ^4J(H,H) = 1.7 Hz, 1H; Ar C4−*H*), 7.39 (overlapping multiplet, 1H; $\mathrm{N}H\mathrm{(CH_2)_4O}$), 7.31 (t, ^3J(H,H) = 7.6 Hz, 1H; Ar C5−*H*), 7.20 (ddd, ^3J(H,H) = 7.4 Hz, ^3J(H,H) = 2.8 Hz, ^4J(H,H) = 1.2 Hz, 2H; trpy C5−*H*, trpy C5”−*H*), 3.59 (t, ^3J(H,H) = 5.8 Hz, 2H; $\mathrm{NHCH_2CH_2CH_2C}H_2\mathrm{O}$), 3.13 (q, ^3J(H,H) = 7.1 Hz, 2H; $\mathrm{NHC}H_2\mathrm{CH_2CH_2CH_2O}$), 1.47 (quintet, ^3J(H,H) = 6.1 Hz, 2H; $\mathrm{NHCH_2CH_2C}H_2\mathrm{CH_2O}$), 1.39 (quintet, 2H; $\mathrm{NHCH_2C}H_2\mathrm{CH_2CH_2O}$); *porphyrin*: 8.88 (br s, 4H; β*H*), 8.72 (br s, 2H; β*H*), 8.64 (br S, 2H; β*H*), 8.09 (AA′BB′ system, 4H; $\mathrm{C_6}H_4\mathrm{CO}$), 7.79–7.83 (m, 3H; di-fluorophenyl C4−*H*), 7.39 (overlapping multiplet, 6H; di-fluorophenyl C3−*H*, di-fluorophenyl C5−*H*), −2.92 ppm (s, 2H; inner N*H*).

Compound 1a: Compound **13a** (16.0 mg, 0.0095 mmol) and zinc acetate dihydrate ($Zn(OAc)_2 \cdot 2H_2O$, 16.7 mg, 0.076 mmol) were dissolved in CH_2Cl_2/EtOH (1:1 wt%, 20 mL) and stirred for 5 h at 50 °C. After the reaction had been completed, the solution was washed once with saturated aqueous disodium dihydrogen ethylenediaminetetraacetate, and the organic phase was separated and evaporated to reduce the volume. The zinc porphyrin compound **14a** was precipitated by the addition of *n*-

hexane as a fine red powder. Compound **14a** (13.6 mg, 0.0077 mmol), $CoCl_2\cdot 6H_2O$ (8.0 mg, 0.034 mmol) and LiCl (2.5 mg, 0.595 mmol) were dissolved in CH_2Cl_2/EtOH (1:1 wt%, 20 mL) and stirred for 8 h at RT under a nitrogen atmosphere. After the reaction had been completed, a solution of ammonium hexafluorophosphate (5.2 mg, 0.032 mmol) in EtOH (3 mL) was added to the reaction mixture, the solution was evaporated to remove CH_2Cl_2, and left to stand overnight. Compound **1a** was obtained as fine purple crystals. Yield: 13.3 mg (0.0067 mmol, 71%); elemental analysis calcd (%) for **1a**$\cdot 6H_2O$ ($C_{102}H_{101}N_{13}O_{18}ClCoF_6PZn$): C 58.29, H 4.84, N 8.66; found: C 58.12, H 4.73, N 8.41.

Compound 1b: This compound was synthesized according to the same procedure as compound **1a** by using compound **13b** (17.4 mg, 0.0094 mmol) and $Zn(OAc)_2\cdot 2H_2O$ (9.9 mg, 0.045 mmol), and then $CoCl_2$**$\cdot 6H_2O$** (8.4 mg, 0.035 mmol) and LiCl (5.2 mg, 0.12 mmol). Yield: 18.3 mg (0.0085 mmol, 90%); elemental analysis calcd (%) for **1b**$\cdot 4H_2O$ ($C_{120}H_{133}N_{13}O_{10}ClCoF_6PZn$): C 64.86, H 6.03, N 8.19; found: C 64.97, H 5.96, N 8.21.

Compound 1c: This compound was synthesized according to the same procedure as compound **1a** by using compound **13c** (15.9 mg, 0.0097 mmol) and $Zn(OAc)_2\cdot 2H_2O$ (7.9 mg, 0.036 mmol), and then $CoCl_2\cdot 6H_2O$ (5.9 mg, 0.025 mmol) and LiCl (5.2 mg, 0.12 mmol). Yield: 15.5 mg (0.0081 mmol, 83%); elemental analysis calcd (%) for **1c**$\cdot 6H_2O$ ($C_{96}H_{83}N_{13}O_{12}ClCoF_{12}PZn$): C 56.81, H 4.12, N 8.97; found: C 56.41, H 3.82, N 8.92.

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[1] J. P. McEvoy and G. W. Brudvig, *Chem. Rev.* **2006**, *106*, 4455–4483.

[2] R. Malkin in *Oxygenic Photosynthesis: The Light Reactions: Photosystem I Electron Transfer Reactions-Components and Kinetics*, (Eds.: D. R. Ort, C. F. Yocus), Klumer, the Netherlands, **1996**, pp. 313–332.

[3] G. M. Brown, S.-F. Chan, C. Creutz, H. A. Schwarz, N. Sutin, *J. Am. Chem. Soc.* **1979**, *101*, 7638–7640.

[4] J. Hawecker, J. M. Lehn, R. Ziessel, *J. Chem. Soc. Chem. Commun.* **1983**, 536–538.

[5] A. Fihri, V. Artero, M. Razavet, C. Baffert, W. Leibel, M. Fontecave, *Angew. Chem. Int. Ed.* **2008**, *47*, 564–567.

[6] M. Elvington, J. Brown, S. M. Arachchige, K. J. Brewer, *J. Am. Chem. Soc.* **2007**, *129*, 10644–10645.

[7] Z.-Y. Bian, K. Sumi, M. Furve, S. Sato, K. Koike, O. Ishitani, *Inorg. Chem.* **2008**, *47*, 10801–10803.

[8] H. Ozawa, M. Haga, K. Sakai, *J. Am. Chem. Soc.* **2006**, *128*, 4926–4927.

[9] *CRC Handbook of Chemistry and Physics, 85th Edition*, (Ed.: D. R. Lide), CRC Press, Boca Raton, **2005**, Section 14.11.

[10] Y. Ooyama, Y. Harima, *Eur. J. Org. Chem.* **2009**, 2903–2934.

[11] S. Matsuoka, K. Yamamoto, T. Ogata, M. Kusaba, N. Nakashima, E. Fujita, S. Yanagida, *J. Am. Chem. Soc.* **1993**, *115*, 601–609.

[12] C. A. Craig, L. O. Spreer, J. W. Otvos, M. Calvin, *J. Phys. Chem.* **1990**, *94*, 7957–7960.

[13] E. Kimura, X. Bu, M. Shionoya, S. Wada, S. Maruyama, *Inorg. Chem.* **1992**, *31*, 4542–4546.

[14] T. L. James, L. Cai, M. C. Muetterties, R. H. Holm, *Inorg. Chem.* **1996**, *35*, 4148–4161.

[15] I. Bhugun, D. Lexa, J.-M. Savéant, *J. Phys. Chem.* **1996**, *100*, 19981–19985.

[16] F. Gloaguen, J. D. Lawrence, T. B. Rauchfuss, M. Benard, M.-M. Rohmer, *Inorg. Chem.* **2002**, *41*, 6573–6582.

[17] L. Sun, B. Åkermark, S. Ott, *Coord. Chem. Rev.* **2005**, *249*, 1653–1663.

[18] H. Minami, *Kinzoku Shigen Report* (ISSN 1349–5003), **2010**, *39*, 909–915.

[19] *Minerals Yearbook, Vol. I, Metals & Minerals*, U.S. Geological Survey, U.S. Government Printing Office, Washington DC, **2007**, to be found under http://minerals.usgs.gov/minerals/pubs/commodity/myb.

[20] H. Kon, T. Nagata, *Inorg. Chem.* **2009**, *48*, 8593–8602.

[21] J. E. Argüello, C. Costentin, S. Griveau, J.-M. Savéant, *J. Am. Chem. Soc.* **2005**, *127*, 5049–5055.

[22] P. Fromme, I. Grotjohann in *Photosynthetic Protein Complexes* (Ed. P. Fromme), Wiley-VCH, Weinheim, **2008**, pp. 1–22.

[23] I. Iwakura, M. Hatanaka, A. Kokura, H. Teraoka, T. Ikeno, T. Nagata, T. Yamada, *Chem. Asian J.* **2006**, *1*, 656–663.

[24] F. Gao, X. Yan, T. Shakya, O. M. Baettig, S. A.-M. -Brunet, A. M. Berghuis, G. D. Wright, K. Auclair, *J. Med. Chem.* **2006**, *49*, 5273–5281.

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