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Synthesis and photoreaction of a porphyrin–Co(III)-complex linked molecule

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Abstract

A dyad molecule composed of a zinc porphyrin and a Co(III) complex that are linked together via a coordination bond underwent intramolecular electron transfer when irradiated with visible light, and subsequent ligand exchange at the Co(II) center led to dissociation of the two moieties.

Keywords: Photoreaction; Porphyrin; Cobalt complexes

1. Introduction

Covalently-linked porphyrin-acceptor systems have been actively studied for past 20 years as model systems for photoinduced electron transfer in photosynthesis [1]. Flash photolysis studies on these systems have provided information on dynamics of the fast, intramolecular electron transfer, especially how the rates of electron transfer are affected by geometrical and energetical factors [2]. More recently, porphyrin-acceptor systems linked via non-covalent bonds (such as hydrogen bonds) have also been studied [3]. On the other hand, one of the fascinating subjects in photosynthetic model chemistry is to achieve real chemical changes (i.e. cleavage/formation of chemical bonds) triggered by photoinduced electron transfer. There have been reported many successful systems that undergo redox chemical reactions in the presence of light and ‘sacrificial’ electron donor (such as tertiary amines [4]) or acceptor (such as Co(III) complexes [5]) reagents. These systems, however, generally include intermolecular electron transfer between photoexcited pigments and electron donor–acceptor reagents, which introduces complication in elucidating reaction mechanisms because of the rate-limiting diffusion process.

In this article, we wish to report synthesis of a dyad molecule in which a porphyrin and a Co(III) complex are linked together via a coordination bond. As shown below, this dyad molecule underwent cleavage of the porphyrin–cobalt bond upon irradiation with visible light. Although Co(III) complexes are well-known electron acceptors that have been used in intramolecular donor-acceptor systems [6], our dyad is the first example of a porphyrin–Co(III) linked molecule in which the Co(III) moiety serves as a sacrificial electron acceptor. Another interesting feature in our dyad is the use of a pentadentate ligand [7] that binds the Co(III) center. Whereas simple Co(III) complexes such as $[Co(NH_3)_5Cl]^{2+}$ often suffer complete solvolysis after initial photoreduction, the Co(III) moiety in our dyad retains the pentadentate ligand even after the detachment from the porphyrin moiety. Such a characteristic may be useful in utilizing the Co(III) complex as an

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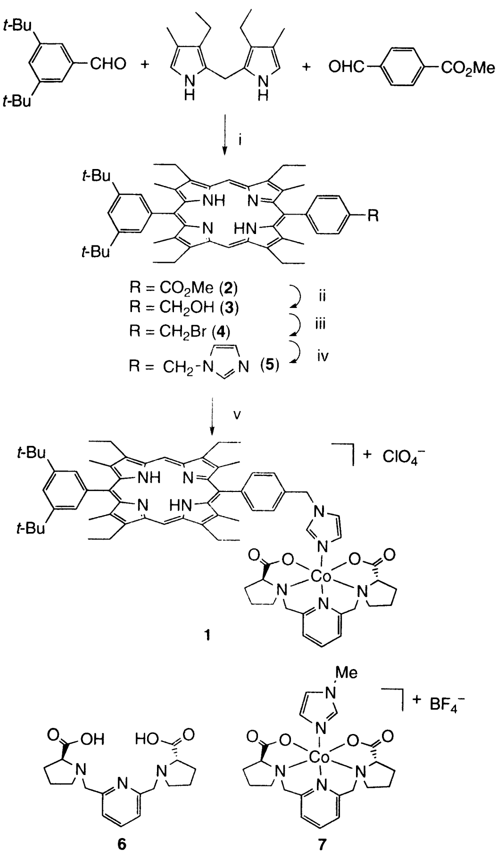

Scheme 1. Reagents and conditions: (i) CCl_3CO_2H, CH_3CN; (ii) $LiAlH_4$, Et_2O; (iii) $SOBr_2$, CH_2Cl_2; (iv) sodium imidazolate, THF; (v) see text.

electron-carrying device in multicomponent redox systems.

2. Results and discussion

2.1. Synthesis of the dyad 1

Synthesis of the dyad **1** is shown in Scheme 1. The imidazole-linked porphyrin **5** was synthesized from a methoxycarbonyl derivative **2**, which was prepared by cross-condensation of dipyrrolylmethane and corresponding aldehydes followed by chromatographic separation. On the other hand, the pentadentate ligand **6**, first developed by Bernauer et al. [7], was prepared by the reaction of L-proline benzyl ester and 2,6-bis(bromomethyl)pyridine, followed by deprotection by hydrogenolysis. Subsequently, the ligand **6** was treated with $[Co(CH_3CN)_6](BF_4)_2$ [8] in CH_3CN in the presence of 2 equiv. of 2,6-lutidine and precipitated from CH_3CN–EtOAc to remove 2,6-lutidine·HBF_4. The resulting '**6**·Co' material was treated with the imidazole-linked porphyrin **5** to give the desired dyad molecule **1**, which was obtained as deep red powders after precipitation from acetone–H_2O–$NaClO_4$ and fully characterized by ^1H NMR (500 MHz), ESI-MS, and elemental analysis (C, H, N).

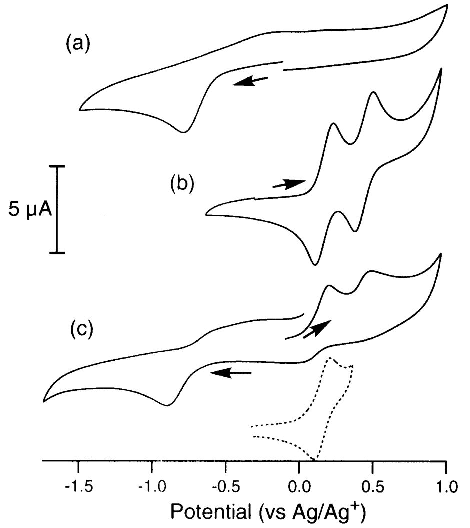

Fig. 1. Cyclic voltammograms of (a) **7**, (b) **2**, and (c) **1**. Conditions: CH_3CN (a) or CH_2Cl_2 (b and c), 0.1 mol dm^{-3} Bu_4NClO_4, Pt working electrode. The broken line below (c) shows the scan for **1** in the range −0.3–0.3 V, which represents the reversibility of the first oxidation wave.

2.2. Electronic properties of the dyad 1

The cyclic voltammogram of **1** (Fig. 1) in CH_2Cl_2 revealed two anodic peaks at +0.20 and +0.47 V (vs. $Fe(C_5H_5)_2$–$[Fe(C_5H_5)_2]^+$) and one cathodic peak at −0.95 V. From comparison with the voltammograms of **2** and **7**, the anodic peaks were assigned to the first and second oxidation of the porphyrin ring, and the cathodic peak was assigned to the reduction of Co(III)–Co(II). The cathodic peaks in **2** and **7** showed marked irreversibility; this can be attributed to the rapid ligand exchange of the substitutionally-labile Co(II) center.

The UV–Vis absorption spectra of **1** and **2** (the reference porphyrin compound) in CH_2Cl_2 (Fig. 2) showed no significant difference in the range of 350–

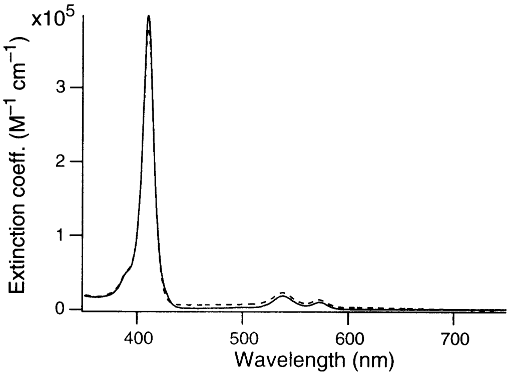

Fig. 2. UV–Vis absorption spectra of **1** (solid line) and **2** (broken line) in CH_2Cl_2 (4.0×10^{-6} mol dm^{-3}) at room temperature.

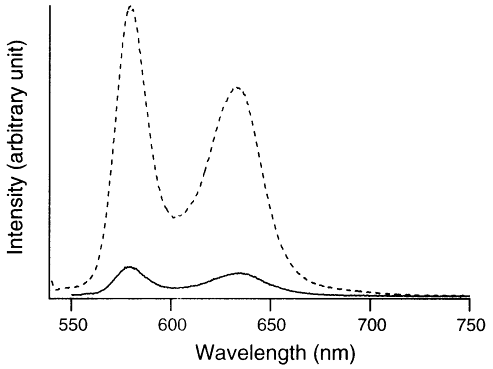

Fig. 3. Steady-state fluorescence spectra of **1** (solid line) and **2** (broken line) in CH_2Cl_2 (4.0×10^{-6} mol dm^{-3}) at room temperature. The excitation wavelength is 543 nm.

600 nm. On the other hand, the relative intensity of the steady-state fluorescence spectrum of **1** was 0.10 compared with that of **2** (Fig. 3). The free energy change (ΔG) calculated by the Rehm–Weller equation [9] was −1.15 eV (−111 kJ mol^{-1}) [10]. The large negative value of ΔG strongly suggests that the fluorescence of **1** was quenched by the intramolecular electron transfer from the singlet excited state of the porphyrin to the Co(III) complex.

2.3. *Photoreaction of the dyad **1***

When a solution of **1** in $CDCl_3+CD_3CN$ (v/v = 1/5) was irradiated with a halogen lamp for 3 min, the red solution turned yellow and red precipitate formed. The ^{1}H NMR and ESI-MS spectra indicated that the yellow supernatant exclusively contained $[Co(III)(\mathbf{6})(CD_3CN)]^+$ (yield 80%). The red precipitate were collected, analyzed by ^{1}H NMR, and found to be the compound **5** (isolated yield 70%). This reaction did not proceed in the absence of light. The reaction is, therefore, the light-induced ligand exchange of the Co(III) center, in which the imidazole (linked to the porphyrin moiety) is replaced by CD_3CN. We assume that the intramolecular electron transfer from the excited porphyrin to the Co(III) moiety is the first step in this reaction. The hypothetical reaction mechanism is as follows:

$$\text{Por–Co}^{\text{III}} \xrightarrow{h\nu} \text{Por}^{+\bullet}\text{–Co}^{\text{II}} \longrightarrow$$

$$\text{Por}^{+\bullet} + \text{Co}^{\text{II}} \longrightarrow \text{Por} + \text{Co}^{\text{III}}$$

Namely, the initial photoinduced electron transfer generates the Co(II), which is substitutionally labile and undergoes fast ligand exchange with the solvent (CD_3CN) molecule. Subsequently, the intermolecular back electron transfer takes place from the Co(II)–CD_3CN complex to the porphyrin cation radical, which results in the observed final products, a Co(III) complex and a neutral porphyrin.

In summary, our new dyad molecule **1** undergoes photoinduced electron transfer to give a 'reactive' state of the cobalt center that eventually leads to a cleavage of the coordination bond. The present system, however, is still non-productive because the transient Co(II) species returns to the Co(III) state by fast intermolecular back-electron transfer. Our next project will be to utilize this transient reactive species for real chemical transformation.

3. Experimental

3.1. *General*

All reagents and solvents were of the commercial reagent grade and were used without further purification unless otherwise noted. Dry CH_2Cl_2 was distilled from calcium hydride. Dry ether and THF were distilled from sodium benzophenone ketyl. Acetnitrile and ethanol were dried over activated molecular sieves 3A. ^{1}H NMR spectra were recorded on a JEOL LAMBDA-500 (500 MHz) spectrometer, and chemical shifts were reported in the delta scale relative to Me_4Si in ppm. UV–Vis absorption spectra were recorded on a Shimadzu UV-2500PC spectrometer. Steady-state fluorescence emission spectra were recorded on a Shimadzu RF-5300PC spectofluorometer. FAB-MS and ESI-MS spectra were recorded on a JEOL HX-110 spectrometer and a Perkin–Elmer SCIEX API 300 spectrometer, respectively. Cyclic voltammograms were obtained with an ALS/CHI Model 660 voltammetric analyzer.

3.2. *5-(3,5-Di-t-butylphenyl)-15-(4-methoxycarbonylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphine zinc complex (**2**)*

Bis(3-ethyl-4-methyl-2-pyrrolyl)methane (1.16 g, 5.04 mmol), 3,5-di-*t*-butylbenzaldehyde (0.548 g, 2.51 mmol) and methyl 4-formylbenzoate (0.384 g, 2.52 mmol) were dissolved in 50 ml of dry acetonitrile. Trichloroacetic acid (0.116 g, 0.710 mmol) was added and the mixture was stirred under N_2 in the dark for 6 h. A suspension of *p*-chloranil (1.97 g, 8.01 mmol) in 30 ml of dry THF was added and the mixture was stirred overnight. After removal of the solvent, the residual solid was dissolved in CH_2Cl_2. The solution was washed with saturated aqueous $NaHCO_3$ solution and water, and concentrated in vacuo. The concentrate was treated with a saturated solution of zinc acetate in MeOH (20 ml). The solution was washed with water, saturated aqueous $NaHCO_3$, and water again. The organic layer was dried over Na_2SO_4 and evaporated. The resulting product was separated by column chromatography (silica gel, CH_2Cl_2 then CH_2Cl_2 +1% MeOH). The second fraction was further purified by repeated flash column chromatography (silica gel, toluene). Red solid. Yield 0.755 g (35%). ^{1}H NMR (500 MHz, $CDCl_3$) 10.20 (s, 2H, meso), 8.44 (d, 2H, phenyl), 8.21 (d, 2H, phenyl), 7.93 (d, 2H, phenyl), 7.82 (t, 1H, phenyl), 4.14 (s, 3H, CO_2CH_3), 4.01 (m, 8H, CH_2CH_3), 2.17 (s, 12H, CH_3), 1.77 (m, 12H, CH_2CH_3), and 1.54 (s, 18H, *t*-butyl). *Anal*. Found: C, 75.13; H, 7.05; N, 6.35 %. Calc: C, 75.02; H, 7.23; N, 6.48%. FAB-MS (3-nitrobenzyl alcohol) $m/z = 862$.

*3.3. 5-(3,5-Di-t-butylphenyl)-15-(4-(hydroxymethyl)phenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphine (**3**)*

The compound **2** (161 mg, 0.186 mmol) was dissolved in 10 ml of dry ether. A suspension of lithium aluminum hydride (16 mg, 0.42 mmol) in 5 ml of dry ether was added in portions to the solution. The mixture was stirred under nitrogen atmosphere for 40 min in the dark. Water (5 ml) was carefully added and the mixture was stirred for 4 h. The organic layer was separated and the aqueous layer was extracted twice with CH_2Cl_2. All of organic layer were combined and dried over anhydrous Na_2SO_4. After removal of the solvent, the resulting solid was dissolved in 10 ml of CH_2Cl_2 and a saturated solution of zinc acetate in MeOH (2 ml) was added to the solution. The mixture was stirred for 1 h in the dark. The resulting solution was poured into water and extracted two times with CH_2Cl_2. The combined extracts were washed with saturated aqueous $NaHCO_3$ solution and water, then dried over anhydrous Na_2SO_4. The solvent was removed in vacuo, the residual solid was purified by column chromatography (silica gel, CH_2Cl_2). The resulting product was dissolved in CH_2Cl_2, treated with 1 N aqueous HCl, and washed with saturated aqueous $NaHCO_3$ solution and water. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was taken off by a rotary evaporator. The resulting purple solid was dried under reduced pressure. Yield 142 mg (99%). ^{1}H NMR (500 MHz, $CDCl_3$) 10.23 (s, 2H, meso), 8.08 (d, 2H, phenyl), 7.92 (d, 2H, phenyl), 7.81 (s, 1H, phenyl), 7.75 (d, 2H, phenyl), 5.10 (s, 2H, CH_2OH), 4.02 (q, 8H, CH_2CH_3), 2.49 (s, 6H, CH_3), 2,46 (s, 6H, CH_3), 2.01 (br, 1H, OH), 1.77 (m, 12H, CH_2CH_3), 1.51 (s, 18H, *t*-butyl), and −2.42 (br, 2H, NH).

*3.4. 5-(4-(Bromomethyl)phenyl)-15-(3,5-di-tert-butylphenyl)-2,8,12,18-tetraethyl-3,7,13,17-tetramethylporphine (**4**)*

The compound **3** (121 mg, 0.157 mmol) was dissolved in 3 ml of dry CH_2Cl_2. Thionyl bromide (69 mg, 0.33 mmol) in 0.20 ml of CH_2Cl_2 was added to the solution. The mixture was stirred under nitrogen in the dark at room temperature (r.t.) overnight. The reaction mixture was poured into water, extracted four times with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ solution and water, and evaporated. The residual solid was purified by column chromatography (silica gel, CH_2Cl_2). Reprecipitation from CH_2Cl_2–MeOH gave a purple solid. Yield 104 mg (80 %). ^{1}H NMR (500 MHz, $CDCl_3$) 10.23 (s, 2H, meso), 8.07 (d, 2H, phenyl), 7.91 (d, 2H, phenyl), 7.81 (s, 1H, phenyl), 7.78 (d, 2H, phenyl), 4.87 (s, 2H, CH_2Br), 4.02 (m, 8H, CH_2CH_3), 2.51(s, 6H, CH_3), 2,46 (s, 6H, CH_3), 1.77 (m, 12H, CH_2CH_3), 1.51 (s, 18H, *t*-butyl), and −2.43 (br, 2H, NH).

*3.5. 5-(3,5-Di-tert-butylphenyl)-2,8,12,18-tetraethyl-15-(4-(1-imidazolylmethyl)phenyl)-3,7,13,17-tetramethylporphine zinc complex (**5**)*

The compound **4** (225 mg, 0.269 mmol) was dissolved in 15 ml of dry CH_2Cl_2 under nitroge, and a suspension of sodium imidazolate (481 mg, 5.46 mmol) was added to the solution. The mixture was stirred at 50 °C in the dark until the starting materials were not visible by TLC. Water (20 ml) was added, and the organic layer was separated and the aqueous layer was extracted twice with CH_2Cl_2. The extracts were combined, washed with 1 N HCl, saturated aqueous $NaHCO_3$ and water. The solution was dried over Na_2SO_4, evaporated, and dried in vacuo. The residual solid was dissolved in 10 ml of CH_2Cl_2 and a saturated solution of zinc acetate in MeOH (2 ml) was added to the solution. The mixture was stirred overnight in the dark. The resulting solution was washed with water, saturated aqueous $NaHCO_3$ solution, and water. The extract was dried over Na_2SO_4, evaporated, and dried in vacuo. The resulting product was reprecipitated from CH_2Cl_2–MeOH. Yield 228 mg (96%). ^{1}H NMR (500 MHz, $CDCl_3$) 10.15 (s, 2H, meso), 7.98 (d, 2H, phenyl), 7.80 (t, 2H, phenyl), 7.68 (br, 2H, phenyl), 6.13 (br, 2H, phenyl), 5.06 (br, 1H, imidazole), 4.03 (m, 8+2H, benzylic CH_2 and CH_2CH_3), 2.45 (s, 6H, CH_3), 2.10 (s, 6H, CH_3), 1.82 (t, 6H, CH_2CH_3), 1.72 (t, 6H, CH_2CH_3), and 1.52 (s, 18H, *t*-butyl). FAB-MS (3-nitrobenzyl alcohol) $m/z = 884$.

3.6. 2,6-Bis(((2S)-2-benzyloxycarbonylpyrrolidin-1-yl)methyl)pyridine

L-proline benzyl ester hydrochloride [11] (5.04 g, 19.0 mmol) was suspended in 200 ml of THF under nitrogen atmosphere. Triethylamine (7.98 g 78.9 mmol) was added to the solution at 0 °C, and the resulting solution was stirred for 10 min. Then a solution of 2,6-bis(bromomethyl)pyridine [12] (2.52 g, 9.50 mmol) in 95 ml of THF was added to the mixture, and the mixture was stirred for 66 h at r.t. The reaction was monitored by NMR. When the reaction stopped, the mixture was poured into 150 ml of water, and extracted with 500 ml of CH_2Cl_2. The organic layer was separated and dried over anhydrous Na_2SO_4. The solvent was removed by a rotary evaporator. The oily residue was separated by column chromatography (silica gel, diameter 4 cm, length 20 cm, CH_2Cl_2, CH_2Cl_2 + 1% MeOH, CH_2Cl_2 + 3% MeOH). Yield 4.33 g (44%). ^1H NMR (500 MHz, $CDCl_3$) 7.53 (t, 2H, 4-H-pyridine), 7.37–7.27 (12H, 3,5-H-pyridine $-CO_2CH_2$*Ph*), 5.12 (dd, 4H, $-CO_2CH_2Ph$), 4.04 (d, 2H, pyridine$-CH_2-$pyrrolidine), 3.79 (d, 2H, pyridine$-CH_2-$pyrrolidine), 3.46 (dd, 2H, pyrrolidine), 3.07 (m, 2H, pyrrolidine), 2.52 (dd, 2H, pyrrolidine), 2.14 (m, 2H, pyrrolidine), and 2.01–1.78 (m, 6H, pyrrolidine).

*3.7. 2,6-Bis(((2S)-2-carboxypyrrolidin-1-yl)methyl)pyridine (**6**)*

Palladium on carbon (10%, 0.80 g) was suspended in 5 ml of ethanol and the suspension was purged with hydrogen. A solution of the dibenzyl ester (see above; 4.08 g, 7.94 mmol) in 20 ml of ethanol was added to the suspension with stirring. The mixture was stirred vigorously for 1 week. The catalyst was removed by filtration and rinsed with ethanol, and the filtrate was evaporated. A yellow solid thus gained was dried in vacuo. Yield 2.14 g (81 %). ^1H NMR (500 MHz, $CDCl_3$) 7.70 (t, 1H, 4-H-pyridine), 7.30 (d, 2H, 3,5-H-pyridine), 4.44 (d, 2H, pyridine-CH_2-pyrrolidine), 4.30 (d, 2H, pyridine-CH_2-pyrrolidine), 3.83 (m, 2H, pyrrolidine), 3.71 (m, 2H, pyrrolidine), 2.99 (m, 2H, pyrrolidine), 2.30 (m, 4H, pyrrolidine), 2.10 (m, 2H, pyrrolidine), and 2.00 (m, 2H, pyrrolidine). FAB-MS (3-nitrobenzyl alcohol) $m/z = 334$ ($M + H^+$).

3.8. Co(III) complex of 6 and 1-methylimidazole (7)

A solution of $[Co(CH_3CN)_6](BF_4)_2$ (152 mg, 0.317 mmol) in 2.5 ml of acetonitrile was added to **6** (106 mg, 0.317 mmol) under argon atmosphere. The mixture was stirred for 20 min till the solid was dissolved, then 2,6-lutidine (75 µl, 0.65 mmol) was added to the solution. The resulting solution was stirred for 7 h. The solvent was taken off in vacuo, and the residue was dried in vacuo. The solid was dissolved in 0.5 ml of acetonitrile, and 5 ml of ethyl acetate was added to the solution. The precipitate was collected by filtration and washed with 10 ml of ethyl acetate. This procedure of precipitation was repeated four times, and the pink product was dried in vacuo at 60 °C for 2.5 h. The product was dissolved in 5 ml of acetonitrile, and 1-methylimidazole (26 µl, 0.33 mmol) was added to the solution. The mixture was heated at 60 °C with stirring overnight, then the solvent was removed under reduced pressure. The residual solid was dissolved in 0.2 ml of acetonitrile, and precipitated with 2 ml of ethyl acetate. The pink solid was collected by filtration and washed with 2 ml of ethyl acetate. Yield 115 mg (65% as tetrafluoroborate salt). ^1H NMR (500 MHz, CD_3CN) 8.14 (t, 1H, 4-H-pyridine), 7.83 (s, 1H, imidazole), 7.65 (d, 2H, 3,5-H-pyridine), 7.33 (s, 1H, imidazole), 7.16(s, 1H, imidazole), 4.80 (d, 2H, pyridine-CH_2-pyrrolidine), 4.31 (d, 2H, pyridine-CH_2-pyrrolidine), 3.82 (s, 3H, $-CH_3$), 3.47 (d, 2H, pyrrolidine), 3.17 (m, 2H, pyrrolidine), 2.70 (m, 2H, pyrrolidine), 2.13 (m, 2H, pyrrolidine), 1.90 (m, 2H, pyrrolidine), 1.69 (m, 2H, pyrrolidine), and 0.56 (m, 2H, pyrrolidine). ESI-MS (in MeOH) $m/z = 472$ ($[Me\text{-}ImCo(III)L]^+$).

*3.9. Porphyrin–Co(III) complex linked molecule **1***

A solution of $[Co(CH_3CN)_6](BF_4)_2$ [8b] (30.7 mg, 63.4 µ mol) in 0.5 ml was added to **6** (21.2 mg, 63.5 µmol) under argon atmosphere. The mixture was stirred for 20 min until the solid was dissolved, then 2,6-lutidine (15 µl, 129 µmol) was added to the solution. The resulting solution was stirred for 7 h. The solvent was taken off in vacuo, and the residue was dried in vacuo. The solid was dissolved in 0.1 ml of acetonitrile, and 1 ml of ethyl acetate was added to the solution to precipitate. The precipitate was collected by filtration and washed with 2 ml of ethyl acetate. This procedure of precipitation was repeated four times, and the pink product was dried in vacuo at 60 °C for 2.5 h. A solution of **5** (34.8 mg, 39.3 mmol) in 7.5 ml of $CHCl_3$ was added to the solid. The mixture was stirred at 60 °C in the dark overnight. To the solution, 1.5 ml of acetonitrile was added and the mixture was heated with stirring in the dark for 1 h. The solvent was taken off by a rotary evaporator in the dark. All of solvents used by the following purification were distilled. The solid was dissolved in 2 ml of CH_2Cl_2, and precipitated with 20 ml of hexane. The red solid was collected by filtration and washed with 10 ml of hexane. A solution of the solid in acetone was filtered and the solvent was removed in vacuo. The residual solid was dissolved in 1 ml of acetone, and 1 ml of water was added. To the solution, a solution of anhydrous sodium perchlorate (405 mg, 3.31 mmol) in 2 ml of water was added. Red solid formed upon cooling at 0 °C overnight was collected by filtration and washed with 2 ml of cold water. The product was dried in vacuo. Yield 27.5 mg (51%). ^1H NMR (500 MHz, $CD_3CN:CDCl_3 = 5:1$); the porphyrin moiety: 10.17 (s, 2H, meso), 8.33 (s, 1H, imidazole), 8.10 (d, 2H, phenyl), 7.87 (s, 1+2H, imidazole and phenyl), 7.70 (m, 3H, phenyl), 5.71 (dd, 4H, benzylic CH_2), 4.01 (q, 8H, CH_2CH_3), 2.45 (s, 6H, CH_3), 2.42 (s, 6H, CH_3), 1.75 (t, 12H, CH_2CH_3), 1.50 (s, 18H, *t*-butyl); the cobalt-complex moiety: 8.20 (t, 1H), 7.70 (m, 2H), 4.92 (d, 2H, benzylic CH_2), 4.38 (d, 2H, benzylic CH_2), 3.56 (m, 2H), 3.38 (m, 2H), 2.81, (m, 2H), 2.32 (m, 2H), 0.68 (m, 2H). ESI-MS (in acetone) $m/z = 1274$. *Anal*. Found: C, 63.50; H, 6.18; N, 8.76%. Calcd for $[C_{73}H_{85}N_9O_4CoZn](ClO_4)(acetone)$: C, 63.64; H, 6.39; N, 8.79%. *Caution!* Perchlorate salts containing organic components are potentially explosive; they should be handled with care and in small amounts.

3.10. Photoreaction of **1**

A solution of **1** (2.07 mg, 1.52 μmol) and 1,1,2,2-tetrachloroethane (1.0 μl, an internal standard) in 0.25 ml of $CDCl_3$ and 1.25 ml of CD_3CN was purged with argon for 20 min in an NMR tube. The solution was irradiated for 3 min with a Shimadzu AT-100 HG light source equipped with a halogen lamp. The red-violet solution became turbid, and red powders precipitated leaving a clear yellow supernatant. The ^1H NMR spectra were measured before and after irradiation. The resulting mixture was filtered, and the precipitate and filtrate were analyzed by ^1H NMR (the precipitate in $CDCl_3$) and ESI-MS (the filtrate in CD_3CN).

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