Synthesis and Nonlinear Optical Absorption of Novel Porphyrin – Osmium-Cluster Complexes

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Abstract: Reaction of azido(tetra-*p*-tolylporphyrinato)indium(III) [TTPInN$_3$] and [Os$_3$(μ-H)$_2$(CO)$_{10}$] in toluene at 80 °C overnight gave two major products, complexes **1** and **2.** Complex **1** had an axial bridge of "NH", while **2** had an axial bridge of "N" between the porphyrin and osmium cluster moieties. Complex **1** could be converted to **2** when refluxed in toluene. These two novel porphyrin – osmium clusters are the first axially linked porphyrin – metal cluster complexes. UV/Vis spectroscopy revealed the significant ground state electronic perturbation in the capped complex **2**, demonstrating that the remarkable electronic interaction of the moieties within the molecule was achieved by this special structural arrangement. In addition, the electrochemistry of **1** and **2** were investigated and their oxidation current voltage curves are similar to those of indium(III) – porphyrins with a metal – metal σ bond such as [TPPInRe(CO)$_5$] (TPP = tetraphenylporphyrin). The two new molecules also exhibit large nonlinear optical absorption at 532 nm with a ns pulse laser and are potential optical limiting materials for sensor protection in the visible region.

Keywords: azido ligands · cluster compounds · indium · nonlinear optics · osmium · porphyrinoids

Introduction

Recently, considerable effort has been devoted to the design and synthesis of supramolecular systems consisting of porphyrins and other organic chromophores (e.g. C$_{60}$) with the aim of exploring their remarkable intramolecular processes such as electron and energy transfer.[1, 2] In most of the porphyrin model compounds studied so far the chromophores are linked at the peripheral positions (*meso or β* positions) of the porphyrin ring. The electronic interaction between the two moieties in the macromolecules has not been explored in detail.[3] To increase the electronic interaction between the two chromophores and to investigate the nonlinear optical properties, we have designed and synthesized hitherto unknown model compounds that contain an axial nitrogen bridge between a porphyrin unit and an osmium metal carbonyl cluster.

Our extension of azidometalloporphyrin chemistry to reactions with osmium carbonyl clusters was based on the observation that the azido group at the center of a metalloporphyrin has shown reactivity similar to that of its organic counterparts.[4] Thus, for example, azidometalloporphyrins undergo 1,3-dipolar cycloadditions to dipolarophiles such as nitriles or alkynes to form metalloporphyrins with tetrazolato or triazolato axial ligands. Also, organic azides were reported to react with [Os$_3$(μ-H)$_2$(CO)$_{10}$] readily to form the bridged cluster [Os$_3$(μ-H)(CO)$_{10}$(HN$_3$R)] (R = Ph, *n*Bu, CH$_2$Ph, *cyclo*-C$_6$H$_{11}$), which was converted to the nitrogen-capped cluster [Os$_3$(μ-H)$_2$(CO)$_9$(μ_3-NR)] by thermolysis.[5] Herein, we report the reaction of azidoindium(III) – porphyrin with the osmium cluster [Os$_3$(μ-H)$_2$(CO)$_{10}$], which results in the formation of novel porphyrin – osmium cluster complexes linked through an axial nitrogen ligand.

Results and Discussion

Scheme 1 shows the synthetic route to the porphyrin – osmium cluster dyads. Reaction of azido(tetra-*p*-tolylporphyrinato)indium(III) [TTPInN$_3$] and [Os$_3$(μ-H)$_2$(CO)$_{10}$][6] in toluene at 80 °C overnight gave two major products, **1** and **2**, both of which were fully characterized by analytical and spectroscopic methods. The IR absorptions in the range of 1900 to 2100 cm^{-1} are characteristic of the metal carbonyl groups in **1** and **2**. The

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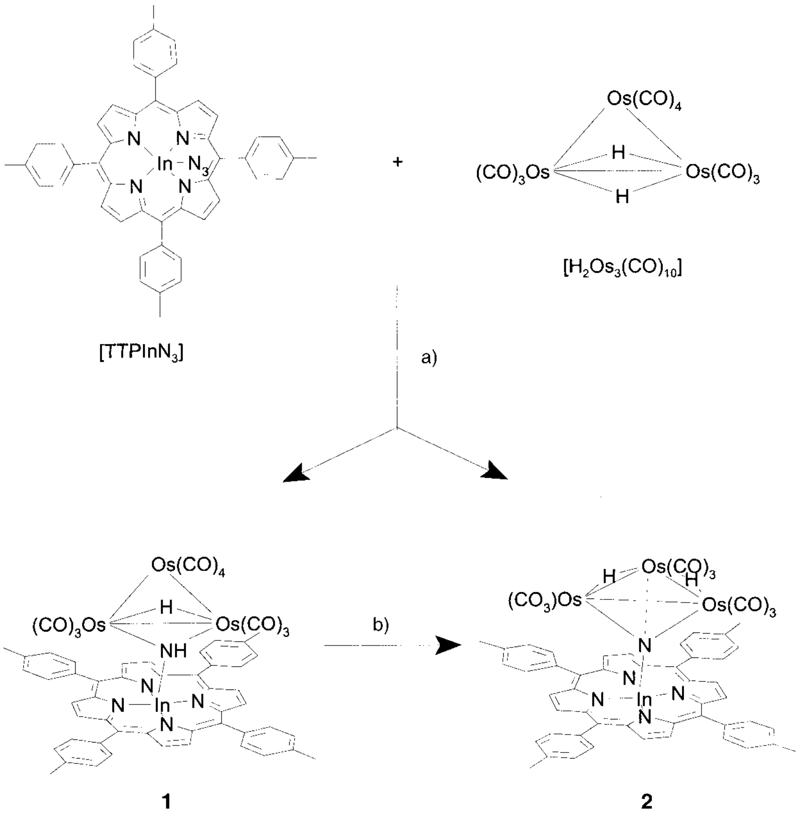

Scheme 1. Synthesis of complexes 1 and 2. a) Toluene, 80 °C, 16 h; b) toluene, refluxing overnight.

β-H atoms and the protons of the tolyl groups in the porphyrin moiety of **1** and **2** are observed with the expected ratio of 2:7 in the ^{1}H NMR spectra of the complexes. The ^{1}H NMR signals of the osmium-bridging hydride and the nitrogen-bonded proton in **1** are located at $\delta = -15.56$ (s, 1 H) and 1.28 (s, 1 H) ppm, respectively. The two osmium-bridging hydrides in **2** are chemically nonequivalent and two ^{1}H NMR signals are observed at $\delta = -14.59$ and -18.21 ppm with a coupling constant of about 3 Hz. In contrast, in the ^{1}H NMR spectrum for the reported cluster $[Os_3(\mu\text{-H})_2(CO)_9(\mu_3\text{-NR})]$ (R = Me), the two hydrides have the same chemical shift ($\delta = -18.74$ ppm).[7] This may be due to the unsymmetrical influence from the bulky porphyrin ring in complex **2**. Although the nitrogen atom is symmetrically capped to the osmium triangle, its coordination configuration could render the two hydrides different distances from the porphyrin plane. The mass spectra of **1** and **2** indicate the protonated parent molecular ion multiplets whose principal peaks were measured at *m/z* 1652.3 and 1624.7, respectively. The chemistry of **1** was also carefully studied. Upon refluxing in toluene solution overnight, the majority of **1** decomposed and **2** was obtained as the major product. It was also found that **2** was much more stable than **1**, the majority of the former remained unchanged in refluxing toluene solution overnight.

Single crystals of **1** were obtained by recrystallization from an *n*-hexane/dichloromethane solvent mixture and its structure was determined by X-ray crystallography (Figure 1). The cluster portion of **1** is similar to that of the cluster $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-NHSiMe}_3)]$.[8] Os1–Os2, the shortest edge of the osmium cluster triangle, is bridged by the μ-NH-InTTP moiety. The Os–N distances of 2.087(6) and 2.084(6) Å and the Os-N-Os angle of 83.7(2)° are similar to the corresponding values of 2.10(1), 2.13(2) Å, and 82.9(6)° in the cluster $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-NHSiMe}_3)]$. Although both the nitrogen-bonded proton and the metal–bridging hydride were not directly located in the crystal structure of **1**, their presence was confirmed by their ^{1}H NMR signals, as discussed above. While the geometry of the indium coordination polyhedron is not greatly influenced by the attachment of the osmium cluster, the In1–N1 bond length (2.053(6) Å) is considerably shorter than the average bond length of 2.163 Å for the indium porphyrin nitrogen bonds In–N(P). This may be attributed to the electronic influences such as the electronic interaction between the porphyrin and the osmium cluster. The distance from the mean plane of four porphinatonitrogen atoms to the indium ion is 0.591 Å, which is within the range of 0.463–0.791 Å reported for indium-containing porphyrins.[4] The dihedral angle between the Os_3 plane and the porphyrin ring is 36.3°. This conformation is defined by the coordination configuration of the axial nitrogen ligand, demonstrated by the similar angles of In1-N1-Os1 (132.4(3)°), In1-N1-Os2 (134.8(3)°), and Os2-N1-Os1 to those of Os1-N1-Si1 (135.1(8)°), Os2-N1-Si1 (135.6(8)°) and Os2-N1-Os1 in the cluster $[Os_3(\mu\text{-H})(CO)_{10}(\mu\text{-NHSiMe}_3)]$, respectively.

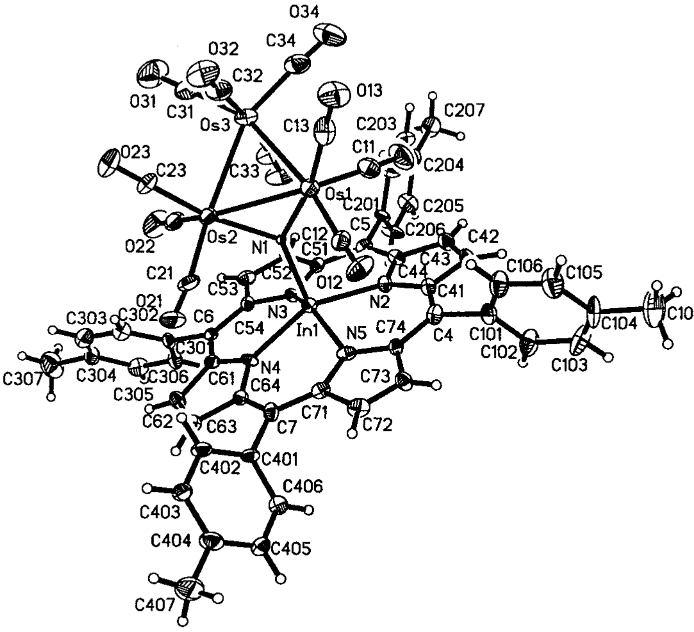

Figure 1. Molecular structure of complex **1**.

The electronic absorption spectra of the starting material $[TTPInN_3]$, complex **1**, and complex **2** are compared in Figure 2. The Soret (B) and Q bands of **1** are almost identical

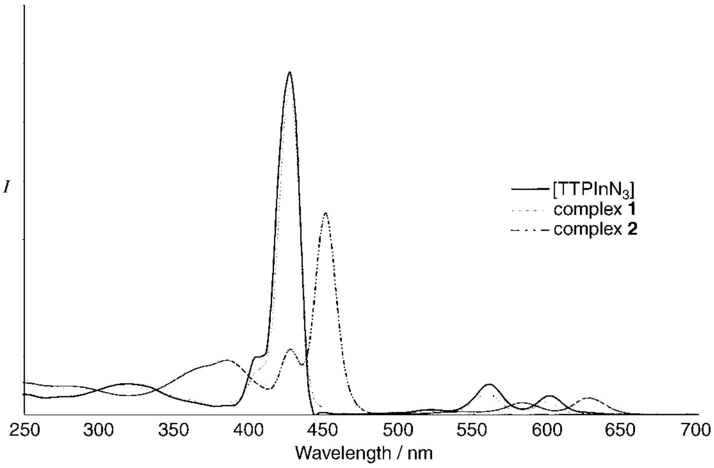

Figure 2. Electronic spectra of [TTPInN$_3$], **1**, and **2**.

to those of [TTPInN$_3$], indicating that the ground-state electronic interaction between the porphyrin and the osmium cluster is not significant. Interestingly, the Soret (B) and Q bands of **2** are clearly perturbed and remarkably shifted. The Soret band I is blue-shifted by 20 nm and the Soret band II is red-shifted by 24 nm. The two Q bands are red-shifted by 24 and 28 nm, respectively. Evidently, the capped structure provides a better configuration for the electronic interaction between the porphyrin and the osmium cluster, and direct interaction between the two moieties is achieved in this particular arrangement. Besides, the molar absorptivity ratio of ε(Soret II)/ε(Soret I) for **1** is greater than that for **2**. As a smaller ε(Soret II)/ε(Soret I) ratio is usually induced by a stronger electron-accepting axial ligand in a given metal–metal or metal–carbon-bonded (P)M(R) species (P = porphyrin, M = metal, R = axial ligand), our observation of a smaller ε(Soret II)/ε(Soret I) ratio for **2** demonstrates that the osmium cluster moiety in **2** is in a better position to function as an electron-accepting unit.

The interaction between the porphyrin and the osmium cluster moieties was also confirmed by the quenching effect of the osmium cluster moiety on the luminescence of the dyads (Figure 3). Porphyrin [TTPInN$_3$], excited at 428 nm, displays fluorescence maxima at 613 and 663 nm. Complex **1**, excited at 428 nm, shows an emission spectrum with characteristic features of the porphyrin.[9] However, the porphyrin emission is quenched by the attached osmium cluster to about half of that for [TTPInN$_3$]. As for complex **2**, excited at 452 nm, the emission from porphyrin is further quenched by a factor of 7 and the emission is red-shifted by about 30 nm. The greater quenching effect observed in dyad **2** is probably attributed to a more efficient electron/energy transfer.

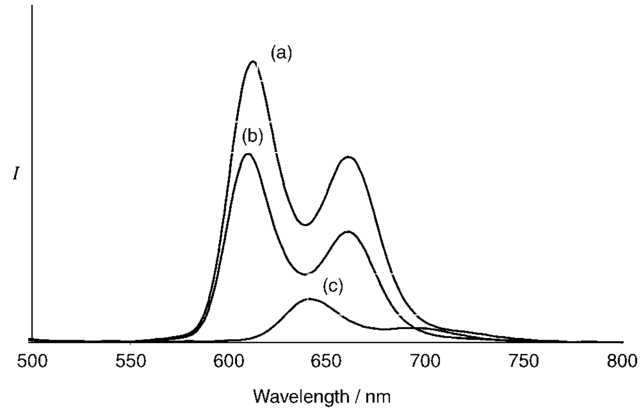

Figure 3. Fluorescence spectra of a) [TTPInN$_3$], b) **1**, and c) **2** (all samples in CH$_2$Cl$_2$; concentration 10^{-5} M). The Soret band was chosen as the excitation wavelength.

The electrochemistry of dyads **1** and **2** was investigated in CH$_2$Cl$_2$ containing 0.1 M tetrabutylammonium hexafluorophosphate (TBA(PF$_6$)) and their cyclic voltammograms are illustrated in Figure 4. Both dyads exhibit similar current–voltage curves with two electroreductions and three electrooxidations. The initial reversible reduction occurs at $E_{1/2} = -1.36$ and -1.28 V for **1** and **2**, respectively, followed by a second irreversible reduction located at $E_p = -1.82$ and -1.72 V, respectively. The absolute potential differences between the first and second reduction are 0.38 and 0.36 V for **1** and **2**, respectively, indicating that the electroreduction most likely occurs at the porphyrin π-ring system.[10] Among the three electrooxidations, the initial oxidation is not coupled to a return reduction peak; however, the value of $|E_p - E_{P/2}|$ is within the range of 65 ±5 mV. It is very likely that a diffusion-controlled one-electron-transfer is involved. The second and the third reversible oxidations of **1** and **2** occur at similar potentials which are similar to that observed for TPPInCl in CH$_2$Cl$_2$.[11] This type of three electrooxidation process has been reported for indium(III)–porphyrins with metal–metal σ bonds, for example [TPPInRe(CO)$_5$] (TPP = tetraphenylporphyrin).[12] As in [TPPInRe(CO)$_5$], the oxidation of **1** and **2** can be rationalized by the initial formation of an unstable singly oxidized product [TTPInL]$^{+\bullet}$ (L = {NH-[HOs$_3$(CO)$_{10}$]} for **1** and {N-[H$_2$Os$_3$(CO)$_9$]} for **2**), followed by a rapid In–N bond cleavage to yield [TTPIn^{III}]$^{2+}$ and further oxidation to [TTPIn^{III}]$^{3+}$. The difference in the half-wave potentials between the first oxidation and the first reduction (ΔE) in both of the dyads falls within the range of 2.25 ±0.15 V, as generally observed for porphyrin ring centered oxidations and reductions.[13] However, the two dyads differ somewhat in that ΔE of **2** is smaller than that of **1** by 0.12 V, consistent with the red-shifted major absorptions of **2** in the UV/Vis spectrum (Figure 2).

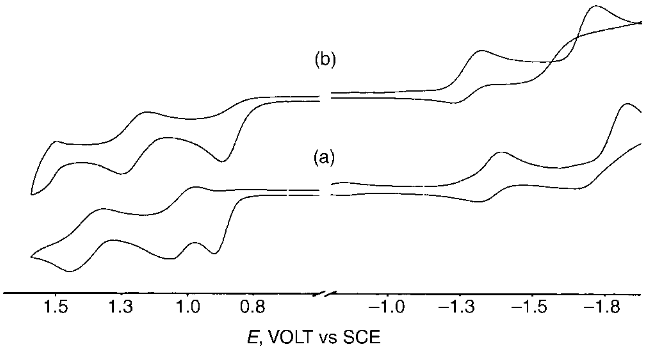

Figure 4. Cyclic voltammograms for the reductions and oxidations of a) **1** and b) **2** in CH$_2$Cl$_2$ containing 0.1 M TBA(PF$_6$) at the scan rate of 50 mV s^{-1}.

To explore the novel features of the new complexes for optical limiting applications, we have measured their nonlinear absorption at 532 nm with a 5 ns laser pulse width using the Z scan[14] technique. Porphyrins and metalloporphryins are important optical limiters that strongly attenuate optical beams at high intensities while exhibiting high transmittance at low intensities.[15] They have the potential to protect human eye and optical sensors from exposure to intense laser pulses. Intense investigations are being conducted in attempt to improve their nonlinear optical performance by molecular modification.[16]

The Z scan technique has been used to study the third-order nonlinear optical processes of many materials including two-photon absorption in zinc selenide and reverse saturable absorption (RSA) in porphyrins[17] and C_{60}.[18] This technique involves moving a sample along the z axis of a focused laser beam. The intensity of light on the sample is maximum when the sample is at the focus of the beam. By moving the sample along the z axis through the focus, the intensity-dependent absorption is measured as a change of the transmission through the sample by using a detector in the far field. If a material exhibits RSA, a decrease in transmission can be observed as the sample moves through the focus.

From the data collected, the open aperture Z scans, the transmittance, T was fitted for the case of RSA behavior[19] to Equation (1), in which where $q_0 = \sigma_{ex}^{eff} \alpha F_0 L_{eff}/2\,h\omega$ and $x = z/z_0$.

$$T = \frac{\ln\left[1 + \left(\frac{q_0}{1+x^2}\right)\right]}{\left(\frac{q_0}{1+x^2}\right)} \tag{1}$$

σ_{ex}^{eff} is the effective excited state cross section, which for the given laser pulse duration of 5 ns, contains contributions from both the singlet and triplet states, assuming that the intersystem crossing (ISC) takes place within the duration of 5 ns. α is the linear absorption coefficient, F_0 is the fluence, L_{eff} is the effective length of the sample $[(L - \exp(-\alpha L)]/(\alpha)$, and z_0 is the Rayleigh range. The σ_{ex}^{eff} values at 532 nm for [TTPInN$_3$], complex **1**, and complex **2** are listed in Table 1. The typical curves obtained for C_{60} and complex **1** are shown in Figure 5. Complex **2** displays a similar curve to that of dyad **1**. As all the samples have the same linear transmission at 532 nm, it is evident that complex **1** and complex **2** exhibited a much better optical limiting effect than that of C_{60}. The transmittances for C_{60}, [TTPInN$_3$], dyad **1**, and dyad **2** decrease from 88% to 73%, 60%, 58%, and 56%, respectively, when the samples are moved from far field to the focal point, where the peak input laser fluence is about 0.18 J cm^{-2}. Figure 5 also shows the theoretical fit (solid line) to Equation (1). The ratio of the excited-state to ground-state absorption cross-section ($\sigma_{ex}^{eff}/\sigma_g$), a figure-of-merit for optical limiting performance, has been calculated. The figure-of-merit for C_{60} obtained from our experiment is 3.70, comparable to that reported by Perry and co-workers.[20] The results for the dyads are consistent with the fact that the optical limiting effects of the two dyads are better than that of C_{60}[21] and the pristine molecular [TTPInN$_3$] at 532 nm. Porphyrins and metalloporphyrins are known to have the RSA at 532 nm, and molecular modifications by incorporating functional groups on the porphyrin ring and insertion of metal ions in the center are adopted to improve their nonlinear optical behavior. Our experiment has demonstrated that the nonlinear optical absorption can also be enhanced by coordinating osmium clusters to the axial position. This enhancement is attributed to the reduced ground-state absorption coefficient of dyad **1** and dyad **2** (as seen in Figure 2), and a probable increased excited-state absorption coefficient at 532 nm. Further study using a time-resolved pump – probe technique will be conducted to reveal how their structure and optical properties are related.

Table 1. Ground-state and excited-state absorption cross-sections for [TTPInN$_3$], **1**, and **2**.

Compound	Ground-state cross-section (σ_g, cm^2)	Excited-state cross-section (σ_{ex}^{eff}, cm^2)	Figure of merit ($\sigma_{ex}^{eff}/\sigma_g$)
[TTPInN$_3$]	1.33×10^{-17}	3.8×10^{-17}	2.86
1	8.73×10^{-18}	3.7×10^{-17}	4.24
2	9.62×10^{-18}	4.4×10^{-17}	4.57

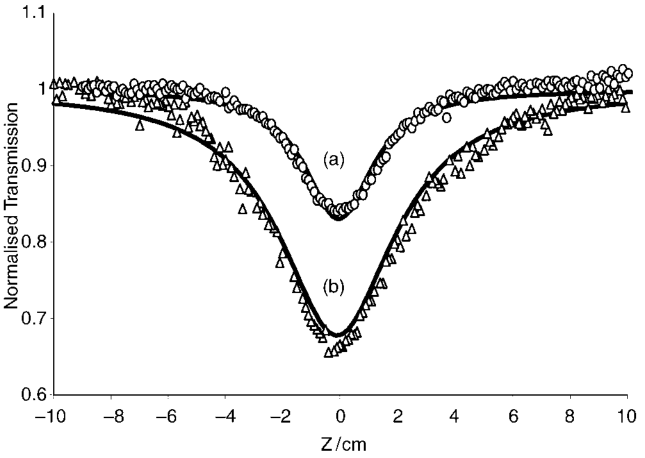

Figure 5. Z scans of a) C_{60} ($T = 88.0\%$ in toluene), b) **1** ($T = 88.0\%$ in CH_2Cl_2) taken at 532 nm with a 5 ns pulse width. The solid line in each case shows the optimized fit to Equation (1).

Conclusion

In conclusion, two novel porphyrin – osmium cluster complexes were synthesized and characterized. By obtaining the complexes with the same nitrogen ligand but different bridging models, the coordination chemistry for both the osmium carbonyl cluster and the porphyrin was further investigated. The significant ground-state electronic perturbation and photoluminescence quenching observed in the capped complex **2** demonstrated the remarkable interaction of the moieties within the molecule. The preliminary nonlinear optical study has shown that both of the two dyads have better optical limiting performance than that of C_{60} at 532 nm. In view of the rich chemistry of porphyrins, the versatility of the osmium carbonyl cluster, and the extensive availability of various axial bridging ligands, the results obtained here have undoubtedly opened the possibilities of design and synthesis of a series of unique porphyrin – metal cluster supramolecules. It should now be possible to establish a relationship between their interesting structures and useful electronic/spectroscopic properties. The establishment of this type of structure – property relationship is desirable to design molecules with improved nonlinear optical properties.

Experimental Section

General: All steps in the synthesis prior to the termination reaction were carried out under a nitrogen atmosphere. Solvents were purified, dried, and distilled under purified nitrogen. FTIR: Perkin-Elmer Spectrum 1600; UV/Vis: Unicam UV 2; fluorescence spectra: Perkin-Elmer LS 50 B spectrofluorophotometer; MS (ESI-TOF): Mariner Biospectrometry Workstation; ^{1}H NMR: Bruker ACF 300 (300 MHz).

Cyclic voltammetric study: Cyclic voltammetric studies at room temperature were performed on an Eco Chemie PGSTAT20 potentiostat/galvanostat in a nitrogen-filled dry box (Vacuum Atmosphere Co.; $O_2 <$ 5 ppm, $H_2O < 10$ ppm). CH_2Cl_2 was distilled from P_2O_5 under nitrogen and $n\mathrm{Bu_4PF_6}$ was dried in vacuo at 80 °C prior to use. The electrochemical cell consisted of platinum working and counter electrodes and a silver wire as a reference electrode. The supporting electrolyte was $n\mathrm{Bu_4PF_6}$ (0.1 M) in CH_2Cl_2 and the $\mathrm{Fc/Fc^+}$ redox couple was used as internal reference standard.

Z scan: Our Z scan experiments were conducted by using 532 nm, 5 ns duration laser pulses at the repetition rate of 20 Hz, generated by a frequency-doubled Q-switched Nd:YAG laser. A small part of the input beam is split using a glass plate to monitor the input energy. The major part of the laser beam is focused with a 250 mm focal length lens, and the sample is scanned across the focus using a micrometer translation stage, which is controlled by a computer. The transmitted energy is collected directly by a photodiode detector for open aperture measurement. All the data points are obtained by averaging the measurements of around 40 shots. All the samples were prepared as solutions and had approximately 88% linear transmission of the materials themselves at 532 nm.

Synthesis of complex 1 and 2: $[\mathrm{TTPInN_3}]$ was synthesized according to reference [4] and characterized by ^{1}H NMR, IR, and UV/Vis spectroscopy, and mass spectrometry. $[\mathrm{TTPInN_3}]$ (82.0 mg, 0.1 mmol) and $[\mathrm{Os_3(\mu\text{-}H)_2(CO)_{10}}]$ (85.0 mg, 0.1 mmol) were dissolved in toluene (20 mL) and heated at 80 °C under a nitrogen atmosphere for 16 h. The reaction mixture was worked up and subjected to flash chromatography on silica gel using *n*-hexane/dichloromethane (v/v = 3:1) as eluent, to yield two major compounds; first fraction: **1** (39.2 mg, 23.7%, red purple), second fraction: **2** (7.2 mg, 4.4%, dark green).

Complex 1: UV/Vis (CH_2Cl_2): $\lambda_{\max}$ ($10^3\varepsilon$, $\mathrm{M^{-1}cm^{-1}}$) = 404.0 (35.0, Soret I), 428.0 (278.6, Soret II), 560.0 (18.3), 600.0 (10.5) nm; fluorescence (λ_{exc} = 428.0 nm, CH_2Cl_2): $\lambda_{\max}$ = 612.0, 662.0 nm; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS): δ = 9.07 (s, 8 H; β H atoms in the porphyrin ring), 8.35, 7.87, 7.67, 7.52 (d, J = 6.6 – 7.4 Hz,4 H each; -*p*-C_6*H_4*-CH_3), 2.73 (s, 12 H; -*p*-C_6H_4-*CH_3*), 1.28 (s, 1 H; NH), – 15.56 ppm (s, 1 H; OsH); IR (CH_2Cl_2): $\tilde{\nu}$ = 2098.0w, 2055.0s, 2045.0m, 2008.0vs, 1981.0sh, 1965.0sh $\mathrm{cm^{-1}}$; ESI-TOF MS: 1652.3 [$M^+ + 1$]; elemental analysis for $C_{58}H_{38}N_5InO_{10}Os_3$: calcd: C 42.21, H 2.30, N 4.24; found: C 41.99, H 2.40, N 3.61.

Complex 2: UV/Vis (CH_2Cl_2): $\lambda_{\max}$ (10^3 ε, $\mathrm{M^{-1}cm^{-1}}$) = 384.0(46.1, Soret I), 452.0 (172.3, Soret II), 584.0 (10.1), 628.0 (14.1) nm; fluorescence (λ_{exc} = 452.0 nm, CH_2Cl_2): $\lambda_{\max}$ = 643.0, 701.0 nm; ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C, TMS):δ = 9.02 (s, 8 H; β H atoms in the porphyrin ring), 8.08, 7.55 (d, J = 7.4 and 8.3 Hz, respectively, 8 H each; -*p*-C_6*H_4*-CH_3),2.71 (s, 12 H; CH_3, -*p*-C_6H_4-*CH_3*), – 14.59 (d, J = 2.5 Hz, 1 H; OsH), – 18.21 ppm (d, J = 3.3 Hz, 1 H; OsH); IR (CH_2Cl_2): $\tilde{\nu}$ = 2098.0m, 2071.0m, 2058.0s, 2008.0vs $\mathrm{cm^{-1}}$; ESI-TOF MS: 1624.7 [$M^+ + 1$], elemental analysis for $C_{57}H_{38}N_5InO_9Os_3 \cdot 0.5\,C_6H_{12}$: calcd: C 43.30, H 2.66, N 4.21; found: C 43.46, H 3.04, N 4.63.

Crystal structure analysis for complex 1: Crystallographic data: $C_{64}H_{48}InN_5O_{10}Os_3$ from cyclohexane/CH_2Cl_2, M_w = 1732.49, monoclinic, space group *P*2(1)/*c*, a = 14.9447(1), b = 28.6076 (5), c = 15.6948 (3) Å, β = 91.103 (1)°, V = 6708.8(2) $Å^3$, Z = 4, ρ = 1.715 $\mathrm{g\,cm^{-3}}$, F(000) = 3296, $\lambda(\mathrm{Mo_{k\alpha}})$ = 0.71073 Å, crystal dimensions 0.26 × 0.22 × 0.08 $\mathrm{mm^3}$. A total of 44046 reflections was collected at room temperature using a Siemens diffractometer equipped with a CCD detector in the range of 1.93 to 29.40°, of which 16717 were unique (R_{int} = 0.0975). The structure was solved by direct methods and the refinement was by the full-matrix, least-squares method with all non-hydrogen atoms refined anisotropically. Two cyclohexane molecules were found to be disordered and were modeled by standard procedures. The largest peak and hole in the difference map were 1.345 and – 1.432 e $Å^{-3}$, respectively. The least-squares refinement converged normally giving residuals of R = 0.0645 and wR^2 = 0.1152. All computations were carried out using a SHELXTL (v. 5.10) program.
CCDC-150092 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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