Electronic Supplementary Information

Two-Photon, Red Light Uncaging of Alkyl Radicals from Organorhodium(III) Phthalocyanine Complexes

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1. General procedures

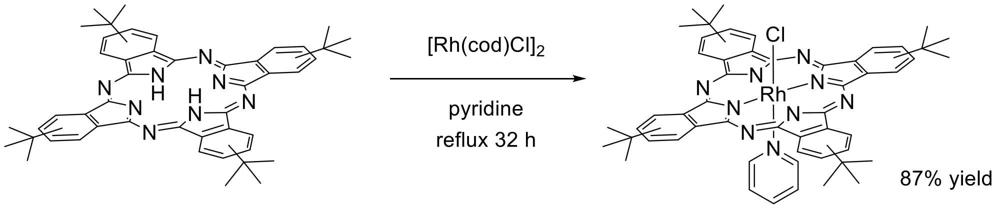
Materials $RhCl_2 \cdot 3H_2O$ was purchased from Tanaka Kikinzoku Kogyo K.K. 4-*Tert*-butyl phthalonitrile and zinc phthalocyanine (Pc) were purchased from Tokyo Chemical Industry Co., Ltd. Chloroform, cyclooctadiene, ethanol (EtOH), ethyl acetate (AcOEt), methanol (MeOH), tetrahydrofuran (THF), and pyridine were purchased from Wako Pure Chemical Industries, Ltd. Toluene, pyridine, acetone-d_6, benzene-d_6 (C_6D_6), and chloroform-*d* ($CDCl_3$) were purchased from Kanto Chemical Co., Inc. Dulbecco's modified Eagle's medium (high glucose; DMEM) was purchased from Merck KGaA (Sigma-Aldrich®). GlutaMAX™ and Penicillin Streptomycin were purchased from Thermo Fisher Scientific Inc. (Gibco®). Fetal bovine serum (FBS) was purchased from Biowest. Cell Counting Kit-8 (CCK-8) was purchased from Dojindo Laboratories Co., Ltd. Apoptotic/Necrotic/Healthy Cells Detection Kit was purchased from PromoCell GmbH (PromoKine). All the chemicals were used as received without further purification. The precursor tetra-*tert*-butyl-29H,31H-phthalocyanine,[1] $[Rh(cod)Cl]_2$ (cod = 1,5-cyclooctadiene),[2] and liposomal zinc Pc[3] were synthesized according to literature procedures. *tert*-Butyl groups were introduced to the macrocycle to improve the solubility in organic solvents, assuming that the electronic structures of the Pc ring remained unaltered upon substitution.

Measurements UV–vis absorption spectra were recorded on a V-570 UV–vis/NIR spectrophotometer (JASCO Co., Ltd.). Magnetic circular dichroism (MCD) measurements were performed using a JASCO E-250 equipped with a JASCO electromagnet (+1.35 – −1.35 T). Near-IR phosphorescence measurements were performed with a monochromator (JASCO CT-25CP) and a photomultiplier (Hamamatsu Photonics R5509-42), which was cooled at 193 K by a cold nitrogen gas flow system (Hamamatsu Photonics R6544-20). The photon signals were amplified by a fast preamplifier (Stanford Research SR445) and measured according to the single-photon counting method using a photon counter (Stanford Research SR400). A dye laser (Sirah CSTR-LG532-TRI-T; 650–653 nm) pumped with an Nd:YAG laser (Spectra Physics INDI 40; 532 nm, 7 ns fwhm) or a diode laser (LDX Optronics LDX-2515-650; 650 nm) was employed as the excitation source. MALDI-TOF-MS spectra were measured using a JEOL JMS-S8000 SpiralTOF spectrometer. NMR spectra were recorded on a JEOL Resonance ECS 400 spectrometer. For the NMR measurements of complexes **1** and **2**, pyridine-d_5 was added to the $CDCl_3$ solution to inhibit the aggregation and observe the NMR signals clearly.

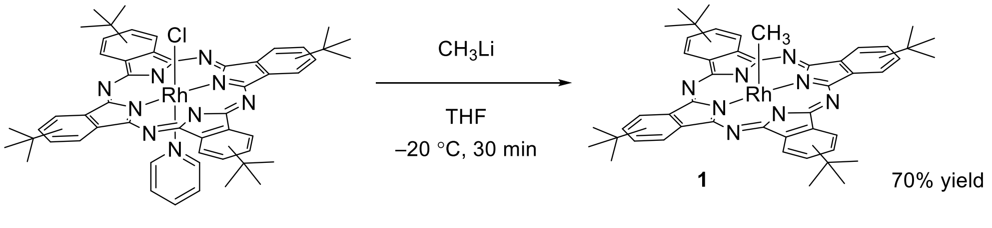
Theoretical study DFT and TD-DFT calculations were performed with the Gaussian 16 package using the B3LYP functional.[4] The Def2-TZVPP basis set was used for all atoms.[5] For validation, the vibrational frequencies were calculated for the optimized geometries. To address solvation effects, the polarizable continuum model (PCM)[6] was used. The orbital plots and graphical representations were produced using the Molekel software.[7]

2. Preparations

RhPc complexes

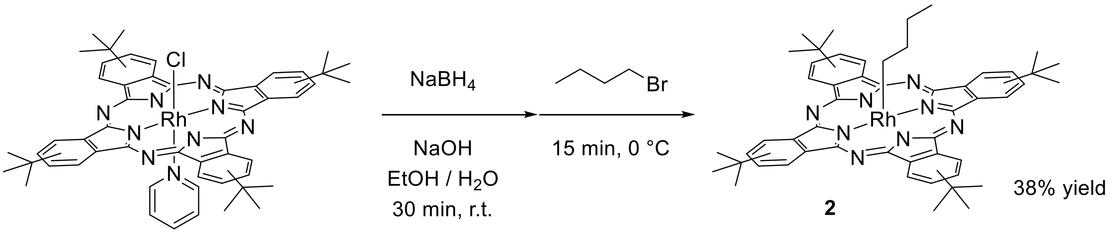


(Tetra-*tert*-butyl-phthalocyaninato)rhodium(III)chloride(pyridine) (**ClRhPc(py)**): Under a nitrogen atmosphere, a mixture of tetra-*tert*-butyl-29H,31H-phthalocyanine (50.0 mg, 0.0676 mmol) and $[Rh(cod)Cl]_2$ (66.6 mg, 0.135 mmol) was refluxed in pyridine (7 mL) for 32 h. After removal of the solvent, the crude product was filtered and washed with H_2O/MeOH (3/1). The filtrate was purified by silica-gel column chromatography (toluene/AcOEt = 20/1) to give **ClRhPc(py)** as an analytically pure product (56.4 mg, 0.0588 mmol, 87.4% yield). ^{1}H NMR (400 MHz, $CDCl_3$, δ / ppm) : 9.58–9.54 (m, 4 H, *Pc*), 9.49–9.39 (m, 4 H, *Pc*), 8.27–8.23 (m, 4 H, *Pc*), 6.18 (t, J = 7 Hz, 1 H, *py*), 5.33 (dd, J = 7 Hz, 7 Hz, 2 H, *py*), 2.00 (d, J = 7 Hz, 2 H, *py*), 1.82–1.80 (m, 36 H, ^{t}*Bu*). ^{13}C NMR (100 MHz, $CDCl_3$, δ / ppm) : 162.7, 153.6–153.5, 146.3, 144.4–144.2, 139.1–139.0, 136.7, 136,4, 127.3–127.2, 123.9, 122.4, 119.4, 36.1, 32.2. HR-MS (MALDI-TOF) : *m/z* calcd for $C_{48}H_{48}ClN_8Rh$: 874.2746 $[M-py]^+$; found: 874.2719. Anal. found (calcd for $C_{53}H_{53}ClN_9Rh$): C, 67.30 (66.70) ; H, 5.85 (5.60) ; N, 12.34 (13.21).



(Tetra-*tert*-butyl-phthalocyaninato)rhodium(III)methyl (**1**): Under a nitrogen atmosphere, MeLi (3.1 M in dimethoxyethane, 18.0 μL, 0.0559 mmol) was added to a THF solution (3 mL) of **ClRhPc(py)** (26.6 mg, 0.0279 mmol) at −20 °C, and the solution was stirred for 30 min.

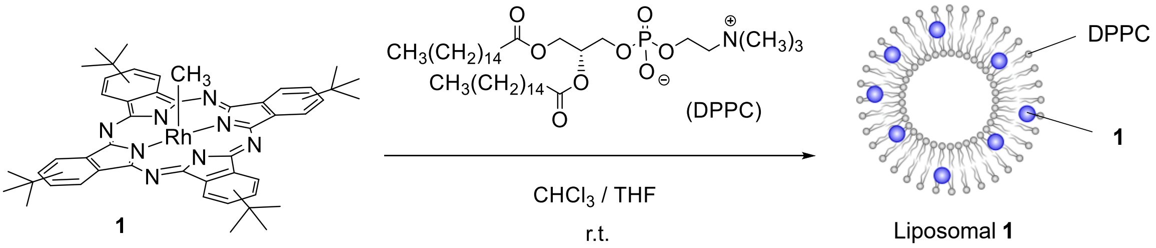
After the removal of the solvent, the crude product was purified by silica-gel column chromatography ($CHCl_3$) and gel-permeation chromatography (Bio-beads®, $CHCl_3$) to give **1** as an analytically pure product (16.6 mg, 0.0194 mmol, 69.5% yield). UV–Vis (toluene + 1% pyridine, $\lambda_{\max}$ / nm (log ε / L mol^{-1}cm^{-1})): 651 (5.4), 628 (4.6), 589 (4.6), 353 (4.5). ^{1}H NMR (600 MHz, $CDCl_3$ + 0.2% pyridine-*d*$_5$, δ / ppm) : 9.48–9.44 (m, 4 H, *Pc*), 9.38–9.31 (m, 4 H, *Pc*), 8.19–8.17 (m, 4 H, *Pc*), 1.79–1.78 (m, 36 H, *^{t}Bu*), −6.11 (m, 3 H, Rh−C*H*$_3$). ^{13}C NMR (150 MHz, $CDCl_3$ + 0.2% pyridine-*d*$_5$, δ / ppm) : 152.9, 144.2–144.0, 139.2–139.1, 136.8, 126.8, 121.9, 118.7, 36.0, 32.2, −12.5. HR-MS (MALDI-TOF) : *m/z* calcd for $C_{49}H_{51}N_8Rh$: 854.3292 [M]$^+$; found: 854.3293. Anal. found (calcd for $C_{49}H_{51}N_8Rh$): C, 69.45 (68.84) ; H, 6.16 (6.01) ; N, 12.34 (13.11).



(Tetra-*tert*-butyl-phthalocyaninato)rhodium(III)butyl (**2**): Under a nitrogen atmosphere, an aqueous NaOH solution (0.1 M, 7.2 mL) containing $NaBH_4$ (72.5 mg, 1.92 mmol) was added to a EtOH (18 mL) solution of **ClRhPc(py)** (30.0 mg, 0.0314 mmol) at room temperature, and the resulting mixture was stirred for 30 min. 1-Bromobutane (33.9 μL, 0.314 mmol) was then added at 0 °C, and the mixture was stirred for another 15 min. The reaction mixture was extracted with CH_2Cl_2, and the combined organic phase was washed with H_2O. After removal of the solvent, the crude product was purified by silica-gel column chromatography (*n*-hexane → $CHCl_3$/*n*-hexane = 2/3) and gel-permeation chromatography (Bio-beads®, $CHCl_3$) to give **2** as an analytically pure product (10.8 mg, 0.0121 mmol, 38.4% yield). UV–Vis (toluene + 1% pyridine, $\lambda_{\max}$ / nm (log ε / L mol^{-1}cm^{-1})): 651 (5.4), 628 (4.6), 589 (4.6), 352 (sh, 4.5), 331 (4.6). ^{1}H NMR (600 MHz, $CDCl_3$ + 0.2% pyridine-*d*$_5$, δ / ppm) : 9.48–9.44 (m, 4 H, *Pc*), 9.37–9.31 (m, 4 H, *Pc*), 8.19–8.17 (m, 4 H, *Pc*), 1.80–1.78 (m, 36 H, *tBu*), −0.87 (t, *J* = 8 Hz, 3 H, -CH_2CH_2C*H*$_3$), −1.32 (tq, *J* = 8 Hz, 8 Hz, 2 H, -CH_2C*H*$_2$$CH_3$), −3.88 (tt, *J* = 8 Hz, 8 Hz, 2 H, -C*H*$_2$$CH_2CH_3$), −5.15–−5.18 (m, 2 H, Rh-C*H*$_2$). ^{13}C NMR (150 MHz, $CDCl_3$ + 0.2% pyridine-*d*$_5$, δ / ppm) : 152.9–152.8, 144.3–144.0, 139.3–139.2, 136.9, 126.9–126.8, 121.9, 118.7, 36.0, 32.2, 28.7, 22.1, 12.6, 12.1. HR-MS (MALDI-TOF) : *m/z* calcd for $C_{52}H_{57}N_8Rh$: 896.3761

$[M]^+$; found: 896.3751. Anal. found (calcd for $C_{52}H_{57}N_8Rh$): C, 68.92 (69.63) ; H, 6.47 (6.41) ; N, 11.84 (12.49).

Liposomal 1



Liposomal **1** was prepared according to a previously reported method.[8,9] Briefly, 1,2-dipalmitoyl-sn-glycero-3-phosphocholine (DPPC, 42 mg, 0.057 mmol) and complex **1** (0.30 mg, 3.5×10^{-4} mmol) were dissolved in 7.6 mL of $CHCl_3$/THF (20/1 v/v), and the solvent was removed by rotary evaporation. After addition of 4.0 mL of 0.1 M phosphate-buffered saline (PBS, pH 7.4), the dried DPPC was hydrated by repeated vortex mixing with glass beads. The obtained suspension was sonicated at 50 °C for 1 h and centrifuged three times, which resulted in a blue supernatant fluid. The concentration of complex **1** in the liposomal dispersions was determined by diluting the solution with an excess of dimethylformamide (DMF) and measuring the absorbance at λ_{max}.

3. Cell experiments

The cell experiments were performed following a previously reported procedure.[8]

Growth of HeLa cells Monolayer cultures of HeLa cells were grown in DMEM medium with 10% FBS. The cultures were maintained at 37 °C in a humidified atmosphere of 5% CO_2 and 95% air.

Cytotoxicity toward HeLa cells For the cytotoxicity experiment, 96-well microplates and a CCK-8 kit were employed. A tetrazolium salt (WST-8: 4-[3-(2-methoxy-4-nitrophenyl)-2-(4-nitrophenyl)-2H-5-tetrazolio]-1,3-benzene disulfonate sodium salt) in CCK-8 produced a highly colored formazan dye solution upon NADH reduction, indicating the presence of living cellular dehydrogenase. To investigate the cytotoxicity, Suspensions of 2×10^3 HeLa cells in 100 μL of medium were inoculated into each well of a 96-well microplate. After culturing in a

CO_2 incubator for 24 h, 20 μL of PBS solutions of liposomal Pc with Pc complex concentrations ranging between 0.6 and 24 μM were added to 40 of the wells of monolayer cultures of HeLa cells, and the remaining wells were used as controls. After incubating for 20 h, the medium in each well was exchanged to remove the extracellular liposomes. After further incubating for 24 h, 10 mL of the CCK-8 solution was added into each well, which were then cultured for 3 h to complete the color reaction. The absorbance at 450 nm of each well was then measured using a microplate reader (Bio-Rad Model 680). To evaluate the cytotoxicity of the Pc complexes, the average absorbance data of the 40 wells containing the Pc complexes was compared with that of the wells without Pc complex.

Phototoxicity toward HeLa cells Suspensions of 2×10^3 HeLa cells in 100 μL of medium were inoculated into each well of a 96-well microplate. After culturing in a CO_2 incubator for 24 h, 20 μL of PBS solutions of liposomal Pc with Pc complex concentrations ranging between 0.6 and 24 μM were added to 40 of the wells of monolayer cultures of HeLa cells, and the remaining wells were used as controls. After incubating for 20 h, the medium in each well was exchanged to remove the extracellular liposomes. The 40 wells treated with the Pc complexes were irradiated for 30 min using the dye laser (653 nm, 5 mJ pulse^{-1}) pumped with the Nd:YAG laser. The dye laser beam was expanded by lenses capable of irradiating 40 wells simultaneously from the bottom of the microplate. After further incubating for 24 h, 10 mL of the CCK-8 solution was added into each well, followed by culturing for 3 h to complete the color reaction. The absorbance at 450 nm of each well was then measured using a microplate reader (Bio-Rad Model 680). The average absorbance data of the 40 wells treated with the Pc complexes and laser irradiation was compared with that of the wells without photodynamic treatment to evaluate the phototoxicity of the Pc complexes.

Uptake by HeLa cells Suspensions of 2.5×10^6 HeLa cells in 9 mL of medium were inoculated into a 10 cm dish. After culturing in a CO_2 incubator for 24 h, 1 mL of liposomal Pc with a Pc complex concentration of 10 μM was added to the monolayer cultures of HeLa cells. After incubating for 20 h, the medium containing the Pc complexes was removed from the dish and repeatedly washed with PBS solutions to remove the extracellular liposomes. Then, the cells were harvested into a tube by tryptic treatment, followed by centrifugation to obtain a colorless supernatant fluid and a blue precipitate. After removal of the supernatant fluid, the Pc complex was extracted with an excess amount of DMF, and the absorbance at the Q band of the Pc complex was then measured to evaluate the uptake amount.

4. Experimental and related data

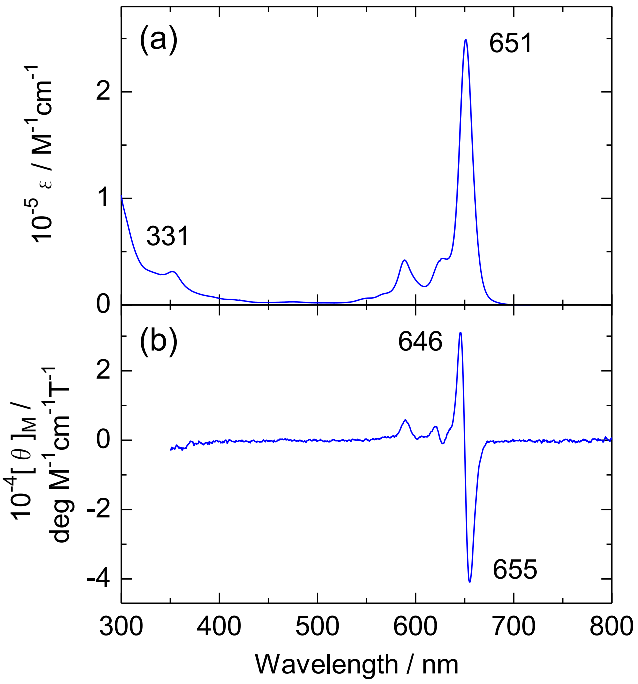


Fig. S1 Electronic absorption and MCD spectra of complex **2** (toluene with 1% pyridine, room temperature).

Table S1 Photouncaging reactions under various conditions.

Entry	Complex	Atmos-phere	Solvent	Conv. [%]	Yield[a] [%]	
					HCHO[b]	CH_3OH
1	**1**	O_2 (1 atm)	acetone-d_6	92	≥30	12
2	**1**	O_2 (1 atm)	C_6D_6	>99	≥34	14
3	**1**	air	C_6D_6	>99	≥29	17

Entry	Complex	Atmos-phere	Solvent	Conv. [%]	Yield[a] [%]		
					butyr-aldehyde	1-butanol	1-butene[b]
4	**2**	O_2 (1 atm)	C_6D_6	>99	50	13	≥21
5	**2**	air	C_6D_6	91	30	8	≥28

Standard condition : 1.0 mM complex, pulsed laser : λ_{irr} = 650 nm, 1.8 mJ/pulse, r.t.

[a]NMR yield. [b]calculated based on the product dissolved in the solution.

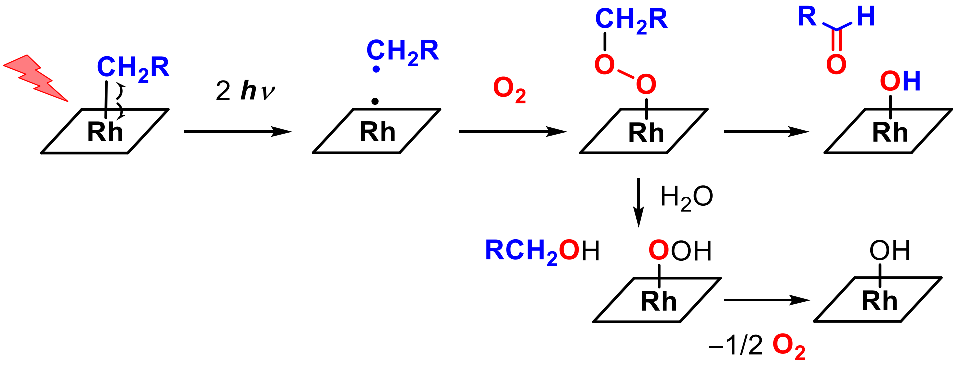


Fig. S2 Proposed mechanism for the photochemical formation of aldehyde and alcohol from the organorhodium(III) complexes.

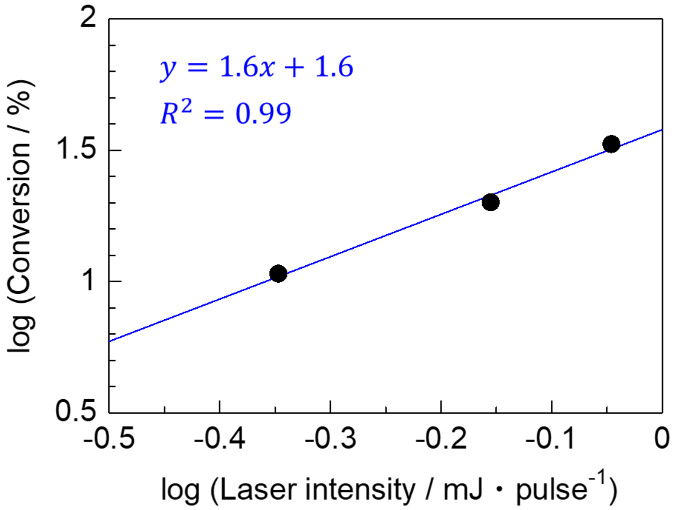


Fig. S3 Photoconversion of complex **1** as a function of the laser intensity (irradiation with a nanosecond pulsed laser of red light at $\lambda_{\text{irr.}}$ = 650 nm for 30 min in acetone-d^6). The slope of the fitting line is ~2 in the range of 0.4–1 mJ pulse^{-1}, which indicates that the reaction involves a two-photon excitation process.

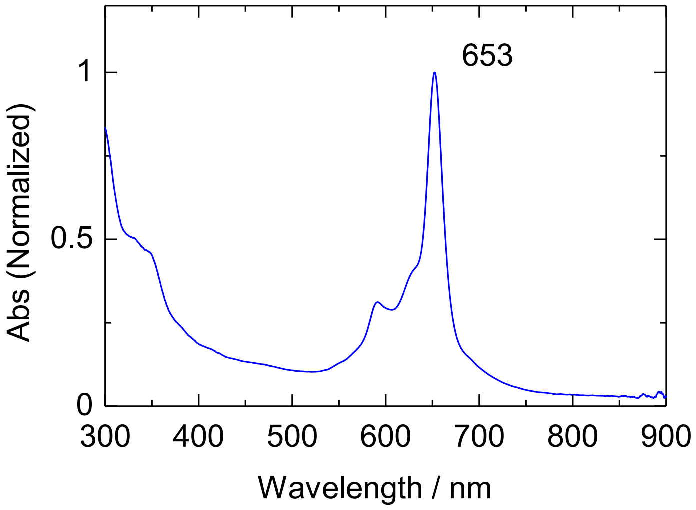


Fig. S4 Electronic absorption spectrum of liposomal **1** (phosphate-buffered saline solution, room temperature, diffuse transmission).

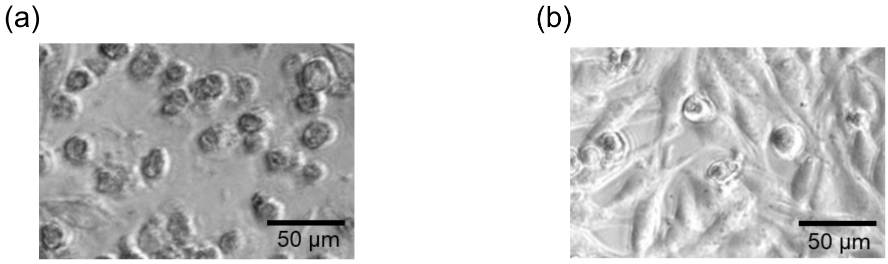


Fig. S5 Microscopy images of HeLa cells treated by liposomal **1** with a complex concentration of 1 μM (a) after irradiation of nanosecond pulsed laser of red light ($\lambda_{\mathrm{irr.}}$ = 653 nm) for 30 min and (b) kept under dark as a control.

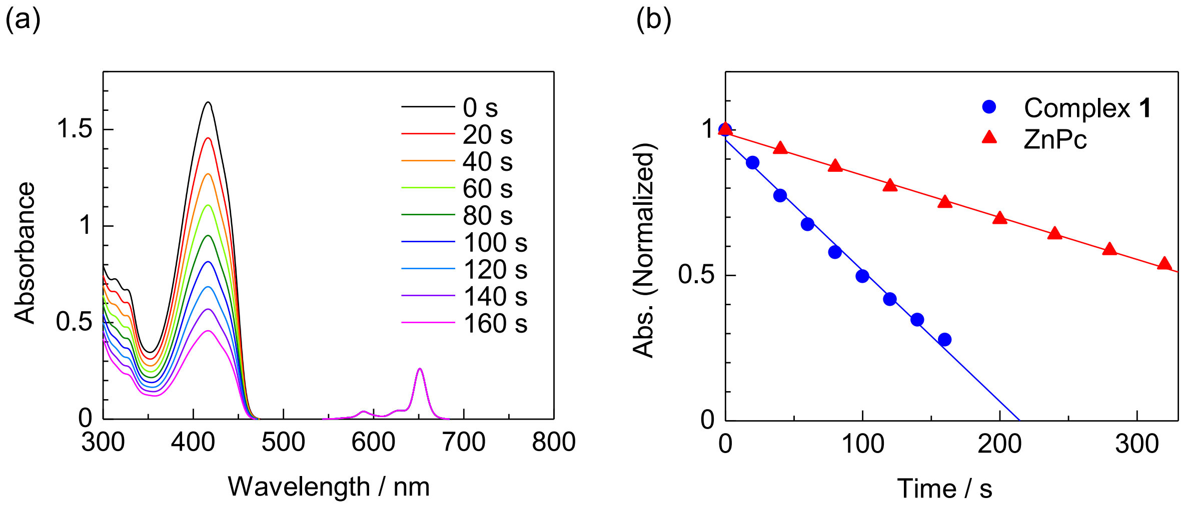


Fig. S6 Singlet-oxygen quantum yield measurement. (a) Electronic absorption spectral changes of DPBF under light irradiation ($\lambda_{\mathrm{irr.}}$ = 650 nm) in the presence of complex **1** (toluene + 1% pyridine, room temperature). (b) Time profiles of the absorbance changes at 412 nm in the presence of complex **1** and zinc phthalocyanine (Φ_{Δ} = 0.54),[10] from which the Φ_{Δ} value of complex **1** was determined to be 0.43.

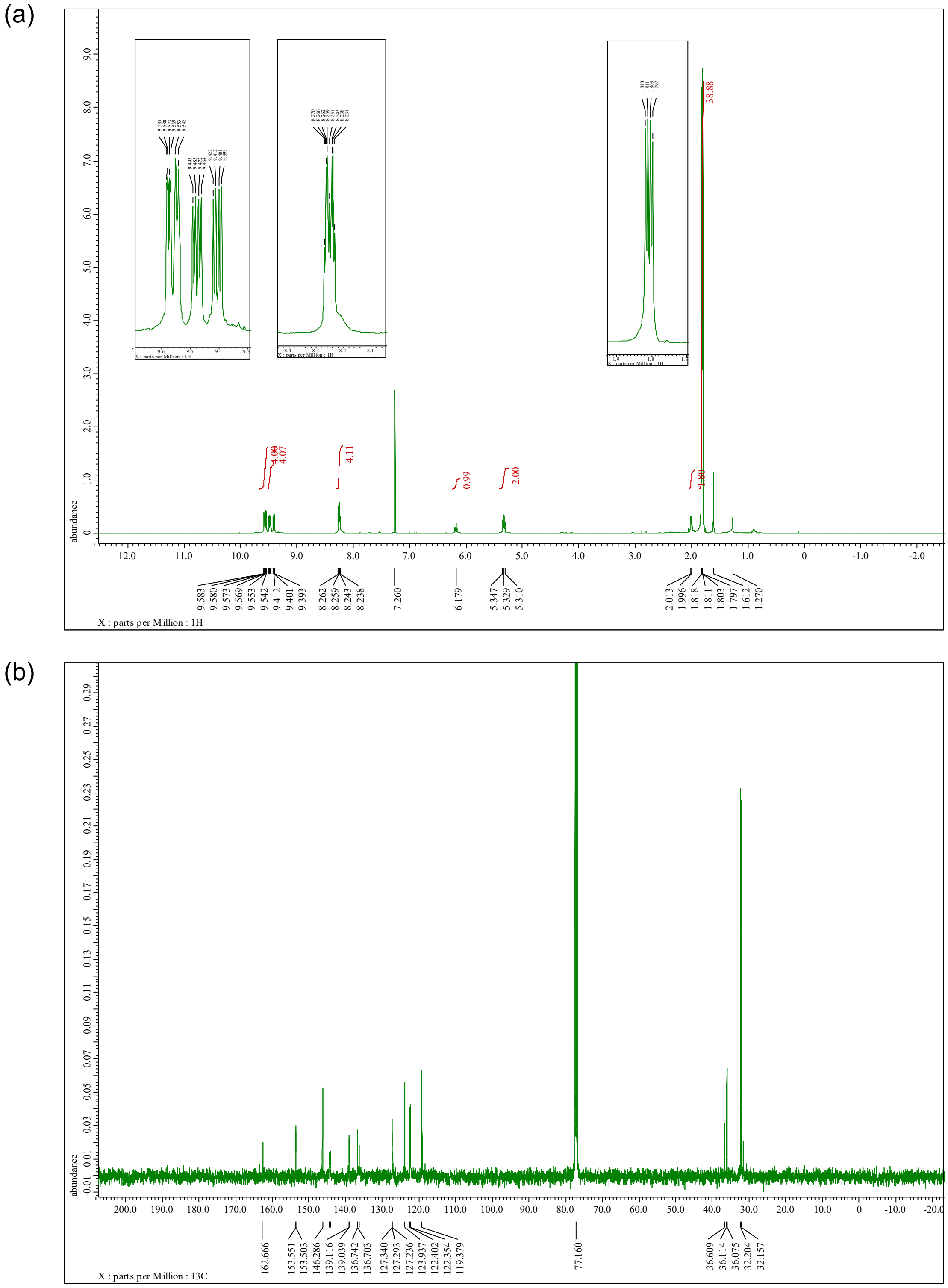


Fig. S7 (a) ^{1}H NMR (400 MHz) and (b) ^{13}C NMR (100 MHz) spectra of ClRhPc(py) (CDCl$_3$, r.t.).

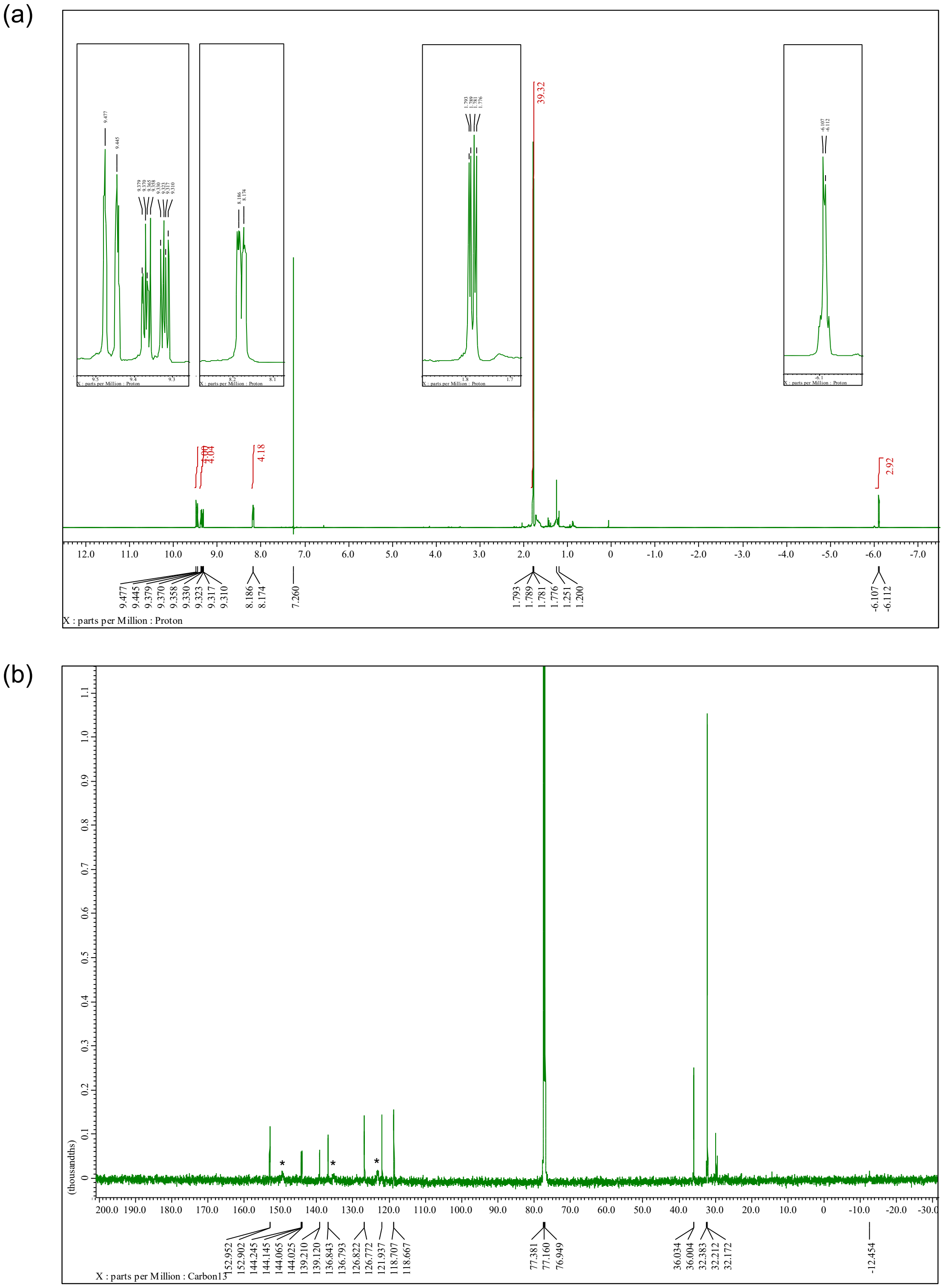


Fig. S8 (a) ^{1}H NMR (600 MHz) and (b) ^{13}C NMR (150 MHz) spectra of complex **1** ($CDCl_3$ + 0.2% pyridine-d_5, r.t.). *Carbon signals of pyridine-d_5.

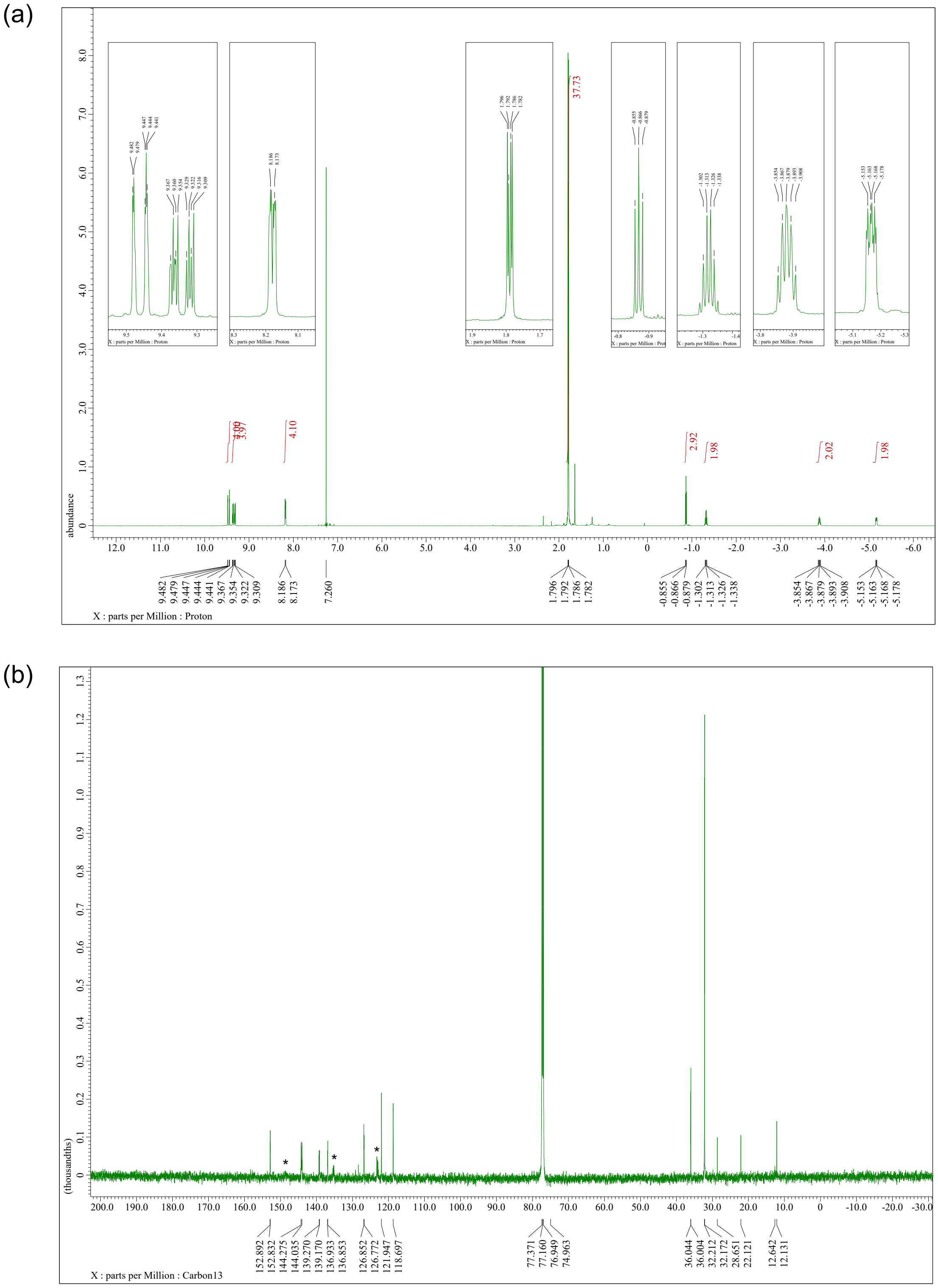


Fig. S9 (a) ^{1}H NMR (600 MHz) and (b) ^{13}C NMR (150 MHz) spectra of complex **2** ($CDCl_3$ + 0.2% pyridine-d_5, r.t.). *Carbon signals of pyridine-d_5.

4. DFT calculation data

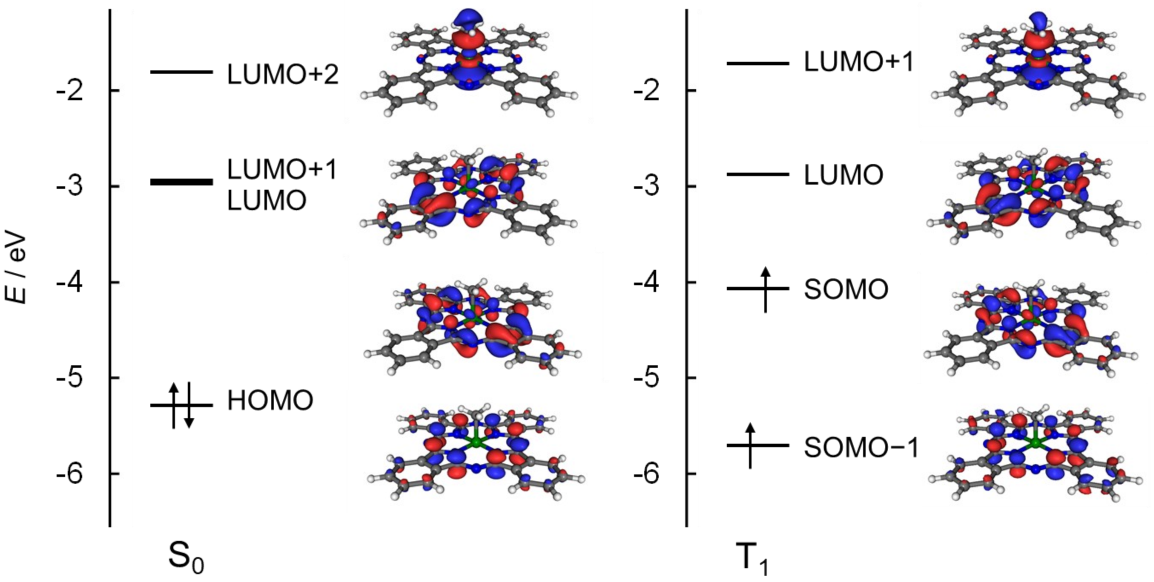


Fig. S10 Selected molecular orbitals of complex **1'** in the S_0 and T_1 optimized geometries. DFT calculation: B3LYP/Def2-TZVPP level with PCM (benzene). Isocontour value ±0.035 (e bohr^{-3})$^{1/2}$.

Table S2 Calculated energies and compositions of the selected excited states of complex **1'** based on the S_0 and T_1 optimized geometries. TD-DFT calculation: B3LYP/Def2-TZVPP level with PCM (benzene).

Geom.	State	*E* / eV	*f*	Compositions[ab]
S_0	S_{1x}	2.069	0.6074	HOMO (a_{1u}(Pc)) → LUMO (e_{gy}(Pc)) (97%)
	S_{1y}	2.070	0.6073	HOMO (a_{1u}(Pc)) → LUMO+1 (e_{gx}(Pc)) (97%)
	S_5	2.791	0.0001	HOMO (a_{1u}(Pc)) → LUMO+2 (σ*(Rh−C)) (99%)
	T_{1x}	1.302	---	HOMO (a_{1u}(Pc)) → LUMO (e_{gy}(Pc)) (100%)
	T_{1y}	1.302	---	HOMO (a_{1u}(Pc)) → LUMO+1 (e_{gx}(Pc)) (100%)
T_1	T_5	1.481	0.0001	SOMO (e_{gy}(Pc)) → LUMO+1 (σ*(Rh−C)) (94%)

[a] Transition percentage ≥5%. [b] Expressions based on D_{4h} symmetry of Pc^{2-} are used for the π-MOs of the Pc ligand.

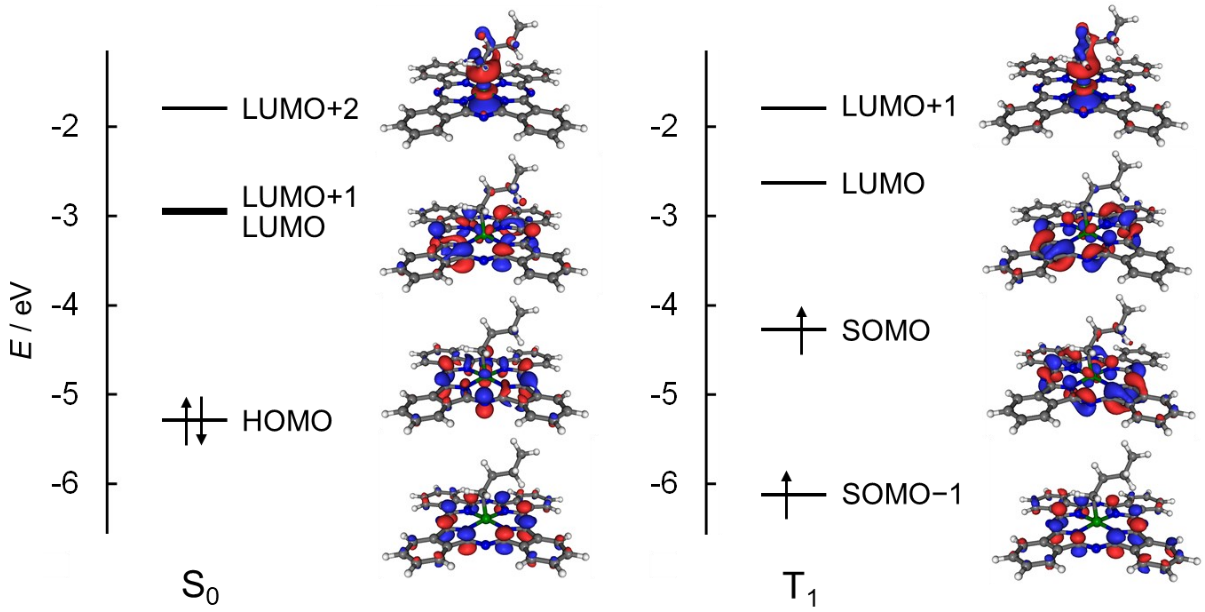


Fig. S11 Selected molecular orbitals of complex **2'** in the S_0 and T_1 optimized geometries. DFT calculation: B3LYP/Def2-TZVPP level with PCM (benzene). Isocontour value ±0.035 (e bohr^{-3})$^{1/2}$.

Table S3 Calculated energies and compositions of the selected excited states of complex **2'** based on the S_0 and T_1 optimized geometries. TD-DFT calculation: B3LYP/Def2-TZVPP level with PCM (benzene).

Geom.	State	E / eV	f	Compositions[a]
S_0	S_{1x}	2.071	0.5901	HOMO (a_{1u}(Pc)) → LUMO (e_{gy}(Pc)) (97%)
	S_{1y}	2.071	0.5887	HOMO (a_{1u}(Pc)) → LUMO+1 (e_{gx}(Pc)) (97%)
	S_5	2.788	0.0008	HOMO (a_{1u}(Pc)) → LUMO+2 (σ*(Rh−C)) (99%)
	T_{1x}	1.309	---	HOMO (a_{1u}(Pc)) → LUMO (e_{gy}(Pc)) (56%) HOMO (a_{1u}(Pc)) → LUMO+1 (e_{gx}(Pc)) (44%)
	T_{1y}	1.309	---	HOMO (a_{1u}(Pc)) → LUMO+1 (e_{gx}(Pc)) (56%) HOMO (a_{1u}(Pc)) → LUMO (e_{gy}(Pc)) (44%)
T_1	T_5	1.473	0.0001	SOMO (e_{gy}(Pc)) → LUMO+1 (σ*(Rh−C)) (94%)

[a] Transition percentage ≥5%. [b] Expressions based on D_{4h} symmetry of Pc^{2-} are used for the π-MOs of the Pc ligand.

Table S4 Cartesian coordinates and ZPE corrected total energy of the optimized structure of the ground state of complex **1**.

1(S_0) E_{tot} = -1818.3812 a.u.

C	-0.03344	0.00300	2.06380
C	2.94642	0.55622	-0.05303
C	4.23362	-0.12712	-0.07158
C	5.54167	0.34288	-0.09034
C	6.56786	-0.59388	-0.10707
C	6.29404	-1.96834	-0.10738
C	4.98716	-2.44027	-0.09089
C	3.95914	-1.50488	-0.07178
C	2.50829	-1.64284	-0.05312
C	-0.55492	2.94520	-0.05486
C	0.12826	4.23255	-0.07432
C	0.55763	-2.94584	-0.05326
C	-0.34184	5.54050	-0.09405
C	0.59484	6.56680	-0.11112
C	1.96929	6.29311	-0.11082
C	2.44134	4.98625	-0.09338
C	1.50605	3.95818	-0.07393
C	1.64408	2.50732	-0.05421
C	-2.94447	-0.55619	-0.05325
C	-4.23185	0.12701	-0.07344
C	-5.53977	-0.34304	-0.09353
C	-6.56606	0.59372	-0.11184
C	-0.12585	-4.23301	-0.07366
C	-6.29231	1.96809	-0.11241
C	-4.98538	2.44008	-0.09463
C	-3.95742	1.50477	-0.07393
C	-2.50648	1.64264	-0.05393
H	1.40482	-5.74902	-0.09436
H	-3.49854	-4.77113	-0.09678
C	0.34397	-5.54103	-0.09400
H	5.74947	1.40376	-0.09095
H	4.77229	-3.49977	-0.09209
C	-0.59295	-6.56712	-0.11264
H	-1.40274	5.74822	-0.09509
H	3.50083	4.77148	-0.09404
C	-1.96732	-6.29311	-0.11330
H	-5.74759	-1.40391	-0.09400
H	-4.77058	3.49958	-0.09611
C	-2.43907	-4.98614	-0.09522
C	-1.50356	-3.95833	-0.07421
C	-1.64119	-2.50742	-0.05393
N	-0.38824	-1.95677	-0.04553
N	-2.79902	-1.86985	-0.05166
N	1.95725	-0.38986	-0.04600
N	1.87122	-2.80082	-0.05134
N	0.39133	1.95630	-0.04696
N	2.80178	1.86993	-0.05164
N	-1.95575	0.38993	-0.04533
N	-1.86872	2.80022	-0.05257
Rh	0.00081	-0.00003	0.01782
H	0.96156	-0.25064	2.41830
H	-0.32010	0.99758	2.39343
H	-0.76036	-0.73616	2.38817
H	7.59668	-0.25955	-0.12028
H	7.11621	-2.67140	-0.12086
H	0.26041	7.59559	-0.12508
H	2.67229	7.11533	-0.12452
H	-7.59485	0.25931	-0.12614
H	-7.11446	2.67115	-0.12715
H	-0.25874	-7.59597	-0.12716
H	-2.67050	-7.11515	-0.12837

Table S5 Cartesian coordinates and ZPE corrected total energy of the optimized structure of the lowest excited triplet state of complex **1**.

1(T$_1$) E_{tot} = −1818.3306 a.u.

C	0.03361	0.00007	2.06932
C	-2.78664	-1.12727	-0.04574
C	-4.19557	-0.69960	-0.05087
C	-5.37872	-1.41706	-0.05828
C	-6.57526	-0.69741	-0.06334
C	-6.57527	0.69738	-0.06351
C	-5.37873	1.41704	-0.05861
C	-4.19557	0.69959	-0.05103
C	-2.78665	1.12726	-0.04600
C	1.11901	-2.78236	-0.05809
C	0.70492	-4.16676	-0.09708
C	-1.12193	2.78276	-0.05987
C	1.41859	-5.36063	-0.13319
C	0.70029	-6.55044	-0.16817
C	-0.70221	-6.55064	-0.16881
C	-1.42082	-5.36102	-0.13458
C	-0.70747	-4.16694	-0.09790
C	-1.12193	-2.78276	-0.05919
C	2.78482	1.12710	-0.04544
C	4.19385	0.69962	-0.05303
C	5.37693	1.41705	-0.06271
C	6.57351	0.69738	-0.06970
C	-0.70749	4.16692	-0.09905
C	6.57352	-0.69735	-0.06956
C	5.37693	-1.41703	-0.06241
C	4.19385	-0.69960	-0.05288
C	2.78482	-1.12708	-0.04518
H	-2.50207	5.35968	-0.13731
H	2.49979	5.35908	-0.13498
C	-1.42085	5.36098	-0.13614
H	-5.37344	-2.49805	-0.05936
H	-5.37346	2.49803	-0.05995
C	-0.70225	6.55059	-0.17079
H	2.49981	-5.35909	-0.13337
H	-2.50205	-5.35973	-0.13577
C	0.70026	6.55041	-0.17016
H	5.37167	2.49805	-0.06402
H	5.37169	-2.49803	-0.06350
C	1.41856	5.36061	-0.13478
C	0.70490	4.16674	-0.09824
C	1.11901	2.78237	-0.05878
N	-0.00153	1.99584	-0.04113
N	2.40451	2.37728	-0.04780
N	-2.00168	-0.00000	-0.04727
N	-2.40707	2.37759	-0.04870
N	-0.00153	-1.99584	-0.04071
N	-2.40707	-2.37760	-0.04814
N	2.00046	0.00001	-0.04476
N	2.40451	-2.37727	-0.04723
Rh	-0.00085	0.00001	0.02750
H	-0.99247	-0.00054	2.42784
H	0.55634	-0.89346	2.40024
H	0.55527	0.89425	2.40018
H	-7.51761	-1.22860	-0.06734
H	-7.51762	1.22856	-0.06763
H	1.22956	-7.49358	-0.19548
H	-1.23120	-7.49392	-0.19657
H	7.51584	1.22859	-0.07547
H	7.51585	-1.22856	-0.07521
H	-1.23125	7.49386	-0.19888
H	1.22952	7.49354	-0.19781

Table S6 Cartesian coordinates and ZPE corrected total energy of the optimized structure of the ground state of complex **2**.

2(S_0) E_{tot} = -1936.3624 a.u.

C	-0.30212	0.00803	1.92849
C	-1.90026	2.42522	-0.18952
C	-1.82981	3.88095	-0.21949
C	-2.81089	4.86554	-0.20495
C	-2.39999	6.19243	-0.24768
C	-1.04075	6.52803	-0.30804
C	-0.05844	5.54517	-0.32709
C	-0.46710	4.21743	-0.27970
C	0.27387	2.96195	-0.28715
C	-2.57929	-1.76002	-0.15748
C	-4.03513	-1.68753	-0.13063
C	2.27590	1.74658	-0.42611
C	-5.02039	-2.66776	-0.11118
C	-6.34709	-2.25461	-0.08716
C	-6.68192	-0.89386	-0.08526
C	-5.69845	0.08782	-0.10734
C	-4.37082	-0.32325	-0.12887
C	-3.11478	0.41643	-0.15299
C	1.59980	-2.43702	-0.36814
C	1.52522	-3.89264	-0.39546
C	2.50101	-4.87724	-0.49806
C	2.08710	-6.20387	-0.50021
C	3.72059	1.67371	-0.60461
C	0.72960	-6.53916	-0.40697
C	-0.24789	-5.55617	-0.30979
C	0.16452	-4.22874	-0.30237
C	-0.57187	-2.97324	-0.22348
H	4.43842	3.70267	-0.71193
H	5.62181	-1.15342	-0.84785
C	4.69766	2.65349	-0.73893
H	-3.85884	4.60363	-0.16085
H	0.99078	5.80117	-0.37592
C	6.01335	2.23945	-0.90776
H	-4.75917	-3.71680	-0.11358
H	-5.95390	1.13832	-0.10684
C	6.34530	0.87833	-0.94604
H	3.54726	-4.61547	-0.57264
H	-1.29613	-5.81164	-0.24115
C	5.36971	-0.10261	-0.81624
C	4.05341	0.30948	-0.64323
C	2.80791	-0.42986	-0.48207
N	1.78573	0.47073	-0.34807
N	2.72293	-1.74883	-0.47613
N	-0.62428	1.93160	-0.22441
N	1.59006	2.87527	-0.37376
N	-2.08566	-0.48479	-0.17752
N	-3.02736	1.73546	-0.14929
N	0.32894	-1.94252	-0.24961
N	-1.88969	-2.88777	-0.16776
Rh	-0.14697	-0.00570	-0.15058
H	-1.19205	0.61219	2.08539
H	-0.52831	-1.02660	2.18289
C	0.86108	0.54217	2.74628
H	-3.13969	6.98183	-0.23494
H	-0.75429	7.57078	-0.34094
H	-7.13694	-2.99374	-0.06963
H	-7.72452	-0.60563	-0.06632
H	2.82292	-6.99337	-0.57588
H	0.44066	-7.58174	-0.41203
H	6.79692	2.97802	-1.01265
H	7.37930	0.58962	-1.08005
H	1.27403	1.44950	2.29996
H	0.43084	0.86781	3.70379
C	1.97770	-0.45669	3.04921
H	1.54180	-1.33354	3.53728
H	2.42325	-0.81675	2.12165
C	3.07078	0.13087	3.94037
H	3.55082	0.98751	3.46272
H	2.66279	0.47104	4.89488
H	3.84626	-0.60583	4.15449

Table S7 Cartesian coordinates and ZPE corrected total energy of the optimized structure of the lowest excited triplet state of complex **2**.

2(T$_1$) E_{tot} = −1936.3153 a.u.

C	0.31509	-0.01759	1.92687
C	1.80165	-2.50200	-0.19994
C	1.67623	-3.94145	-0.24837
C	2.61573	-4.96769	-0.24994
C	2.15288	-6.27755	-0.30743
C	0.78035	-6.55924	-0.36599
C	-0.16305	-5.53788	-0.36868
C	0.29388	-4.22525	-0.30734
C	-0.39115	-2.95218	-0.29495
C	2.64932	1.66297	-0.15231
C	4.11506	1.52668	-0.10792
C	-2.35065	-1.66355	-0.41360
C	5.13037	2.46602	-0.07235
C	6.44624	2.00009	-0.03578
C	6.72534	0.63359	-0.03786
C	5.69738	-0.31067	-0.07646
C	4.39522	0.15571	-0.11011
C	3.10064	-0.54482	-0.15260
C	-1.50397	2.49984	-0.37576
C	-1.37206	3.93861	-0.42540
C	-2.30414	4.96439	-0.54686
C	-1.83621	6.27349	-0.56909
C	-3.80767	-1.52754	-0.57666
C	-0.46540	6.55470	-0.47653
C	0.47101	5.53369	-0.35951
C	0.00824	4.22187	-0.33198
C	0.68614	2.94930	-0.22990
H	-4.59739	-3.52526	-0.66715
H	-5.58664	1.36979	-0.80694
C	-4.81669	-2.46709	-0.69494
H	3.67383	-4.74939	-0.20644
H	-1.22149	-5.75364	-0.41568
C	-6.12386	-2.00135	-0.85023
H	4.90938	3.52422	-0.07214
H	5.90829	-1.37091	-0.07926
C	-6.40027	-0.63478	-0.88957
H	-3.36054	4.74620	-0.62076
H	1.52838	5.74877	-0.29073
C	-5.37828	0.30955	-0.77429
C	-4.08518	-0.15674	-0.61574
C	-2.79887	0.54408	-0.46959
N	-1.81148	-0.40215	-0.34053
N	-2.67743	1.84536	-0.47488
N	0.54608	-1.95660	-0.22405
N	-1.72945	-2.81267	-0.37146
N	2.10785	0.40225	-0.19013
N	2.97848	-1.84624	-0.14966
N	-0.25436	1.95390	-0.24578
N	2.02536	2.81113	-0.15925
Rh	0.14509	-0.00122	-0.14461
H	1.17819	-0.66033	2.08416
H	0.58892	1.00548	2.18341
C	-0.86474	-0.49851	2.75586
H	2.86139	-7.09513	-0.30753
H	0.45280	-7.58936	-0.41029
H	7.26283	2.70895	-0.00544
H	7.75444	0.30144	-0.00917
H	-2.53911	7.09082	-0.66026
H	-0.13364	7.58422	-0.49777
H	-6.93569	-2.71031	-0.94256
H	-7.42251	-0.30279	-1.01205
H	-1.31812	-1.38942	2.31540
H	-0.44570	-0.83723	3.71379
C	-1.93738	0.54761	3.05816
H	-1.46318	1.40840	3.53919
H	-2.37122	0.92180	2.13059
C	-3.05023	0.01188	3.95755
H	-3.56739	-0.82747	3.48776
H	-2.65256	-0.33921	4.91249
H	-3.79372	0.78133	4.17040

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