Giant Shape-Persistent Tetrahedral Porphyrin System: Light-Induced Charge Separation

Marianna Marchini, Alessandra Luisa, Giacomo Bergamini, Nicola Armaroli, Barbara Ventura,* Massimo Baroncini,* Nicola Demitri, Elisabetta Iengo,* and Paola Ceroni*
# Table of Contents

| Section                                                                 | Page |
|------------------------------------------------------------------------|------|
| Self-assembly process                                                  | S2   |
| NMR characterization                                                   | S3   |
| X-ray analysis and structural characterization                          | S9   |
| Photophysical measurements                                             | S17  |
| Electrochemical measurements                                           | S26  |
| References                                                             | S30  |
Self-assembly process.

Scheme S1. Schematization of the supramolecular arrays’ formation between 1⁺ and 2⁺ with Ru(CO)FTPP.

Scheme S2. Schematization of the supramolecular arrays’ formation between 1⁺⁺ and 2⁺⁺ with Ru(CO)OEP.
NMR characterization.

Figure S1. $^1$H NMR spectrum (acetone-$d_6$, 500 MHz) of $2^+\rightarrow$Ru(CO)FTPP, with labeling scheme.

Figure S2. FF-COSY NMR spectrum (acetone-$d_6$, 500 MHz) of $[2^+\rightarrow$Ru(CO)FTPP]PF$_6^-$, see Figure S1 for labeling scheme.
Figure S3. $^1$H NMR spectrum (acetone-$d_6$, 500 MHz) of 1$^{4+}$→4Ru(CO)FTPP, with labeling scheme (only one of the four arms is depicted, for simplicity).

Figure S4. HH-COSY NMR spectrum (acetone-$d_6$, 500 MHz) of 1$^{4+}$→4Ru(CO)FTPP, see Figure S3 labeling scheme.
Figure S5. FF-COSY NMR spectrum (acetone-$d_6$, 500 MHz) of [$1^{4+}$→$4$Ru(CO)FTPP][PF$_6$]$_4$, see Figure S3 for labeling scheme.

Figure S6. HF-HOESY NMR spectrum (acetone-$d_6$, 500 MHz) of [$1^{4+}$→$4$Ru(CO)FTPP][PF$_6$]$_4$, with relevant special couplings, see Figure S3 for labeling scheme.
Figure S7. $^1$H NMR spectrum (acetone-$d_6$, 500 MHz) of $2^+\equiv$Ru(CO)OEP, with labeling scheme.

Figure S8. HH-COSY NMR spectrum (acetone-$d_6$, 500 MHz) of $2^+\equiv$Ru(CO)OEP, see Figure S7 for labeling scheme.
Figure S9. HC-HSCQ NMR spectrum (acetone-$d_6$, 500 MHz) of 2$^+$$\rightarrow$Ru(CO)OEP, see Figure S7 for labeling scheme.

Figure S10. $^1$H NMR spectra (acetone-$d_6$, 500 MHz) of 1$^+$ (top), Ru(CO)OEP (center) and 1$^+$$\rightarrow$4Ru(CO)OEP (bottom), with labelling scheme (only one of the four arms is depicted, for simplicity).
Figure S11. HC-HSCQ NMR spectrum (acetone-\textit{d}_6, 500 MHz) of 1^{4-\text{Ru}}(CO)OEP (bottom), 2^{4-\text{Ru}}(CO)OEP, see Figure S10 for labeling scheme.

Figure S12. Superimposition of the 2D $^1$H-DOSY spectra (Bayesian transform, acetone-\textit{d}_6, 500 MHz) of Ru(CO)OEP (red), 2^{4-\text{Ru}}(CO)OEP, and 2^{4-\text{Ru}}(CO)OEP (green). On the horizontal axis, only the 1D $^1$H trace for 2^{4-\text{Ru}}(CO)OEP is shown for simplicity.
Figure S13. Superimposition of the 2D $^1$H-DOSY spectra (Bayesian transform, acetone-$d_6$, 500 MHz) of Ru(CO)OEP (red), $^{1+}$ (blue), and $^{1+}$$\rightarrow$$^{4}$Ru(CO)OEP (green). On the horizontal axis, only the 1D $^1$H trace for $^{1+}$$\rightarrow$$^{4}$Ru(CO)OEP is shown for simplicity.

Table S1. Diffusion coefficient values derived from the $^1$H-DOSY NMR experiments.

| compound | $D_t$ a (cm$^2$s$^{-1}$) | $r_H$ b (Å) |
|----------|-----------------|-----------|
| $^{2+}$  | 1.98±0.01 x 10^{-5} | 3.4 |
| Ru(CO)OEP | 1.46±0.02 x 10^{-5} | 4.7 |
| Ru(CO)FTPP | 1.25±0.04 x 10^{-5} | 5.5 |
| $^{2+}$$\rightarrow$$^{4}$Ru(CO)OEP | 1.15±0.04 x 10^{-5} | 5.9 |
| $^{2+}$$\rightarrow$$^{4}$Ru(CO)FTPP | 1.05±0.01 x 10^{-5} | 6.5 |
| $^{1+}$  | 8.86±0.03 x 10^{-6} | 7.7 |
| $^{1+}$$\rightarrow$$^{4}$Ru(CO)OEP | 5.82±0.03 x 10^{-6} | 11.7 |
| $^{1+}$$\rightarrow$$^{4}$Ru(CO)FTPP | 5.33±0.04 x 10^{-6} | 12.8 |

aaverage of $D_t$ values obtained from the $^1$H signal decay analysis;
bcalculated from Stokes-Einstein equation for linear diffusion.

X-ray analysis and structural characterization.

Data collections were performed at the X-ray diffraction beamline (XRD1) of the Elettra Synchrotron, Trieste (Italy). Complete datasets were collected at 100 K (nitrogen stream supplied through an Oxford Cryostream 700 - Oxford Cryosystems Ltd., Oxford, United Kingdom) using a monochromatic wavelength of 0.700 Å through the rotating crystal method. Images were acquired on a Pilatus 2M hybrid-pixel area detector (DECTRIS Ltd., Baden-Daettwil, Switzerland). The crystals of compounds [$^{2+}$$\rightarrow$$^{4}$Ru(CO)FTPP][PF$_6$],
[2\*\(\supset\)Ru(CO)OEP][PF\(_6\)] and [1\(^{4+}\)\(\supset\)4Ru(CO)FTPP][PF\(_6\)]\(_4\) were dipped in N-paratone and mounted on the goniometer head with a nylon loop (Hampton Research, Aliso Viejo, California). The diffraction data were indexed, integrated and scaled using XDS.\([25]\) The structures were solved by direct methods using SIR2014\([33]\) and/or the dual space algorithm implemented in the SHELXT code.\([45]\) Fourier analysis and refinement were performed by the full-matrix least-squares methods based on F\(^2\) implemented in SHELXL-2014.\([55]\) The Coot program was used for modeling.\([65]\) Anisotropic thermal motion modeling was applied to atoms with occupancy greater or equal to 50%. Restraints on bond lengths, angles and thermal motion parameters (DFIX, DANG, SIMU and DELU) have been applied on disordered and poorly defined fragments. Hydrogen atoms were included at calculated positions with isotropic U\(_{factors}\) = 1.2 U\(_{eq}\) or U\(_{factors}\) = 1.5 U\(_{eq}\) for methyl and hydroxyl groups (U\(_{eq}\) being the equivalent isotropic thermal factor of the bonded non hydrogen atom). Pictures were prepared using ORTEP-3\([75]\) and Pymol\([85]\) softwares. Essential crystal and refinement data are reported below (Table S2).

**Single crystal X-ray structure of [2\*\(\supset\)Ru(CO)FTPP][PF\(_6\)].**

[2\*\(\supset\)Ru(CO)FTPP][PF\(_6\)] crystallizes in a monoclinic P2\(_1\)/n crystal form with one complex molecule (Figure S14) in the crystallographic asymmetric unit (ASU). Electroneutrality requires the presence of one PF\(_6\) \(^-\) counterion that remains close to the positively charged pyridinium nitrogen (shorter F\(\cdots\)N\(^+\) distance is 3.121(2) Å). Furthermore, fluorines form orthogonal halogen bonds with the perfluorinated phenyls of neighbor porphyrins (Figure S15; shortest d\(_{F\cdots F}\) = 3.001(2) Å). Weak hydrophobic contacts keep distinct molecules loosely packed. Voids can be identified and each cavity is filled by two acetone and one disordered water molecule, weakly coordinated to CO oxygen (d\(_{O\cdots O}\) = 3.43(2) Å).

Another polymorphic crystalline form of [2\*\(\supset\)Ru(CO)FTPP][PF\(_6\)] was identified ([2\*\(\supset\)Ru(CO)FTPP][PF\(_6\)]\(_{alt}\)) during crystals screening. These crystals formed as thinner red plates from the hexane-acetone mixtures and showed a bigger orthorhombic Pca2\(_1\) unit cell. The volume is three times larger than monoclinic [2\*\(\supset\)Ru(CO)FTPP][PF\(_6\)] crystal form and three crystallographically independent complex molecules are present in the [2\*\(\supset\)Ru(CO)FTPP][PF\(_6\)]\(_{alt}\) ASU (Figure S16). The crystal packing appears different compared to [2\*\(\supset\)Ru(CO)FTPP][PF\(_6\)] and underlines some torsional flexibility on phenyl groups; larger cavities can be identified. These voids contain five well defined acetones molecules, but most of the volume has disordered solvent and no model could be built in the blurred electron density. The contribution of this region to the scattering was estimated as ca. 470 electrons/cell, in a volume of ca. 1871 Å\(^3\) (29 % of cell volume) and it was removed with the SQUEEZE routine of PLATON.\([95]\) The formula mass and unit-cell characteristics reported for [2\*\(\supset\)Ru(CO)FTPP][PF\(_6\)] take into account this disordered solvent, which corresponds to one hexane and two acetone additional molecules in the ASU. Semi-empirical absorption correction and scaling was performed on [2\*\(\supset\)Ru(CO)FTPP][PF\(_6\)]\(_{alt}\) dataset, exploiting multiple measures of symmetry-related reflections, using SADABS program.\([105]\) The ruthenium coordination sphere (Table S3) is equivalent to
Ru(CO)FTPP bearing other axially bound pyridine-based ligands, recently published (CCDC IDs 1999059 and 1999060).\(^{115}\)

**Figure S14.** Asymmetric unit content for \([2\supseteq\text{Ru(CO)FTPP}][\text{PF}_6]\) (50% probability ellipsoids). Two molecules of acetone and one disordered water have been modeled in the crystal voids. Color code: Ru, violet; N, blue; O, red; F, green; P, orange.

**Figure S15.** Stick representation of \([2\supseteq\text{Ru(CO)FTPP}][\text{PF}_6]\) crystal packing, showing contacts of \(\text{PF}_6^-\) counterions. Hydrogen bonds between solvent water molecules and CO coordinated to ruthenium atom are also visible. Color code: Ru, violet; N, blue; O, red; F, green; P, orange.

**Figure S16.** Asymmetric unit content for \([2\supseteq\text{Ru(CO)FTPP}][\text{PF}_6]\) (50% probability ellipsoids). Five molecules of acetone were modeled in the ASU crystal voids. Color code: Ru, violet; N, blue; O, red; F, green; P, orange.
Single crystal X-ray structure of $[2^+\rightarrow\text{Ru(CO)OEP}][\text{PF}_6]$. $[2^+\rightarrow\text{Ru(CO)OEP}][\text{PF}_6]$ crystallizes with a triclinic $P\overline{1}$ unit cell; complete dataset was obtained by merging two data collections obtained from two different orientations of the same crystal. Asymmetric unit contains a full complex with a $\text{PF}_6^-$. Contacts with neighboring molecules are characterized by weak hydrophobic interactions among ethylene sidechains of the porphyrins. Compared to $[2^+\rightarrow\text{Ru(CO)FTPP}][\text{PF}_6]$, the presence of less bulky porphyrin substituents keeps symmetry related complexes closer, therefore smaller voids are present and only one, well ordered, acetone molecule is present in the ASU (Figure S17). The ruthenium coordination sphere (Table S3) is equivalent to that found for the neutral Ru(CO)(pyridine)OEP complex, already published (CCDC ID 1245082 and 1876317).

![Figure S17. Asymmetric unit content for $[2^+\rightarrow\text{Ru(CO)OEP}][\text{PF}_6]$ (50% probability ellipsoids). One acetone molecule was modeled in the crystal voids. Color code: Ru, violet; N, blue; O, red; F, green; P, orange.](image)

Single crystal X-ray structure of $[1^4\rightarrow4\text{Ru(CO)FTPP}][\text{PF}_6]_4$. $[1^4\rightarrow4\text{Ru(CO)FTPP}][\text{PF}_6]_4$ crystallizes with a monoclinic $C2/c$ unit cell. The crystals appeared as small plates prone to radiation damage; a complete dataset could be obtained only merging two data collections obtained from two different crystals. The presence of loose contacts in the crystal packing and big channels is in agreement with the poor diffracting power of these crystals that diffracted not better than $\sim1.1$ Å. This limit explains why the data/parameter ratio for the refinement of this model is only 6.3 and why extensive restraints on disordered moieties have been used. Half tetrameric complex is crystallographically independent and the full object is generated through a twofold proper rotation axis bisecting the tetramer $sp^3$ carbon (Figure S18).

Small cavities contains two hexane and one acetone well-ordered molecules, while larger voids contain severely disordered solvent. In this region only half hexane could be modeled while the remaining density (estimated as ca. 772 electrons/cell, in a volume of ca. 6828 Å$^3$ - 21 % of cell volume) was removed with the
SQUEEZE routine of PLATON.\textsuperscript{[95]} The formula mass and unit-cell characteristics reported for [1\textsuperscript{4+}→4Ru(CO)FTPP][PF\textsubscript{6}]\textsubscript{4} take into account this disordered solvent, which corresponds to additional 1.25 hexane and 1 acetone molecules in the ASU. Semi-empirical absorption correction and scaling was performed merging two independent [1\textsuperscript{4+}→4Ru(CO)FTPP][PF\textsubscript{6}]\textsubscript{4} datasets, exploiting multiple measures of symmetry-related reflections, using SADABS program.\textsuperscript{[105]}

[1\textsuperscript{4+}→4Ru(CO)FTPP][PF\textsubscript{6}]\textsubscript{4} shows a distorted structure, compressed on two sides (Figure S19) with two ordered PF\textsubscript{6}\textsuperscript{−} in the middle of the shorter sides and two heavily disordered counterions outside (these latter were modeled in three alternative positions). The distortions from the ideal tetrahedral angle observed may be imputed to packing effects (angles of ~85° and ~126° on the narrower and on the wider sides, respectively, Figure S19).

*Figure S18. Asymmetric unit content for [2\textsuperscript{−}→Ru(CO)FTPP][PF\textsubscript{6}]\textsubscript{4} (50% probability ellipsoids). One acetone and 2.5 hexane molecules were modeled in the crystal voids. Color code: Ru, violet; N, blue; O, red; F, green; P, orange.*

*Figure S19. Stick representation of the structure of [1\textsuperscript{4+}→4Ru(CO)FTPP][PF\textsubscript{6}]\textsubscript{4} with tetrahedral distortions highlighted in yellow dotted lines (PF\textsubscript{6}\textsuperscript{−} omitted for clarity). Color code: Ru, violet; N, blue; O, red; F, green; P, orange.*
### Table S2. Crystallographic data and refinement details for [2^2=Ru(CO)FTPP][PF_6], [2^2=Ru(CO)OEP][PF_6] and [1^4=4Ru(CO)FTPP][PF_6].

| CCDC Number    | 2089855 | 2089854 |
|----------------|---------|---------|
| **Chemical Formula** | C_{67}H_{35}F_{26}N_{6}O_{4}Pr | C_{70}H_{39.67}F_{26}N_{6}O_{3.33}Pr |
| **Formula weight (g/mol)** | 1614.05 | 1644.12 |
| **Temperature (K)** | 100(2) | 100(2) |
| **Wavelength (Å)** | 0.700 | 0.700 |
| **Crystal system** | Monoclinic | Orthorhombic |
| **Space Group** | P 2_1/n | P ca2_1 |
| **Unit cell dimensions** | | |
| a = 15.989(1) Å | a = 25.100(20) Å |
| b = 23.638(1) Å | b = 26.516(15) Å |
| c = 16.899(1) Å | c = 29.653(14) Å |
| α = 90° | α = 90° |
| β = 92.921(5)° | β = 90° |
| γ = 90° | γ = 90° |
| **Volume (Å³)** | 6378.6(6) | 19738(24) |
| **Z** | 4 | 12 |
| **Density (calculated) (g·cm⁻³)** | 1.681 | 1.660 |
| **Absorption coefficient (mm⁻¹)** | 0.382 | 0.372 |
| **F(000)** | 3216 | 9856 |
| **Resolution (Å)** | 0.72 | 0.84 |
| **Index ranges** | -22 ≤ h ≤ 22, -32 ≤ k ≤ 32, -23 ≤ l ≤ 23 | -29 ≤ h ≤ 28, -31 ≤ k ≤ 31, -35 ≤ l ≤ 35 |
| **Reflections collected** | 97131 | 111283 |
| **Independent reflections (data with I>2σ(I))** | 17701 (17544) | 34584 (28556) |
| **Data completeness (max resln)** | 99.2% (98.8%) | 99.9% (100.0%) |
| **Data multiplicity (max resln)** | 5.38 (5.21) | 6.11 (6.01) |
| **I/σ(I) (max resln)** | 58.01 (52.15) | 16.21 (7.40) |
| **R_{merge} (max resln)** | 0.0272 (0.0232) | 0.0645 (0.1917) |
| **Absorption correction** | None | Multi-scan |
| **Max. and min. transmission** | 0.981 and 0.963 | 0.746 and 0.645 |
| **Refinement method** | Full-matrix least-squares on F² | Full-matrix least-squares on F² |
| **Data / restraints / parameters** | 17701 / 12 / 959 | 34584 / 385 / 2679 |
| **Goodness-of-fit on F²** | 1.012 | 1.029 |
| **Δ/σ_{max}** | 0.006 | 0.028 |
| **Final R indices (I>2σ(I))** | R₁ = 0.0410, wR₂ = 0.1055 | R₁ = 0.0891, wR₂ = 0.2328 |
| **R indices (all data)** | R₁ = 0.0412, wR₂ = 0.1056 | R₁ = 0.1058, wR₂ = 0.2475 |
| **Largest diff. peak and hole (eÅ⁻³)** | 0.981 and -1.080 | 1.867 and -0.943 |
| **R.M.S. deviation from mean (eÅ⁻³)** | 0.136 | 0.121 |

\[
R_1 = \frac{\sum |F_{o}|-|F_{c}|}{\sum |F_{o}|}, \quad wR_2 = \left(\frac{\sum [w(F_{o}^{2} - F_{c}^{2})^{2}]}{\sum [w(F_{o}^{2})]}\right)^{1/2}
\]
|                      | CCDC Number | Chemical Formula | C29H20F104N24O8P4Ru4 | C29H20F104N24O8P4Ru4 |
|----------------------|-------------|------------------|----------------------|----------------------|
| **Crystallographic data and refinement details for** |             |                  |                      |                      |
| **[2’=Ru(CO)FTPP][PF6]** & **[2’=Ru(CO)OEP][PF6]** & **[14+=4Ru(CO)FTPP][PF6]** |             |                  |                      |                      |
|                      | 2089856     |                  |                      |                      |
|                      | 2089853     |                  |                      |                      |
| **CCDC Number**      |             |                  |                      |                      |
| **Chemical Formula** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Formula weight (g/mol)** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Temperature (K)**  |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Wavelength (Å)**   |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Crystal system**   |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Space Group**      |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Unit cell dimensions** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Volume (Å³)**      |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Z**                |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Density (calculated) (g·cm⁻³)** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Absorption coefficient (mm⁻¹)** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **F(000)**           |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Resolution (Å)**   |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Index ranges**     |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Reflections collected** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Independent reflections** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Data completeness (max resln)** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Data multiplicity (max resln)** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **l/σ (l) (max resln)** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **R_{merge} (max resln)** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Absorption correction** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Max. and min. transmission** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Refinement method** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Data / restraints / parameters** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Goodness-of-fit on F²** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **A(rms)**           |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Final R indices [l>2σ(l)]** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **R indices (all data)** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **Largest diff. peak and hole (eÅ⁻³)** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **R.M.S. deviation from mean (eÅ⁻³)** |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **a** = Σ ||Fo|−|Fc|| / Σ |Fo|, wR₂ = {Σ [w(Fo²−Fc²)]²} / Σ [w(Fo²)]₁/² |                      |                      |
|                      |             |                  |                      |                      |
| **R₁ = 0.0244, wR₂ = 0.0616 |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **R₁ = 0.1370, wR₂ = 0.2953 |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **R₁ = 0.1777, wR₂ = 0.3160 |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **R₁ = 0.1909, wR₂ = 0.3475 |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **R₁ = 0.1512, wR₂ = 0.3057 |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **R₁ = 0.1350, wR₂ = 0.2953 |             |                  |                      |                      |
|                      |             |                  |                      |                      |
| **R₁ = 0.1280, wR₂ = 0.2937 |             |                  |                      |                      |
Table S3. Average bond distances and angles (Å and °) for ruthenium coordination spheres of crystallographically independent moieties in $[2^+\text{Ru(CO)FTPP}]\text{[PF}_6\text{]}$, $[2^+\text{Ru(CO)FTPP}]\text{[PF}_6\text{]}_{alt}$, $[2^+\text{Ru(CO)OEP}]\text{[PF}_6\text{]}$ and $[1^{4+}\text{4Ru(CO)FTPP}]\text{[PF}_6\text{]}_4$ ASUs.

|                  | Distances (Å) | Angles ° |
|------------------|---------------|----------|
| $[2^+\text{Ru(CO)FTPP}]\text{[PF}_6\text{]}$ |               |          |
| Ru-C(CO)         | 1.854(2)      | C(CO)-Ru-N(Py) 178.59(5) |
| Ru-N(Porphyrin)  | 2.052(1)      | C(CO)-Ru-N(Porphyrin) 91.51(6) |
| Ru-N(Py)         | 2.230(1)      | N(Py)-Ru-N(Porphyrin) 88.49(5) |

|                  | Distances (Å) | Angles ° |
|------------------|---------------|----------|
| $[2^+\text{Ru(CO)FTPP}]\text{[PF}_6\text{]}_{alt}$ |               |          |
| Ru-C(CO)         | 1.797(14)     | C(CO)-Ru-N(Py) 174.71(59) |
| Ru-N(Porphyrin)  | 2.034(15)     | C(CO)-Ru-N(Porphyrin) 92.28(62) |
| Ru-N(Py)         | 2.207(6)      | N(Py)-Ru-N(Porphyrin) 87.75(61) |

|                  | Distances (Å) | Angles ° |
|------------------|---------------|----------|
| $[2^+\text{Ru(CO)OEP}]\text{[PF}_6\text{]}$ |               |          |
| Ru-C(CO)         | 1.836(2)      | C(CO)-Ru-N(Py) 176.48(50) |
| Ru-N(Porphyrin)  | 2.057(14)     | C(CO)-Ru-N(Porphyrin) 91.47(60) |
| Ru-N(Py)         | 2.182(6)      | N(Py)-Ru-N(Porphyrin) 88.50(50) |

|                  | Distances (Å) | Angles ° |
|------------------|---------------|----------|
| $[1^{4+}\text{4Ru(CO)FTPP}]\text{[PF}_6\text{]}_4$ |               |          |
| Ru-C(CO)         | 1.865(14)     | C(CO)-Ru-N(Py) 177.14(52) |
| Ru-N(Porphyrin)  | 2.028(12)     | C(CO)-Ru-N(Porphyrin) 92.10(54) |
| Ru-N(Py)         | 2.173(10)     | N(Py)-Ru-N(Porphyrin) 87.90(40) |

|                  | Distances (Å) | Angles ° |
|------------------|---------------|----------|
|                  |               |          |
| Ru-C(CO)         | 1.811(15)     | C(CO)-Ru-N(Py) 178.23(43) |
| Ru-N(Porphyrin)  | 2.037(9)      | C(CO)-Ru-N(Porphyrin) 92.06(47) |
| Ru-N(Py)         | 2.087(12)     | N(Py)-Ru-N(Porphyrin) 87.95(37) |
Photophysical measurements.

*Formation of [2−Ru(CO)FTPP].*

![Figure S20](image_url)

**Figure S20.** Complete absorption spectra (plot a) recorded after the addition of increasing amounts of 2⁺ (up to 2.5 equivalents) to a solution of Ru(CO)FTPP in acetone; Soret band (b) and Q-bands (c) regions enlarged. The black solid line is the spectrum of the free porphyrin in solution; the black dashed line is the spectrum recorded after the addition of 2.5 equivalents of 2⁺.

The trend obtained from absorbance versus 2⁺ equivalents added (Figure S20) shows a plateau after the addition of ca. 1 equivalent of 2⁺; that suggests a stoichiometry of 1:1. As expected, a ruthenium porphyrin is able to complex one molecule of 2⁺. By global fitting of the absorption changes it was estimated that the formation of the supramolecular system had a constant of 3x10⁷ M⁻¹.
Figure S21. Global fitting of the absorption changes at 554 nm upon addition of 2⁺.

Formation of [1₄⁺→4Ru(CO)FTPP].

Figure S22. Complete absorption spectra recorded after the addition of increasing amounts of 1⁺ (up to 0.78 equivalents) to a solution of Ru(CO)FTPP in acetone. Inset: Soret band region enlarged. The black solid line is the spectrum of the free porphyrin in solution; the black dashed line is the spectrum recorded after the addition of 0.78 equivalents of 1⁺.
The $1^{4+}$ fluorescence is completely quenched when less than four equivalents of Ru(CO)FTPP are added in solution: indeed one porphyrin quenches almost the 30% of the tetramer emission. An approximation is to estimate the association constant for the complexation of one subunit and one Ru(CO)FTPP (1:1 stoichiometry), considering four times the concentration of the tetramer. It is a good approximation, as long as the four subunits behave independently in the association with the ruthenium porphyrins. The value obtained is $4\times10^6$ M$^{-1}$, one order of magnitude lower than the one estimate for the model compound: this could be explained since the subunits are sterically hindered in the tetramer structure.

![Figure S23](image_url)  
**Figure S23.** Normalized emission intensity changes at 600 nm upon addition to acetone solution of $1^{4+}$ of increasing amounts of Ru(CO)FTPP (up to 6.5 equivalents, $\lambda_{ex}$=330 nm).

![Figure S24](image_url)  
**Figure S24.** Phosphorescence emission spectra of the free ruthenium porphyrin Ru(CO)FTPP in CH$_2$Cl$_2$:CH$_3$Cl 1:1 (black solid line) and after the addition of an excess of $1^{4+}$, added from acetone (black dashed line) at 77K.
Formation of $[2^+\rightleftharpoons \text{Ru(CO)}\text{OEP}]$.

![Figure S25](image_url)

**Figure S25.** Complete absorption spectra (plot a) recorded after the addition of increasing amounts of $2^+$ (up to 4.4 equivalents) to a solution of Ru(CO)OEP in acetone; Soret band (b) and Q-bands (c) regions enlarged. The black solid line is the spectrum of the free porphyrin in solution; the black dashed line is the spectrum recorded after the addition of 4.4 equivalents of $2^+$. Global fitting of the normalized absorption changes at 547 nm upon addition of $2^+$ (d).

As expected, the trend obtained from absorbance versus $2^+$ equivalents added (Figure S25d) show a plateau coming after the addition of ca. 1 equivalent of $2^+$ which suggests a stoichiometry of 1:1. By global fitting of the absorption changes it was estimated that the formation of the supramolecular system had a constant of $8 \times 10^5 \text{ M}^{-1}$. 
Formation of $[1^{4+} \rightarrow 4\text{Ru(CO)OEP}]$. 

Upon addition of increasing amount of $1^{4+}$ to a Ru(CO)OEP solution, the adduct $1^{4+} \rightarrow 4\text{Ru(CO)OEP}$ was formed, as confirmed by the trend obtained from absorbance versus $1^{4+}$ equivalents (Figure S26d). The $1^{4+}$ fluorescence is completely quenched when less than four equivalents of Ru(CO)OEP are added in solution: one porphyrin is enough to quench 70% of the tetramer emission. We can assume that the four subunits behave independently in the association with the ruthenium porphyrins: the association constant obtained for the complexation of one subunit and one Ru(CO)OEP (1:1 stoichiometry) is $2 \times 10^4 \text{ M}^{-1}$, one order of magnitude lower than the one estimate for the model compound, due to the sterically hindered subunits in the tetramer structure.
Figure S27. Normalized emission intensity changes at 600 nm upon addition to acetone solution of 1\textsuperscript{4+} of increasing amounts of Ru(CO)OEP (up to 6 equivalents, \(\lambda_{ex}=330\) nm).

Figure S28. Phosphorescence emission spectra of the free ruthenium porphyrin Ru(CO)OEP in CH\textsubscript{2}Cl\textsubscript{2} (black solid line) and after the addition of an excess of 1\textsuperscript{4+} (2 equivalents), added from acetone (black dashed line) at room temperature (a); phosphorescence emission spectra of Ru(CO)OEP in CH\textsubscript{2}Cl\textsubscript{2}:CH\textsubscript{3}Cl 1:1 (black solid line) and after the addition of an excess of 1\textsuperscript{4+} (2 equivalents), added from acetone (black dashed line) at 77K.

Table S4. Photophysical data of tetramer 1\textsuperscript{4+} and monomer 2\textsuperscript{+} in CH\textsubscript{3}CN; photophysical data of Ru(CO)FTPP, Ru(CO)OEP and assembled system in CH\textsubscript{2}Cl\textsubscript{2}; room temperature.

|             | \(\varepsilon\) (M\textsuperscript{-1} cm\textsuperscript{-1}) | \(\lambda\) (nm) |
|-------------|-------------------|-----------------|
| Ru(CO)FTPP  | 18800             |                 |
| 2\textsuperscript{+}:Ru(CO)FTPP | 16700             |                 |
| 1\textsuperscript{4+}:4Ru(CO)FTPP | 15800             |                 |
| Ru(CO)OEP   | 27200             |                 |
| 2\textsuperscript{+}:Ru(CO)OEP | 16500             |                 |
Transient absorption spectroscopy.

**Figure S29.** Transient absorption spectra of Ru(CO)FTPP in CH₂Cl₂ at the end-of-pulse (blue thick curve) and at different delays. Excitation at 550 nm ($A_{550} = 0.20$, 0.2 cm optical path, 2 µJ/pulse). In the inset the kinetic analysis at 479 nm is reported.

**Figure S30.** Transient absorption spectra of 2⁺:Ru(CO)FTPP in CH₂Cl₂ at the end-of-pulse (brown thick curve) and at different delays. Excitation at 550 nm ($A_{550} = 0.18$, 0.2 cm optical path, 2 µJ/pulse). In the inset is reported the kinetic analysis at 470 nm and 575 nm.
Figure S31. Transient absorption spectra of Ru(CO)FTPP in CH₂Cl₂ at the end-of-pulse (blue thick curve) and at different delays. Excitation at 300 nm ($A_{300} = 0.20$, 0.2 cm optical path, 2 μJ/pulse). In the inset is reported the kinetic analysis at 488 nm and 572 nm.

Figure S32. Transient absorption spectra of 1⁺⁺ in CH₃CN at the end-of-pulse (dark green thick curve) and at different delays. Excitation at 300 nm ($A_{300} = 0.16$, 0.2 cm optical path, 2 μJ/pulse). In the inset is reported the kinetic analysis at 463 nm and 519 nm.
Figure S33. Transient absorption spectra of $2^*$ in CH$_3$CN at the end-of-pulse (dark green thick curve) and at different delays. Excitation at 300 nm ($A_{300} = 0.19$, 0.2 cm optical path, 2 $\mu$J/pulse). In the inset is reported the kinetic analysis at 474 nm and 598 nm.

Figure S34. Transient absorption spectra of $2^*$Ru(CO)FTPP in CH$_2$Cl$_2$ at the end-of-pulse (brown thick curve) and at different delays. Excitation at 300 nm ($A_{300} = 0.23$, 0.2 cm optical path, 2 $\mu$J/pulse). In the inset is reported the kinetic analysis at 471 nm and 570 nm.
**Electrochemical measurements.**

**Figure S35.** Cyclic voltammetry of an argon-purged solution of $2^+$ (1mM) in CH$_3$CN in the presence of 0.1M tetrabutylammonium hexafluorophosphate (TBAPF$_6$) (red solid line) and $1^{4+}$ (0.5mM) in CH$_3$CN in the presence of 0.0.5M TBAPF$_6$. Scan rate=0.2Vs$^{-1}$; working electrode: glassy carbon. Ferrocene (Fc) was used as internal standard.

**Figure S36.** Cyclic voltammetry of an argon-purged solution of Ru(CO)FTPP (0.5mM) in CH$_2$Cl$_2$ in the presence of 0.05M tetrabutylammonium hexafluorophosphate (TBAPF$_6$). Scan rate=0.2Vs$^{-1}$; working electrode: glassy carbon. Ferrocene (Fc) was used as internal standard.
**Figure S37.** Cyclic voltammetry of an argon-purged solution of $\text{2}^{+}\rightleftharpoons \text{Ru(CO)FTPP}$ (0.5mM) in $\text{CH}_2\text{Cl}_2$ in the presence of 0.05M tetrabutylammonium hexafluorophosphate (TBAPF$_6$). Scan rate=0.2Vs$^{-1}$; working electrode: glassy carbon. Ferrocene (Fc) was used as internal standard.

**Figure S38.** Cyclic voltammetry of an argon-purged solution of $\text{1}^{+}\rightleftharpoons 4\text{Ru(CO)FTPP}$ (0.5mM) in $\text{CH}_2\text{Cl}_2$ in the presence of 0.05M tetrabutylammonium hexafluorophosphate (TBAPF$_6$). Scan rate=0.2Vs$^{-1}$; working electrode: glassy carbon. Ferrocene (Fc) was used as internal standard.
Figure S39. Cyclic voltammetry of an argon-purged solution of Ru(CO)OEP (0.6mM) in CH$_2$Cl$_2$ in the presence of 0.05M tetrabutylammonium hexafluorophosphate (TBAPF$_6$). Scan rate=0.5Vs-1; working electrode: glassy carbon. Decamethylferrocene (FcMe$_{10}$) was used as internal standard.

Figure S40. Cyclic voltammetry of an argon-purged solution of 2$^+$$\rightarrow$Ru(CO)OEP (0.6mM) in CH$_2$Cl$_2$ in the presence of 0.05M tetrabutylammonium hexafluorophosphate (TBAPF$_6$). Scan rate=0.5Vs-1; working electrode: glassy carbon. Decamethylferrocene (FcMe$_{10}$) was used as internal standard.
Figure S41. Cyclic voltammetry of an argon-purged solution of $1^+\Leftrightarrow$Ru(CO)OEP (0.3mM) in CH$_2$Cl$_2$ in the presence of 0.05M tetrabutylammonium hexafluorophosphate (TBAPF$_6$). Scan rate=0.2Vs$^{-1}$; working electrode: glassy carbon. Decamethylferrocene (FcMe$_{10}$) was used as internal standard.

Table S5. Redox potentials estimated from cyclic voltammetry performed in argon-purged CH$_2$Cl$_2$ solutions with tetrabutylammonium hexafluorophosphate (TBAPF$_6$). Working electrode: glassy carbon.

|          | $E_{1/2}$ (V vs SCE) |
|----------|----------------------|
| Ru(CO)FTPP | +1.30                |
| Ru(CO)OEP  | +0.65; +1.30         |
| $2^+$     | -0.78$^a$            |
| $2^+\Leftrightarrow$Ru(CO)FTPP | -0.56; +1.34          |
| $2^+\Leftrightarrow$Ru(CO)OEP  | -0.61; +0.63; +1.23   |
| $1^{4+}$  | -0.70$^{a,b}$        |
| $1^{4+}\Leftrightarrow$4Ru(CO)FTPP | -0.55; +1.35          |
| $1^{4+}\Leftrightarrow$4Ru(CO)OEP | -0.61; +0.64; +1.23   |

$^a$ In CH$_3$CN; $^b$ chemical irreversible process, $E_{pc}$ at 0.2V/s.
Figure S42. Diagram of the redox potentials of $1^{4+}$ (light-blue empty circle, chemical irreversible process, $E_{pc}$ at 0.2V/s in CH$_3$CN), $2^+$ (red circle, in CH$_3$CN), Ru(CO)OEP (light blue triangles, in CH$_2$Cl$_2$), $2^+\rightarrow$Ru(CO)OEP (green diamonds, in CH$_2$Cl$_2$) and $1^{4+}\rightarrow$Ru(CO)OEP (yellow diamonds, in CH$_2$Cl$_2$).

References.

[1S] A. Lausi, M. Polentarutti, S. Onesti, J. R. Plaisier, E. Busetto, G. Bais, L. Barba, A. Cassetta, G. Campi, D. Lamba, A. Pifferi, S. C. Mande, D. D. Sarma, S. M. Sharma, G. Paolucci, Eur. Phys. J. Plus 2015, 130(3), 1-8.

[2S] W. Kabsch, Acta Cryst. D 2010, 66, 125–132.

[3S] M. C. Burla, R. Caliandro, B. Carrozzini, G. L. Cascarano, C. Cuocci, C. Giacovazzo, M. Mallamo, A. Mazzone, G. Polidori, J. Appl. Cryst. 2015, 48 (1), 306–309.

[4S] G. M. Sheldrick, Acta Cryst. A, 2015, 71, 3-8.

[5S] G. M. Sheldrick, Acta Cryst. C, 2015, 71, 3-8.

[6S] P. Emsley, B. Lohkamp, W. G. Scott, K. Cowtan, Acta Cryst. D 2010, 66(4), 486–501.

[7S] L. J. Farrugia, J. Appl. Cryst. 2012, 45, 849-854.

[8S] L. Schrodinger, 2015, The PyMOL Molecular Graphics System. Schrodinger, LLC. http://www.pymol.org.

[9S] A. L. Spek, Acta Cryst. D 2009, 65, 148–155.

[10S] G. M. Sheldrick, SADABS Version 2014/5, University of Göttingen, Germany, 2014.

[11S] Y. Gao, V. Walter, M. J. Ferguson, R. R. Tykwinski, Chem. Eur. J. 2020, 26, 16712-16720.

[12S] R. G. Little, J. A. Ibers, JACS 1973, 95, 8583-8590; V. V. Shirokova, V. S. Tyurin, N. M. Stanetskaya, M. N. Sokolova, A. O. Shkirdova, and I. A. Zamilatskov, Prot. Met. Phys. Chem. Surf. 2019, 55, 1104-1112.