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 $\text{I}^{4+}\cdot4\text{Cl}^{-}$ was prepared according to the literature procedures.\textsuperscript{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$_2$Cl$_2$ 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$_2$Cl$_2$ solutions containing 0.1 M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) in a standard one-component cell under an N$_2$ 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 N$_2$ bubbling for at least 10 min. Obtained $E^\circ$ vs. Ag/AgCl were converted to those vs. Fc/Fc$^+$ based on measured redox potential of ferrocene.

$\text{S2}$
Synthesis of $1^{4+} [\text{Au(III)TPPS}]^{3-} \cdot \text{Cl}^-$.

To the solution of $1^{4+} \cdot 4\text{Cl}^- \ (18.3 \text{ mg}, \ 4.20 \mu\text{mol})$ in CH$_2$Cl$_2 \ (5.0 \text{ mL})$ was added the 3(“Bu$_4$N)$^+$·[Au(III)TPPS]$^{3-} \ (8.00 \text{ mg}, \ 4.24 \mu\text{mol})$ and stirred. The resulting solution was evaporated, dissolved in CHCl$_3$; MeOH = 1:1, and then filtered through fine cellulose powder. After the filtrate was concentrated, reprecipitation from CHCl$_3$ : MeOH = 4:1 / Et$_2$O (vapor diffusion) at room temperature yielded a brown solid. Then reprecipitation from CHCl$_3$ : MeOH = 4:1 / Et$_2$O (vapor diffusion) at –15 ºC 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: C$_{264}$H$_{300}$N$_{24}$O$_{60}$P$_4$S$_4$Cu$_2$AuNa$_2$ ([$1^{4+} [\text{Au(III)TPPS}]^{3-} \cdot \text{Cl}^- + 2\text{Na}^+ - \text{Cl}^-$]$^{3+}$), found: 1896.8.

Synthesis of $1^{4+} [\text{Au(III)TPPS}]^{3-} \cdot \text{PF}_6^-$.

To the solution of $1^{4+} [\text{Au(III)TPPS}]^{3-} \cdot \text{Cl}^- \ (19.9 \text{ mg}, \ 3.70 \mu\text{mol})$ and KPF$_6$ (68.0 mg, 370 μmol) in MeOH (14 mL) was added H$_2$O (30 mL). The resulting precipitate was collected by centrifugation and then redissolved in MeOH (2 mL). This reprecipitation procedure was repeated twice to afford yellowish brown solid (16.8 mg, 3.14 μmol), which was further purified by reprecipitation from CHCl$_3$ : MeOH = 4 : 1 / Et$_2$O (vapor diffusion) at room temperature (16.2 mg, 3.03 μmol, 82%).

MS (ESI-TOF) $m/z$ : calcd for 1896.9: C$_{264}$H$_{300}$N$_{24}$O$_{60}$P$_4$S$_4$Cu$_2$AuNa$_2$ ([$1^{4+} [\text{Au(III)TPPS}]^{3-} \cdot \text{PF}_6^- + 2\text{Na}^+ - \text{PF}_6^-$]$^{3+}$), found: 1896.8. Anal. Calcd for C$_{276}$H$_{312}$AuCl$_6$Cu$_2$F$_6$N$_{24}$O$_{61}$P$_5$S$_4$ ([$1^{4+} [\text{Au(III)TPPS}]^{3-} \cdot \text{PF}_6^- + 2\text{CHCl}_3 + \text{Et}_2\text{O}$]): C, 55.88; H, 5.42; N, 5.79. Found: C, 55.57; H, 5.72; N, 5.89 (0.31% error).

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

To the solution of $1^{4+} \cdot 4\text{Cl}^- \ (17.9 \text{ mg}, \ 4.10 \mu\text{mol})$ in CH$_2$Cl$_2 \ (7.0 \text{ mL})$ was added the solution of 4(“Bu$_4$N)$^+$·[Pd(II)TPPS]$^{4+} \ (8.44 \text{ mg}, \ 4.10 \mu\text{mol})$ in CH$_2$Cl$_2 \ (3.0 \text{ mL})$ and stirred. The resulting solution was evaporated, dissolved in CHCl$_3$ : 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_{4}S_{4}Cu_{2}PdNa_{3} ([\text{I}^{4+}\cdot\text{Pd(II)TPPS}]^{3+} + 3\text{Na}^{3+}), \text{found}: 1774.5. \text{Anal. Calcd for } C_{275}H_{327}Cl_{9}Cu_{2}N_{24}O_{64}P_{4}PdS, (C_{264}H_{300}N_{24}O_{60}P_{4}S_{4}Cu_{2}Pd + 3\text{CHCl}_{3} + 2\text{Et}_{2}O + 2\text{H}_{2}O): \text{C}, 56.87; \text{H}, 5.58; \text{N}, 5.87. \text{Found: C}, 56.53; \text{H}, 5.64; \text{N}, 5.97 (0.35\% \text{ error}).
Figure S1. ESI-TOF mass spectra of (a) $\text{I}^{4+}\cdot[\text{Au(III)TPPS}]^{3-}\cdot\text{Cl}^-$ (M for $[\text{I}^{4+}\cdot[\text{Au(III)TPPS}]^{3-} + 2\text{Na}^+]^{5+} = C_{264}H_{300}N_{24}O_{60}P_{4}S_{4}Cu_{2}AuNa_{2}$), and (b) $\text{I}^{4+}\cdot[\text{Pd(II)TPPS}]^{4-}$ (M for $[\text{I}^{4+}\cdot[\text{Pd(II)TPPS}]^{4-} + 3\text{Na}^+]^{5+} = C_{264}H_{300}N_{24}O_{60}P_{4}S_{4}Cu_{2}PdNa_{3}$). 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 $[2\cdot(\text{I}^{4+}\cdot[\text{Au(III)TPPS}]^{3-}) + 3\text{Na}^+]^{5+} = C_{528}H_{600}N_{48}O_{120}P_{8}S_{8}Na_{3}Au_{2}Cu_{4}$), (b) (M for $[2\cdot(\text{I}^{4+}\cdot[\text{Pd(II)TPPS}]^{4-}) + 5\text{Na}^+]^{5+} = C_{528}H_{600}N_{48}O_{120}P_{8}S_{8}Na_{5}Pd_{2}Cu_{4}$).
Synchrotron single crystal X-ray diffraction study of $1^{4+}$-[Au(III)TPPS]$^3$-$\text{Cl}^-$

The synchrotron X-ray diffraction study for cage $1^{4+}$-[Au(III)TPPS]$^3$-$\text{Cl}^-$ 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 $1^{4+}$-[Au(III)TPPS]$^3$-$\text{Cl}^-$ (CCDC deposit number: 1520369).

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<td></td>
<td>$c = 52.527(11)$ Å</td>
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<td>Theta range for data collection</td>
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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 $\text{1}^{4+}[\text{Au(III)TPPS}]^{3-}\cdot\text{Cl}^-\,$ 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-}$$\cdot$Cl$^-$ (red line), amd $1^{4+}$·[Pd(II)TPPS]$^{4-}$ (blue line). Each compounds were dissolved in CH$_2$Cl$_2$ at a concentration of 2.0 × 10$^{-6}$ M at 20 °C.
Figure S4. A cyclic voltammogram (CV) of $1^{4+} \cdot [\text{Cu(II)TPPS}]^{4+}$ (bottom) alongside of CVs of each components, $4(\text{tBu}_4\text{N})^+ \cdot [\text{Cu(II)TPPS}]^{4+}$, Cu(II)Pc, and Cu(II)Por at a scan rate of 0.1 V s$^{-1}$ at 20 °C ([Substrate] = 400 μM in CH$_2$Cl$_2$ containing 0.1 M TBAPF$_6$)
Figure S5. A cyclic voltammogram (CV, scan rate : 0.1 Vs\(^{-1}\)) and a differential pulse voltammogram (DPV, scan rate : 0.01 Vs\(^{-1}\)) of (a) \(1^{4+} \cdot [\text{Cu(II)TPPS}]^{4-}\) and (b) \(1^{4+} \cdot [\text{Pd(II)TPPS}]^{4-}\) at 20 °C ([Substrate] = 400 µM in CH\(_2\)Cl\(_2\) containing 0.1 M TBAPF\(_6\)).
Figure S6. UV-Vis Spectra of (a) $\mathbf{1}^{\text{+}}-[\text{Cu(II)TPPS}]^{4-}$ (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 CH$_2$Cl$_2$ including 0.1 M $\text{Bu}_4\text{NPF}_6$ at 20 °C. [Substrate] = 20 μM.
Reference.