Supporting Information

Phase-Dependent Reactivity and Host–Guest Behaviors of a Metallo-Macrocycle in Liquid and Solid-State Photosensitized Oxygenation Reactions

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1. Abbreviation

COSY: correlated spectroscopy, Et₂O: diethyl ether, ESI-TOF: electrospray ionization-time-of-flight, IR: infrared, HRMS: high resolution mass spectrum, MeCN: acetonitrile, MeOH: methanol, M.p.: melting point, NIR: near infrared, NMR: nuclear magnetic resonance, pCp: [2.2]paracyclophane, PET: polyethylene terephthalate, PXRD: powder X-ray diffraction, ROESY: rotating frame Overhauser effect spectroscopy, r.t: room temperature TBABr: tetra-*n*-butylammonium bromide, TMS: tetramethylsilane, TOCSY: total correlated spectroscopy, UV-Vis: Ultraviolet-Visible, XRD: X-ray diffraction.

2. Materials and methods

All solvents, organic and inorganic reagents are commercially available and were used without further purification. Macrocyclic ligand L0, dinuclear Ag^I complex $[Ag_2L0X_2](SbF_6)_2$ (X = Et₂O and H₂O), and pCp $\subset [Ag_2L0](SbF_6)_2$ were prepared according to previously reported procedures.¹

NMR spectroscopic measurements were performed using a Bruker AVANCE 500 (500 MHz for ¹H; 126 MHz for ¹³C) spectrometer. NMR spectra were calibrated as below; tetramethylsilane (Si(CH₃)₄) = 0 ppm for ¹H in CDCl₃; CHDCl₂ = 5.30 ppm for ¹H in CD₂Cl₂, CD₂Cl₂/CDCl₃ = 20/1, and CD₂Cl₂/(CD₃)₂CO = 20/1; $CD_2Cl_2 = 53.8$ ppm for ¹³C in CD_2Cl_2 ; $CHD_2CN = 1.94$ ppm for ¹H in $CD_2Cl_2/CD_3CN = 19/1$. p-Dimethoxybenzene was added as an internal standard for the calibration of the concentration of samples. ESI-TOF mass spectra were recorded on a Micromass LCT spectrometer and a Micromass LCT Premier spectrometer. NIR emission and excitation spectroscopies were performed with a HORIBA FluoroMax Plus. UV-vis spectroscopy was performed using a HITACHI U-3500 spectrophotometer. Fluorescent spectroscopy was performed using a HITACHI F-4500 spectrometer. Melting points were measured using a Yanaco MP-500D apparatus. Single-crystal X-ray crystallographic analyses were performed using a Rigaku RAXIS-RAPID imaging plate diffractometer with MoK α radiation, and the obtained data were calculated using a CrystalStructure crystallographic software package, SHELXL-2013,² except for refinement. Molecular modeling was performed by a Spartan'08. PXRD measurement was performed using a Rigaku MiniFlex diffractometer with CuK α radiation. Photochemical reactions were performed using an incandescent lamp (Panasonic, type-60, 100 V, 54 WI) as a light source, which is placed ca. 10–20 cm away from the sample. Solution or solid materials for photoreaction were placed in test tubes or NMR tubes made by borosilicate. For reactions with a red light ($\lambda > 600$ nm), a red colored PET plate was used as a filter. For reactions with visible light ($\lambda > 400$ nm), no filter was used and the samples were cooled by a water bath.

3. Oxygenation of macrocyclic ligand L0



Bulk scale preparation of macrocyclic endoperoxide L4

L0 (14.76 mg, 10.4 µmol, 1.0 eq), methylene blue hydrate (PS1) (0.21 mg, 0.66 µmol, 0.06 eq), and CHCl₃ (2.0 mL) were placed in a test tube to provide a blue solution with a pale yellow precipitate. The inner gas was replaced by oxygen. The mixture was irradiated by an incandescent lamp through a red filter ($\lambda > 600$ nm) at room temperature for 8 h. After irradiation, the mixture was dissolved in CHCl₃ (50 mL) and passed through Al₂O₃ ($\phi = 1.5$ cm, h = 1.0 cm). The solution was once evaporated under reduced pressure, and the resulting solid was successively washed with CHCl₃ (0.5 mL × 4), MeOH (0.5 mL × 2), Et₂O (0.5 mL × 2), and *n*-hexane (0.5 mL × 5) to afford L4 (9.05 mg, 5.87 µmol, 56.4%) as a colorless solid.

¹H NMR (500 MHz, CDCl₃, 300 K): δ (ppm) = 8.54 (d, *J* = 8.5 Hz, 4H, Ar*H*), 8.06 (s, 4H, Ar*H*), 8.05 (d, *J* = 9.5 Hz, 4H, Ar*H*), 7.40 (d, 4H, 1.0 Hz, Ar*H*), 7.28 (d, *J* = 7.5 Hz, 8H, Ar*H*), 7.18 (d, *J* = 7.5 Hz, 8H, Ar*H*), 7.06–7.01 (m, 8H, Ar*H*), 6.96–6.91 (m, 10H, Ar*H*), 4.04 (t, *J* = 6.5 Hz, 4H, C*H*₂), 1.84 (m, 4H, C*H*₂), 1.58–1.46 (m, 4H, C*H*₂), 1.38–1.33 (m, 8H, C*H*₂), 0.91 (t, *J* = 6.8 Hz, 6H, C*H*₃). HRMS (ESI) mass: calcd. for [C₁₀₄H₇₆N₄O₁₀ + H]⁺: *m*/*z* = 1542.5673, found: *m*/*z* = 1542.5698. M.p.: > 300 °C (decomp.)

Due to the low solubility of L4 in general organic solvents, it was difficult to detect clear ¹³C NMR signals.



Figure S1. ¹H NMR spectra of L4 (500 MHz, CDCl₃, 300 K).



Figure S2. HRMS (ESI) mass spectrum of L4 in CHCl₃/CH₃CN = 1/5.



Figure S3. Partial spectrum of ¹H–¹H COSY of L4 (500 MHz, CDCl₃, 300 K).



Figure S4. Partial spectrum of ¹H–¹H COSY of L4 (500 MHz, CDCl₃, 300 K).



Figure S5. Partial spectrum of ¹H–¹H ROESY of L4 (500 MHz, CDCl₃, 300 K).



Figure S6. Partial spectrum of ¹H-¹H ROESY of L4 (500 MHz, CDCl₃, 300 K).



Figure S7. a) UV-Vis absorption (5 μ M, l = 1.0 cm, 293 K in CHCl₃) and b) fluorescent (5 μ M, 293 K, $\lambda_{exc} = 365$ nm in CHCl₃) spectra of **L0** (blue lines) and **L4** (red lines). c) Appearances of **L0** and **L4** under UV irradiation (r.t., $\lambda_{exc} = 365$ nm in CDCl₃).

Monitoring of the photo oxygenation of L0 in CDCl₃ by ¹H NMR spectroscopy

A solution of L0 in CDCl₃ (1000 μ L, 0.07 mM, 0.07 μ mol, 1.0 eq) was placed in an NMR tube. To the solution was added a solution of methylene blue hydrate (PS1) in CDCl₃ (ca. 5 mM, 1.0 μ L, ca. 5 nmol, ca. 0.07 eq). The inner gas was replaced by oxygen. The mixture was irradiated by an incandescent lamp through a red filter ($\lambda > 600$ nm) at room temperature. ¹H NMR spectra during the reaction were shown in Figure S8.



Figure S8. Time-course observation by ¹H NMR spectroscopy (300 K, 500 MHz in CDCl₃) using a mixture of **L0** (0.07 mM) and a catalytic amount of **PS1** under photoirradiation ($\lambda > 600$ nm) for a) 0 min, b) 25 min, c) 60 min, and d) 80 min in an oxygen atmosphere.

4. Oxygenation of dinuclear Ag^I-macrocycle, $[Ag_2L0X_2](SbF_6)_2$ (X = Et₂O or H₂O) in solution

Preparation of 3,7-bis(dimethylamino)phenothiazinium hexafluoroantimonate (PS2)

Methylene blue hydrate (**PS1**) (8.6 mg, 27 μ mol 1.0 eq as anhydrous) and MeOH solution of AgSbF₆ (340 mM, 0.2 mL, 68 μ mol, 2.5 eq) are mixed in MeOH (5.0 mL). A resulting suspension was once evaporated under reduced pressure to obtain a dark blue solid, which was suspended in Et₂O (3.0 mL) and filtrated. The residual solid was washed with Et₂O (1 mL × 2) and extracted with CH₂Cl₂ (ca. 10 mL). After slow Et₂O vapor diffusion into the resulted CH₂Cl₂ solution in dark at room temperature, dark blue needle crystals suitable for single-crystal XRD measurement were obtained. The crystals were collected by decantation, washed by Et₂O (1 mL × 3), and dried under reduced pressure to afford **PS2**·0.5CH₂Cl₂ as dark blue needle crystals (7.09 mg, 12.6 μ mol, 47%).

¹H NMR (500 MHz, CD₂Cl₂, 300 K): δ (ppm) = 8.00 (d, *J* = 10.0 Hz, 2H, Ar*H*), 7.30 (dd, *J* = 9.5, 2.5 Hz, 2H, Ar*H*), 7.07 (d, *J* = 3.0 Hz, 2H, Ar*H*), 3.37 (s, 12H, C*H*₃).

¹³C NMR (126 MHz, CD₂Cl₂, 300 K): δ (ppm) = 157.6, 154.7, 139.3, 136.4, 135.2, 118.9, 106.1, 41.7. Elemental analysis: calcd for C₂₉H₃₈Cl₂F₁₂N₆S₂Sb₂ (**PS2**·0.5CH₂Cl₂): C, 35.23; H, 3.40; N, 7.47. Found: C, 35.45; H, 3.64; N; 7.37.

Crystal data for PS2·0.5CH₂Cl₂

Crystal data for C₂₉H₃₈Cl₂F₁₂N₆S₂Sb₂: $F_w = 1125.21$, crystal dimensions $0.3 \times 0.1 \times 0.1$ mm, monoclinic, space group $P2_1/n$, a = 14.8707(7), b = 17.7171(7), c = 16.5554(7) Å, $\beta = 112.1544$ (11)°, V = 4039.8(3) Å³, Z = 4, $\rho_{calcd} = 1.850$ gcm⁻³, $\mu = 1.6611$ mm⁻¹, T = 101 K, λ (MoK α) = 0.71075 Å, $2\theta_{max} = 55.0^{\circ}$, 9239/62618 reflection collected/unique ($R_{int} = 0.0647$), $R_1 = 0.0347$ ($I > 2\sigma(I)$), $wR_2 = 0.0815$ (for all data), GOF = 1.087, largest diff. peak and hole 0.71/-1.17 eÅ⁻³. CCDC deposit number 2048657.



Figure S9. ORTEP view (50% probability level) of **PS2**·0.5CH₂Cl₂. C atoms of two crystallographically non-equivalent **PS2** are shown in different colors for clarity. (C: grey or red, Cl: pale green, F: yellow, H: white, N: pale blue, O: red, S: orange, Sb: pink)

Monitoring of the photo oxygenation of [Ag₂L0X₂](SbF₆)₂ in CD₂Cl₂/CDCl₃ by ¹H NMR spectroscopy



A solution of $[Ag_2L0X_2](SbF_6)_2$ (0.2 mM, 525 µL, 0.11 µmo1 1.0 eq) in CD₂Cl₂/CDCl₃ = 20/1 was places in an NMR tube. To the solution was added a solution of **PS2**·0.5CH₂Cl₂ (10 mM, 0.5 µL, 5 nmol, 0.05 eq) in CD₂Cl₂. The inner gas was replaced by oxygen. The mixture was irradiated by an incandescent lamp through a red filter ($\lambda > 600$ nm) at room temperature. *p*-Dimethoxybenzene (25 nmol) was added as an internal standard. ¹H NMR spectra during the reaction were shown in Figure S10.



Figure S10. Time-course observation by ¹H NMR spectroscopy (300 K, 500 MHz in CD₂Cl₂/CDCl₃ = 20/1) of the mixtures of $[Ag_2L0X_2](SbF_6)_2$ (0.2 mM) and a catalytic amount of **PS2** after photoirradiation ($\lambda > 600$ nm) under oxygen atmosphere for a) 0 min, b) 4 min, c) 10 min, d) 15 min, e) 20 min, and f) 80 min. Asterisks show signals of *p*-dimethoxybenzene used as an internal standard.

Characterization of [Ag₂L4X_n](SbF₆)₂

The mixture of $[Ag_2L0X_2](SbF_6)_2$ (0.1 mM, 500 µL, 0.05 µmol 1.0 eq) and PS2 (0.1 eq) in CD₂Cl₂ was irradiated by an incandescent lamp through a red filter ($\lambda > 600$ nm) at room temperature for 1 h under oxygen atmosphere. NMR spectra of the product shown in Figures S11–S20 were measured without further purification.



Figure S11. ¹H NMR spectra (500 MHz, CD_2Cl_2 , 300 K) of the product of photosensitized oxygenation of $[Ag_2L0X_2](SbF_6)_2$ in solution to afford $[Ag_2L4X_n](SbF_6)_2$. The procedure for the sample preparation is described on the top of page S10.



Figure S12. Partial spectrum of ${}^{1}\text{H}{-}{}^{1}\text{H}$ COSY (500 MHz, CD₂Cl₂, 300 K) of the product of photosensitized oxygenation of [Ag₂L0X₂](SbF₆)₂ in solution to afford [Ag₂L4X_n](SbF₆)₂. The procedure for the sample preparation is described on the top of page S10.



Figure S13. Partial spectrum of ${}^{1}H{-}^{1}H$ COSY (500 MHz, CD₂Cl₂, 300 K) of the product of photosensitized oxygenation of [Ag₂L0X₂](SbF₆)₂ in solution to afford [Ag₂L4X_n](SbF₆)₂. The procedure for the sample preparation is described on the top of page S10.



Figure S14. Partial spectrum of ${}^{1}H{-}^{1}H$ COSY (500 MHz, CD₂Cl₂, 300 K) of the product of photosensitized oxygenation of [Ag₂L0X₂](SbF₆)₂ in solution to afford [Ag₂L4X_n](SbF₆)₂. The procedure for the sample preparation is described on the top of page S10.



Figure S15. Partial spectrum of ${}^{1}H{-}^{1}H$ ROESY (500 MHz, CD₂Cl₂, 300 K) of the product of photosensitized oxygenation of [Ag₂L0X₂](SbF₆)₂ in solution to afford [Ag₂L4X_n](SbF₆)₂. The procedure for the sample preparation is described on the top of page S10.



Figure S16. Partial spectrum of ${}^{1}H-{}^{1}H$ ROESY (500 MHz, CD₂Cl₂, 300 K) of the product of photosensitized oxygenation of [Ag₂L0X₂](SbF₆)₂ in solution to afford [Ag₂L4X_n](SbF₆)₂. The procedure for the sample preparation is described on the top of page S10.



Figure S17. Partial spectrum of ${}^{1}H-{}^{1}H$ ROESY (500 MHz, CD₂Cl₂, 300 K) of the product of photosensitized oxygenation of [Ag₂L0X₂](SbF₆)₂ in solution to afford [Ag₂L4X_n](SbF₆)₂. The procedure for the sample preparation is described on the top of page S10.



Figure S18. Partial spectrum of ${}^{1}H{-}^{1}H$ TOCSY (500 MHz, CD₂Cl₂, 300 K) of the product of photosensitized oxygenation of [Ag₂L0X₂](SbF₆)₂ in solution to afford [Ag₂L4X_n](SbF₆)₂. The procedure for the sample preparation is described on the top of page S10.



Figure S19. Partial spectrum of ${}^{1}H{-}^{1}H$ TOCSY (500 MHz, CD₂Cl₂, 300 K) of the product of photosensitized oxygenation of [Ag₂L0X₂](SbF₆)₂ in solution to afford [Ag₂L4X_n](SbF₆)₂. The procedure for the sample preparation is described on the top of page S10.



Figure S20. Partial spectrum of ${}^{1}H-{}^{1}H$ TOCSY (500 MHz, CD₂Cl₂, 300 K) of the product of photosensitized oxygenation of [Ag₂L0X₂](SbF₆)₂ in solution to afford [Ag₂L4X_n](SbF₆)₂. The procedure for the sample preparation is described on the top of page S10.



Figure S21. ESI-TOF mass spectrum of the product of photosensitized oxygenation of $[Ag_2L0X_2](SbF_6)_2$ in solution to afford $[Ag_2L4X_n](SbF_6)_2$. The mixture of $[Ag_2L0X_2](SbF_6)_2$ (0.08 mM, 450 µL, 0.04 µmol, 1.0 eq) and **PS2** (0.2 eq) in CDCl₃ was irradiated by an incandescent lamp through a red filter ($\lambda > 600$ nm) at room temperature for 1 h under oxygen atmosphere. ESI-TOF mass spectrum was measured without further purification.

Complexation of L4 and AgSbF₆ in CD₂Cl₂/(CD₃)₂CO

A solution of L4 (0.15 mM, 450 μ L, 0.07 μ mo1, 1.0 eq) in CDCl₃ was placed in an NMR tube, which was evaporated under reduced pressure to obtain a colorless solid. The residue was dissolved in CD₂Cl₂ (450 μ L). To the mixture was added a solution of AgSbF₆ (100 mM) in (CD₃)₂CO to afford a colorless solution. *p*-Dimethoxybenzene (25 nmol) was added as an internal standard. ¹H NMR spectra during the reaction were shown in Figure S22.



Figure S22. Partial ¹H NMR spectra (500 MHz, $CD_2Cl_2/(CD_3)_2CO = 340/0-1$, 300 K) of L4 (0.15 mM, 450 µL, 0.07 µmol, 1.0 eq) in the presence of a) 0 eq, b) 2 eq, and c) 4 eq of AgSbF₆. d) Partial ¹H NMR spectra (500 MHz, CD_2Cl_2 , 300 K) of $[Ag_2L4X_n](SbF_6)_2$ shown on Figure S11.

Figures S22c and S22d show identical ¹H NMR signal patterns. These results suggest that a product obtained by photo oxygenation of $[Ag_2L0X_2](SbF_6)_2$ (Figure S22d) is $[Ag_2L4X_n](SbF_6)_2$, which can also be prepared by complexation between AgSbF₆ and L4 (Figure S22c).

Reaction between [Ag₂L4X₂](SbF₆)₂ and tetra-*n*-butylammonium bromide

First, a solution of $[Ag_2L4X_n](SbF_6)_2$ in CD₂Cl₂/CDCl₃ = 20/1 was prepared by photo irradiation of a solution of $[Ag_2L0X_2](SbF_6)_2$ (0.2 mM, 525 µL, 0.11 µmol 1.0 eq) and PS2·0.5CH₂Cl₂ (0.05 eq) in CD₂Cl₂/CDCl₃ = 20/1 by an incandescent lamp through a red filter ($\lambda_{exc} > 600$ nm) under oxygen atmosphere at room temperature for 80 min (Figure S23a). Then, to the resulting solution was added a solution of tetra-*n*-butylammonium bromide (TBABr) (100 mM, 4 µL, 0.4 µmol, 4 eq) in CDCl₃. *p*-Dimethoxybenzene (25 nmol) was added as an internal standard. ¹H NMR spectra during the reaction were shown on Figure S23.



Figure S23. Partial ¹H NMR spectra (500 MHz, $CD_2Cl_2/CDCl_3 = 20/1$, 300 K) of a) $[Ag_2L4X_n](SbF_6)_2$ in the presence of a) 0 eq and b) 4 eq of TBABr. c) Partial ¹H NMR spectrum (500 MHz, CDCl_3, 300 K) of the same sample of Figure S23b measured in CDCl₃ (the sample of Figure S23b was once evaporated under reduced pressure, and the resulting residue was dissolved in CDCl₃ (450 µL)).

On the ¹H NMR spectrum in Figure S23c, only one set of signals assignable to L4 was observed. This result suggests that a product obtained by photo oxygenation of $[Ag_2L0X_2](SbF_6)_2$ (Figures S23a) is $[Ag_2L4X_n](SbF_6)_2$, which provides L4 upon removal of Ag¹ by reacting with TBABr.

Complexation of L4 and AgSbF₆ in CD₃CN/CD₂Cl₂ = 19/1

A solution of L4 (0.13 mM, 475 μ L, 0.06 μ mol, 1.0 eq) in CDCl₃ was placed in an NMR tube, which was evaporated under reduced pressure to obtain a colorless solid. The residue was suspended in CD₃CN/CD₂Cl₂ = 19/1 (500 μ L). To the mixture was added a solution of AgSbF₆ (0.1 M, 2.5 μ L, 0.25 μ mol 4.0 eq) in CD₃CN to obtain a clear colorless solution. *p*-Dimethoxybenzene (25 nmol) was added as an internal standard. ¹H NMR spectra of the resulting mixture were shown in Figures S24–S28.



Figure S24. ¹H NMR spectra (500 MHz, CD₃CN/CD₂Cl₂ = 19/1, 300 K) of the mixture of L4 (0.12 mM, 500 μ L, 0.06 μ mol, 1.0 eq) and AgSbF₆ (4.0 eq). Asterisks indicate peaks of *p*-dimethoxybenzene.



Figure S25. Partial spectrum of ${}^{1}\text{H}{-}^{1}\text{H}$ COSY (500 MHz, CD₃CN/CD₂Cl₂ = 19/1, 300 K) of the mixture of L4 (0.12 mM, 500 μ L, 0.06 μ mol, 1.0 eq) and AgSbF₆ (4.0 eq). Asterisks indicate peaks of *p*-dimethoxybenzene.



Figure S26. Partial spectrum of ${}^{1}\text{H}{-}^{1}\text{H}$ COSY (500 MHz, CD₃CN/CD₂Cl₂ = 19/1, 300 K) of the mixture of L4 (0.12 mM, 500 µL, 0.06 µmol, 1.0 eq) and AgSbF₆ (4.0 eq). Asterisks indicate peaks of *p*-dimethoxybenzene.



Figure S27. Partial spectrum of ${}^{1}\text{H}-{}^{1}\text{H}$ ROESY (500 MHz, CD₃CN/CD₂Cl₂ = 19/1, 300 K) of the mixture of L4 (0.12 mM, 500 µL, 0.06 µmol, 1.0 eq) and AgSbF₆ (4.0 eq). Asterisks indicate peaks of *p*-dimethoxybenzene.



Figure S28. Partial spectrum of ${}^{1}\text{H}-{}^{1}\text{H}$ ROESY (500 MHz, CD₃CN/CD₂Cl₂ = 19/1, 300 K) of the mixture of L4 (0.12 mM, 500 µL, 0.06 µmol, 1.0 eq) and AgSbF₆ (4.0 eq). Asterisks indicate peaks of *p*-dimethoxybenzene.



Figure S29. Summary of ¹H–¹H ROESY of $[Ag_2L4X_n](SbF_6)_2$ measured in a) CD₂Cl₂ (Figures S15–17) and b) CD₂Cl₂/CD₃CN (Figures S27–28). ¹H NMR signal pattern on Figure S11 and ROE correlations (g-i, c'-d', and g'-h') shown on Figure S29a suggest $[Ag_2L4X_n](SbF_6)_2$ forms a C_{2h} -symmetrical *alternate* conformer in CD₂Cl₂. Whereas, ¹H NMR signal pattern on Figure S24 and an ROE correlation (g-i) shown on Figure S29b suggest $[Ag_2L4X_n](SbF_6)_2$ forms a D_{2h} -symmetrical *all out* conformer in CD₂Cl₂/CD₃CN.

5. Oxygenation of pCp inclusion complex pCp \subset [Ag₂L0](SbF₆)₂ in solution



Monitoring of the photo oxygenation of pCp \subset [Ag₂L0](SbF₆)₂ by ¹H NMR spectroscopy

A solution of pCp \subset [Ag₂L0](SbF₆)₂ (0.3 mM, 525 µL, 0.16 µmol, 1.0 eq) in CD₂Cl₂/CDCl₃ = 20/1 was places in an NMR tube. To the solution was added a solution of **PS2**·0.5CH₂Cl₂ (10 mM, 0.8 µL, 8 nmol, 0.05 eq) in CD₂Cl₂. The inner gas was replaced by oxygen. The mixture was irradiated by an incandescent lamp through a red filter ($\lambda > 600$ nm) at room temperature. *p*-Dimethoxybenzene (25 nmol) was added as an internal standard. ¹H NMR spectra during the reaction were shown in Figures S30–31.



Figure S30. Time-course analysis by ¹H NMR spectroscopy (300 K, 500 MHz in CD₂Cl₂/CDCl₃ = 20/1) using a mixtures of pCp \subset [Ag₂L0](SbF₆)₂ (0.3 mM) and a catalytic amount of **PS2** after photoirradiation ($\lambda > 600$ nm) under oxygen atmosphere for a) 0 min, b) 10 min, c) 15 min, d) 20 min, e) 40 min, f) 45 min, and g) 140 min. Asterisks indicate peaks of *p*-dimethoxybenzene. A_{in} and B_{in} indicate peaks of included pCp within [Ag₂L0]²⁺. A_{out} and B_{out} indicate peaks of free pCp.



Figure S31. Time-course analysis by ¹H NMR spectroscopy (300 K, 500 MHz in CD₂Cl₂/CDCl₃ = 20/1) using a mixtures of pCp \subset [Ag₂L0](SbF₆)₂ (0.3 mM) and a catalytic amount of **PS2** after photoirradiation ($\lambda > 600$ nm) under oxygen atmosphere for a) 0 min, b) 10 min, c) 15 min, d) 20 min, e) 40 min, f) 45 min, and g) 140 min. Asterisks indicate peaks of *p*-dimethoxybenzene. A_{out} and B_{out} indicate peaks of free pCp.

6. Oxygenation of pCp inclusion complex pCp \subset [Ag₂L0](SbF₆)₂ in the solid states

Representative procedure for the preparation of the single crystals (SC) and amorphous solid (AS) of $pCp \subset [Ag_2L0](SbF_6)_2$

To a suspension of **L0** (2.00 mg, 1.41 µmol, 1.0 eq) in CHCl₃ (4.0 mL) was added a solution of AgSbF₆ in acetone (80 mM, 80 µL, 6.4 µmol, 4.5 eq) and a solution of pCp in CHCl₃ (40 mM, 37 µL, 0.5 µmol, 1.0 eq) to form clear yellow solution, which was concentrated to ca. 1.5 mL by evaporation under reduced pressure. To the solution was added Et₂O (ca. 6 mL) to form a pale yellow solid as precipitate. The resulting solid was collected by centrifugation and washed by Et₂O (ca. 0.8 mL × 3), and then dissolved again in CHCl₃ (2.0 mL). To the resulting solution was added a solution of AgSbF₆ in Et₂O (40 mM, 5.0 µL, 0.2 µmol, 0.1 eq). Then, 500 µL of the resulting solution was placed in a test tube. To the solution was added CHCl₃ (150 µL) and Et₂O (500 µL). Pale yellow single crystals of pCp⊂[Ag₂L0](SbF₆)₂·3CHCl₃·3.5C₄H₁₀O (**SC**) suitable for single-crystal XDR measurements were obtained after leaving the mixture in dark around 15 °C for a day (Figures S32–35). To isolate amorphous solid (**AS**), the crystals were collected by decantation, and then washed by Et₂O (ca. 0.5 mL × 3). After being kept in dark for a day, **AS** was obtained as a pale yellow solid (0.57 mg, 0.25 µmol, 71%). Powder X-ray diffraction pattern and a solution phase ¹H NMR spectrum of **AS** are shown in Figure S36 and Figure S37, respectively.



Single crystal structure of pCp⊂ [Ag₂L0](SbF₆)₂·3CHCl₃·3.5C₄H₁₀O (SC)

Figure S32. ORTEP view (50% probability level) of $pCp \subset [Ag_2L0](SbF_6)_2 \cdot 3CHCl_3 \cdot 3.5C_4H_{10}O$ (SC). C atoms of two crystallographically non-equivalent complexes are shown in different colors. Hydrogen atoms are omitted for clarity. (Ag: magenta, C of solvent: grey, C of macrocycle: orange or blue, C of pCp: green, Cl: pale green, F: yellow, N: pale blue, O: red, Sb: pink)



Figure S33. ORTEP view (50% probability level) of the partial structures of $pCp \subset [Ag_2L0](SbF_6)_2 \cdot 3CHCl_3 \cdot 3.5C_4H_{10}O$ (SC). (Ag: magenta, C of macrocycle: orange or blue, C of pCp: green, H: white, N: pale blue, O: red, Sb: pink)



Figure S34. Crystal packing of $pCp \subset [Ag_2L0](SbF_6)_2 \cdot 3CHCl_3 \cdot 3.5C_4H_{10}O(SC)$. A space-fill view without showing a) solvents and b) without showing $pCp \subset [Ag_2L0](SbF_6)_2$, respectively. Hydrogen atoms are omitted for clarity. (Ag: magenta, C of solvent: grey, C of macrocycle: orange or blue, C of pCp: green, Cl: pale green, F: yellow, N: pale blue, O: red, Sb: pink)



Figure S35. a) A crystal packing arrangement of the host-guest complex $pCp \subset [Ag_2L0](SbF_6)_2 \cdot 3CHCl_3 \cdot 3.5C_4H_{10}O(SC)$. Three-dimensional void spaces excluding crystalline solvents are described in a yellowish-green texture. Hydrogen atoms and crystalline solvents (CHCl₃ and Et₂O) are omitted for clarity. (Ag: magenta, C of solvent: grey, C of macrocycle: orange or blue, C of pCp: green, Cl: pale green, F: yellow, N: pale blue, O: red, Sb: pink) b) Three-dimensional void spaces of SC excluding crystalline solvents without showing $pCp \subset [Ag_2L0](SbF_6)_2$.

Crystal data for pCp⊂[Ag₂L0](SbF₆)₂·3CHCl₃·3.5C₄H₁₀O

Crystal data for C₂₇₄H₂₆₀Ag₄Cl₁₈F₂₄N₈O₁₁Sb₄: $F_w = 5853.70$, crystal dimensions $0.4 \times 0.2 \times 0.2$ mm, triclinic, space group *P*-1, *a* = 12.8173(6), *b* = 22.4169(10), *c* = 22.9960(11) Å, $\alpha = 91.0025(14)$, $\beta = 90.3926(13)$, $\gamma = 106.5012(14)^\circ$, V = 6333.7(5) Å³, Z = 1, $\rho_{calcd} = 1.535$ gcm⁻³, $\mu = 0.9895$ mm⁻¹, T = 93 K, λ (MoK α) = 0.71075 Å, $2\theta_{max} = 55.0^\circ$, 55623/27796 reflection collected/unique ($R_{int} = 0.0442$), $R_1 = 0.0650$ ($I > 2\sigma(I)$), $wR_2 = 0.2018$ (for all data), GOF = 1.047, largest diff. peak and hole 2.58/-2.08 eÅ⁻³. The data was refined based on a single domain of the twinning crystals. CCDC deposit number 2048656.



Figure S36. Powder X-ray diffraction pattern of pCp \subset [Ag₂L0](SbF₆)₂ (λ (CuK α) = 1.5418 Å). a) An experimental diffraction pattern of **AS** measured at r.t. and b) a simulated diffraction pattern of **SC** calculated based on the single crystal structure of pCp \subset [Ag₂L0](SbF₆)₂·3CHCl₃·3.5C₄H₁₀O measured at 93 K (Figure S32–35).



Figure S37. ¹H NMR spectra (500 MHz, 300 K in CD₂Cl₂) of AS.

Characterization of pCp⊂[Ag₂L1](SbF₆)₂



The solid sample of **AS** (0.37 mg) prepared by the procedure described on page S23 was placed in an NMR tube. After replacement of the inner gas by oxygen, the solid sample was irradiated by an incandescent lamp without filter ($\lambda > 400$ nm) at room temperature for 36 h. The ¹H NMR spectra of the resulting product shown in Figures S38–S44, S47, and S48 are measured without further purification. Alphabets and numbering denote signals assignable to pCpC[Ag2L1](SbF6)₂.



Figure S38. ¹H NMR spectra (500 MHz, CD₂Cl₂, 300 K) of the product of the photosensitized oxygenation of **AS** in the solid state to afford $pCp \subset [Ag_2L1](SbF_6)_2$. The procedure for the sample preparation is described on the top of page S26.



Figure S39. Partial spectrum of ¹H–¹H COSY (500 MHz, CD₂Cl₂, 300 K) of the product of the photosensitized oxygenation of **AS** in the solid state to afford pCp \subset [Ag₂L1](SbF₆)₂. The procedure for the sample preparation is described on the top of page S26.



Figure S40. Partial spectrum of ¹H–¹H COSY (500 MHz, CD₂Cl₂, 300 K) of the product of the photosensitized oxygenation of **AS** in the solid state to afford $pCp \subset [Ag_2L1](SbF_6)_2$. The procedure for the sample preparation is described on the top of page S26.



Figure S41. Partial spectrum of ${}^{1}\text{H}{-}{}^{1}\text{H}$ TOCSY (500 MHz, CD₂Cl₂, 300 K) of the product of the photosensitized oxygenation of **AS** in the solid state to afford pCp \subset [Ag₂L1](SbF₆)₂. The procedure for the sample preparation is described on the top of page S26.



Figure S42. Partial spectrum of ${}^{1}\text{H}{-}{}^{1}\text{H}$ TOCSY (500 MHz, CD₂Cl₂, 300 K) of the product of the photosensitized oxygenation of **AS** in the solid state to afford pCp \subset [Ag₂L1](SbF₆)₂. The procedure for the sample preparation is described on the top of page S26.



Figure S43. Partial spectra of ¹H–¹H ROESY (500 MHz, CD₂Cl₂, 300 K) of the product of the photosensitized oxygenation of **AS** in the solid state to afford $pCp \subset [Ag_2L1](SbF_6)_2$. The procedure for the sample preparation is described on the top of page S26.



Figure S44. Partial spectrum of ¹H–¹H ROESY (500 MHz, CD₂Cl₂, 300 K) of the product of the photosensitized oxygenation of **AS** in the solid state to afford pCp \subset [Ag₂L1](SbF₆)₂. The procedure for the sample preparation is described on the top of page S26.



Figure S45. Summary of 2D NMR spectra of pCp \subset [Ag₂L1](SbF₆)₂ (500 MHz, CD₂Cl₂, 300 K) shown in Figures S39– 44. Correlations d2-e2-f2-g2 (TOCSY), g2-i2 (ROESY), h2-h3-i2 (TOCSY), h2-j2 (ROESY), h3-j2 (ROESY), h1-j1 (ROESY), h1-h2-i1 (TOCSY) shown in Figure S45 determined the assignments of some of the signals shown in Figure S37 and provide information about the conformation of EPO part of pCp \subset [Ag₂L1](SbF₆)₂, in which peroxide oxygen atoms locate on the outer surface of the macrocyclic skeleton.



Figure S46. ESI-TOF mass spectrum (in CH_2Cl_2) of the product of the photosensitized oxygenation of **AS** in the solid state to afford pCp \subset [Ag₂L1](SbF₆)₂. The procedure for the sample preparation is described on the top of page S26.



Figure S47. ¹H NMR spectra (500 MHz, CD₂Cl₂, 300 K) of the product of the photosensitized oxygenation of **AS** in the solid state in different irradiation times to afford pCp \subset [Ag₂L1](SbF₆)₂. The procedure for the sample preparation is described on the top of page S26. Irradiation time: a) 22 h, b) 41 h.



Figure S48. a) ¹H NMR spectrum (500 MHz, CD₂Cl₂, 300 K) of pCp \subset [Ag₂L0](SbF₆)₂ and ¹H NMR spectra (500 MHz, CD₂Cl₂) of the product of the photosensitized oxygenation of **AS** in the solid state to afford pCp \subset [Ag₂L1](SbF₆)₂ measured at b) 300 K and c) 220 K, respectively. The procedure for the sample preparation is described on the top of page S26.

Photo-oxygenation of solid sample of pCp⊂ [Ag₂L0](SbF₆)₂ prepared from rapid reprecipitation

A powder sample of pCp \subset [Ag₂L0](SbF₆)₂ (0.13 mg, 0.06 µmol) was placed in an NMR tube, which was dissolved with CD₂Cl₂ (450 µL) to obtain a clear yellow solution. After condensation of the solution into ca. 100 µL by evaporation under reduced pressure, to the solution was added *n*-hexane (400 µL) to immediately afford pale yellow precipitate. Then, the solvent was completely removed by evaporation under reduced pressure. After replacement of the inner gas of the NMR tube with oxygen, the resulting solid sample was irradiated by an incandescent lamp without filter ($\lambda > 400$ nm) for 2 days at room temperature. ¹H NMR spectrum of the resulting solid is shown in Figure S49a.

Photo-oxygenation of solid sample of [Ag₂L0X₂](SbF₆)₂

A powder sample of $[Ag_2L0X_2](SbF_6)_2$ (0.36 mg, 0.06 µmol, 0.17 µmol) was placed in an NMR tube. After replacement of the inner gas with oxygen, the solid sample was irradiated by an incandescent lamp without filter ($\lambda > 400$ nm) at room temperature for 22 h. The ¹H NMR spectra of the resulting product are shown in Figure S49b.



Figure S49. ¹H NMR spectra (500 MHz, CD₂Cl₂, 300 K) of the product of the photo oxygenation reaction of the solid sample of a) $pCp \subset [Ag_2L0](SbF_6)_2$ prepared by fast reprecipitation and b) that of the solid sample of $[Ag_2L0X_2](SbF_6)_2$.



Figure S50. Modeling structures of a) $pCp \subset [Ag_2L1]^{2+}$ and b) $pCp \subset [Ag_2L4]^{2+}$.

7. Photochemical properties of macrocycles

NIR emission and excitation spectra of L0 and [Ag₂L0X₂](SbF₆)₂

Solutions of L0 or $[Ag_2L0X_2](SbF_6)_2$ in CHCl₃ (5 μ M, 3.0 mL) were placed in a fluorescent cell. After bubbled with oxygen for a few min, the samples were sealed by plastic caps. Then, the emission and excitation spectra of each solution were measured at room temperature.



Figure S51. NIR emission spectra of a) **L0** and c) $[Ag_2L0X_2](SbF_6)_2$ (5 μ M, r.t., $\lambda_{exc} = 392$ nm in CHCl₃) and excitation spectra of b) **L0** and d) $[Ag_2L0X_2](SbF_6)_2$ (5 μ M, r.t., $\lambda_{obs} = 1275$ nm in CHCl₃) observed under oxygen atmosphere, respectively. On Figure S51a,c sharp peaks characteristic to the phosphorescent of ¹O₂ were observed around 1275 nm (marked by red arrows), the excitation spectrum of which have maximal around 400 nm (Figure S51b,d). These results suggest both **L0** and $[Ag_2L0X_2](SbF_6)_2$ can work as photosensitizers to produce ¹O₂ upon irradiation around 400 nm.³ Broad bands around 800–1200 nm observed in figure S49a and c probably are derived from secondary scattering of the emission of macrocycles around 400–600 nm (Figure S7).

Photosensitized oxygenation of macrocycles in the absence of photosensitizer

· Oxygenation of L0

A solution of L0 (525 μ L, 0.1 mM, 0.05 μ mol) in CDCl₃ in an NMR tube was irradiated by an incandescent lamp without filter ($\lambda > 400$ nm) at room temperature under O₂ atmosphere.



Figure S52. ¹H NMR spectra (500 MHz, CDCl₃, 300 K) of the reaction mixture of the photo oxygenation reaction of **L0** to afford **L4** measured after photoirradiation for a) 0 min, b) 10 min, c) 50 min. Asterisks indicate peaks of p-dimethoxybenzene.

· Oxygenation of [Ag₂L0X₂](SbF₆)₂

A solution of $[Ag_2L0X_2](SbF_6)_2$ in CD_2Cl_2 in an NMR tube was irradiated by an incandescent lamp without filter ($\lambda > 400$ nm) at room temperature under O₂ atmosphere.



Figure S53. ¹H NMR spectra (500 MHz, CD₂Cl₂, 300 K) of the reaction mixture of the photo oxygenation reaction of [Ag₂L0X₂](SbF₆)₂ to afford [Ag₂L4X₂](SbF₆)₂ measured after photoirradiation for a) 0 min, b) 10 min, c) 60 min.

According to the results shown in Figures S52 and S53, oxygenation reactions of L0 and $[Ag_2L0X_2](SbF_6)_2$ proceeded in the absence of photosensitizer upon irradiation by an incandescent lamp without filter ($\lambda > 400$ nm). These results suggest L0 and $[Ag_2L0X_2](SbF_6)_2$ themselves can work as photosensitizers to activate the oxygenation reaction of anthracene parts in this condition.

8. References

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