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Supplementary Information for

Electronic Perturbation of Supramolecular Conjugates of Porphyrins and Phthalocyanines

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General Methods.

All reagents and solvents were purchased at the highest commercial quality available and used without further purification, unless otherwise stated. The four-fold rotaxane 1^{4+.4}Cl⁻ was prepared according to the literature procedures.¹ Elemental analysis were performed on a Yanaco MT-6 analyzer. ESI mass spectrometry was performed with a Waters LCT-Premier XE Spectrometer controlled using Masslynx software.

The absorption spectra were recorded with a Hitachi U-4100 spectrophotometer in CH_2Cl_2 solutions at 20 ± 0.1 °C in 1.0 cm quartz cells. Cyclic voltammetry measurements were performed with a BAS Electrochemical Analyzer Model 750Ds at room temperature in CH_2Cl_2 solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF₆) in a standard one-component cell under an N₂ atmosphere equipped with a 3 mm-O.D. glassy carbon disk working electrode, platinum wire counter electrode as Ag/AgCl reference electrode. All solutions were deoxygenated by N₂ bubbling for at least 10 min. Obtained E^{0° vs. Ag/AgCl were converted to those vs. Fc/Fc⁺ based on measured redox potential of

Synthesis.

Synthesis of 1⁴⁺·[Au(III)**TPPS**]³⁻·Cl⁻.

To the solution of $1^{4+.4}Cl^-$ (18.3 mg, 4.20 µmol) in CH₂Cl₂ (5.0 mL) was added the $3({}^{n}Bu_{4}N)^{+}\cdot[Au(III)TPPS]^{3-}$ (8.00 mg, 4.24 µmol) and stirred. The resulting solution was evapolated, dissolved in CHCl₃:MeOH = 1:1, and then filtered through fine cellulose powder. After the filtrate was concentrated, repricipitation from CHCl₃ : MeOH = 4:1 / Et₂O (vapor diffusion) at room temperature yielded a brown solid. Then repricipitation from CHCl₃ : MeOH = 4:1 / Et₂O (vapor diffusion) at -15 °C yielded the title compound as a yellow brown solid (19.9 mg, 3.70 µmol, 88%). MS (ESI-TOF) *m/z* : calcd for 1896.9: C₂₆₄H₃₀₀N₂₄O₆₀P₄S₄Cu₂AuNa₂ ([$1^{4+}\cdot$ [Au(III)TPPS]³⁻·Cl⁻ + 2Na⁺ -Cl⁻]³⁺), found: 1896.8.

Synthesis of $1^{4+} \cdot [Au(III)TPPS]^{3-} \cdot PF_6^{-}$.

To the solution of 1^{4+} [Au(III)**TPPS**]³⁻·Cl⁻ (19.9 mg, 3.70 µmol) and KPF₆ (68.0 mg, 370 µmol) in MeOH (14 mL) was added H₂O (30 mL). The resulting precipitate was collected by centrifugation and then redissolved in MeOH (2 mL). This repricipitation procedure was repeated twice to afford yellowish brown solid (16.8 mg, 3.14 µmol), which was further purified by repricipitation from CHCl₃ : MeOH = 4 : 1 / Et₂O (vapor diffusion) at room temperature (16.2 mg, 3.03 µmol, 82%). MS (ESI-TOF) *m/z* : calcd for 1896.9: C₂₆₄H₃₀₀N₂₄O₆₀P₄S₄Cu₂AuNa₂ ([1⁴⁺·[Au(III)**TPPS**]³⁻·PF₆⁻ + 2Na⁺ -PF₆⁻]³⁺), found: 1896.8. Anal. Calcd for C₂₇₀H₃₁₂AuCl₆Cu₂F₆N₂₄O₆₁P₅S₄ (1⁴⁺·[Au(III)**TPPS**]³⁻·PF₆⁻ + 2PF₆⁻ + 2CHCl₃ + Et₂O): C, 55.88; H, 5.42; N, 5.79. Found: C, 55.57; H, 5.72; N, 5.89 (0.31% error).

Synthesis of $1^{4+} \cdot [Pd(II)TPPS]^{4-}$.

To the solution of $1^{4+} 4Cl^-$ (17.9 mg, 4.10 µmol) in CH₂Cl₂ (7.0 mL) was added the solution of $4(^{n}Bu_{4}N)^{+} [Pd(II)TPPS]^{4-}$ (8.44 mg, 4.10 µmol) in CH₂Cl₂(3.0 mL) and stirred. The resulting solution was evapolated, dissolved in CHCl₃ : MeOH = 1:1, and then filtered through fine cellulose powder.

The filtrate was subjected to recycling GPC-HPLC (eluent: CHCl₃) to obtain a redish brown solid. Finally, repricipitation from CHCl₃: MeOH = 4:1 / Et₂O yielded the title compound as a redish brown solid (10.7 mg, 2.04 µmol, 50%). MS (ESI-TOF) *m/z* : calcd for 1774.5: $C_{264}H_{300}N_{24}O_{60}P_4S_4Cu_2PdNa_3$ ([1⁴⁺·[Pd(II)**TPPS**]⁴⁻ + 3Na]³⁺), found: 1774.5. Anal. Calcd for $C_{275}H_{327}Cl_9Cu_2N_{24}O_{64}P_4PdS$, ($C_{264}H_{300}N_{24}O_{60}P_4S_4Cu_2Pd$ + 3CHCl₃ + 2Et₂O + 2H₂O): C, 56.87; H, 5.58; N, 5.87. Found: C, 56.53; H, 5.64; N, 5.97 (0.35% error).



Figure S1. ESI-TOF mass spectra of (a) $1^{4+} [Au(III)TPPS]^{3-} Cl^{-}$ (M for $[1^{4+} [Au(III)TPPS]^{3-} + 2Na^{+}]^{3+} = C_{264}H_{300}N_{24}O_{60}P_4S_4Cu_2AuNa_2$), and (b) $1^{4+} [Pd(II)TPPS]^{4-}$ (M for $[1^{4+} [Pd(II)TPPS]^{4-} + 3Na^{+}]^{3+} = C_{264}H_{300}N_{24}O_{60}P_4S_4Cu_2PdNa_3$). The inset is the comparisons of the calculated and the observed isotopic distribution patterns. The peaks labeled as black circle are the signals correspond to the dimer of each ionic complexes; (a) (M for $[2 \cdot (1^{4+} \cdot [Pd(II)TPPS]^{3-}) + 3Na^{+}]^{5+} = C_{528}H_{600}N_{48}O_{120}P_8S_8Na_3Au_2Cu_4$), (b) (M for $[2 \cdot (1^{4+} \cdot [Pd(II)TPPS]^{4-}) + 5Na^{+}]^{5+} = C_{528}H_{600}N_{48}O_{120}P_8S_8Na_5Pd_2Cu_4$).

Synchrotron single crystal X-ray diffraction study of 1⁴⁺.[Au(III)TPPS]³⁻.Cl⁻

The synchrotron X-ray diffraction study for cage $1^{4+} [Au(III)TPPS]^{3-} Cl^-$ was carried out at the BL02B1 beam-line in SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) with a diffractometer equipped with a Rigaku Mercury2CCD detector. A data set was obtained by merging two data sets measured with 1.0 degrees oscillation ($\omega = 0 - 180^\circ$) for 1.0 and 8.0 seconds radiation with 60.5 mm detector distance, $\phi = 0$ and 180°, and $\chi = 45^\circ$, and $2\theta = -25^\circ$. The collected diffraction data were processed with the *WinGX* software program. The structure was solved by charge flipping method and refined by full-matrix least-squares on F^2 using the SHELXT program suite. The crystals were diffracting very weakly due to flipping of flexible crown ether moieties, phosphoramidate stoppers. Geometrical restraints, i.e. DFIX, SADI, FLAT, DELU, and ISOR on rotaxane ligand as well as porphyrin and phthalocyanine units, were used in the refinements.

Table S1. Crystal data and structure refinement for cage 1⁴⁺·[Au(III)**TPPS**]³⁻·Cl⁻ (CCDC deposit number: 1520369).

| Identification code | 1520369 |
|---------------------------------|-------------------------------------------------|
| Empirical formula | C273.90 H317.40 Au Cl29.20 Cu2 N24 O63.50 P4 S4 |
| Formula weight | 6573.01 |
| Temperature | 298 К |
| Wavelength | 0.69990 Å |
| Crystal system | monoclinic |
| Space group | <i>P</i> 21/n |
| Unit cell dimensions | a = 36.595(7) Å |
| | b = 37.093(7) Å |
| | c = 52.527(11) Å |
| Volume | 68108(25) Å ³ |
| Ζ | 8 |
| Density (calculated) | 1.282 g/m ³ |
| F(000) | 27154 |
| Crystal size | 0.15 x 0.15 x 0.05 mm ³ |
| Theta range for data collection | 0.672 to 15.616° |

| Index ranges | -28<=h<=28, -28<=k<=27, -40<=l<=40 |
|-----------------------------------------|------------------------------------|
| Reflections collected | 249699 |
| Independent reflections | 32424 [R(int) = 0.1247] |
| Completeness to theta = 15.62° | 99.9 % |
| Absorption correction | Semi-empirical from equivalents |
| Refinement method | Full-matrix least-square on F^2 |
| Data / restraints / parameters | 32424 / 8290/ 18130 |
| Goodness-of-fit on F ² | 1.834 |
| Final R indices [I>2sigma(I)] | R1 = 0.1068, wR2 = 0.2600 |
| R indices (all data) | R1 = 0.1493, $wR2 = 0.2780$ |
| Largest diff. peak and hole | 0.498 and -0.363 e.Å ⁻³ |



Figure S2. Crystal structure of $1^{4+} \cdot [Au(III)TPPS]^{3-} \cdot Cl^{-}$ in a unit cell. The rotaxane porphyrin, rotaxane phthalocyanine, and TPPS are shown in pink, orange, and green, respectively. Solvent molecules and hydrogen atoms have been omitted for clarity.



Figure S3. UV-Vis spectrum of $1^{4+} [Cu(II)TPPS]^{4-}$ (black line), $1^{4+} [Au(III)TPPS]^{3-} Cl^{-}$ (red line), amd $1^{4+} [Pd(II)TPPS]^{4-}$ (blue line). Each compounds were dissolved in CH_2Cl_2 at a concentration of 2.0×10^{-6} M at 20 °C.



Figure S4. A cyclic voltammogram (CV) of $1^{4+} [Cu(II)TPPS]^{4-}$ (bottom) alongside of CVs of each components, $4({}^{n}Bu_{4}N)^{+} [Cu(II)TPPS]^{4-}$, Cu(II)Pc, and Cu(II)Por at a scan rate of 0.1 Vs⁻¹ at 20 °C ([Substrate] = 400 μ M in CH₂Cl₂ containing 0.1 M TBAPF₆)



Figure S5. A cyclic voltammogram (CV, scan rate : 0.1 Vs⁻¹) and a differential pulse voltlammogram (DPV, scan rate : 0.01 Vs⁻¹) of (a) $1^{4+} \cdot [Cu(II)TPPS]^{4-}$ and (b) $1^{4+} \cdot [Pd(II)TPPS]^{4-}$ at 20 °C ([Substrate] = 400 µM in CH₂Cl₂ containing 0.1 M TBAPF₆).



Figure S6. UV-Vis Spectra of (a) 1^{4+} [Cu(II)**TPPS**]⁴⁻ (black), its singly oxidized species generated by oxidation at 0.21 V vs Fc/Fc⁺ (red), and doubly oxidized species generated by oxidation at 0.39 V vs Fc/Fc⁺ (blue line), (b) a Cu(II)phthalocyanine Cu(II)**Pc** (black) and its singly-oxidized species generated by oxidation at 0.40 V vs. Fc/Fc⁺ (red), and (c) a Cu(II)porphyrin Cu(II)**Por** (black) and its singly-oxidized species generated by oxidation at 0.38 V vs. Fc/Fc⁺ (red) in CH₂Cl₂ including 0.1 M *ⁿ*Bu₄NPF₆ at 20 °C. [Substrate] = 20 μ M.

Reference.

1. Y. Yamada, M. Okamoto, K. Furukawa, T. Kato, K. Tanaka, *Angew. Chem. Int. Ed.* 2012, **51**, 709-713.