Supporting Information

Tripodal Osmium Polypyridyl Complexes for Self-Assembly on Platinum Nano-Particles

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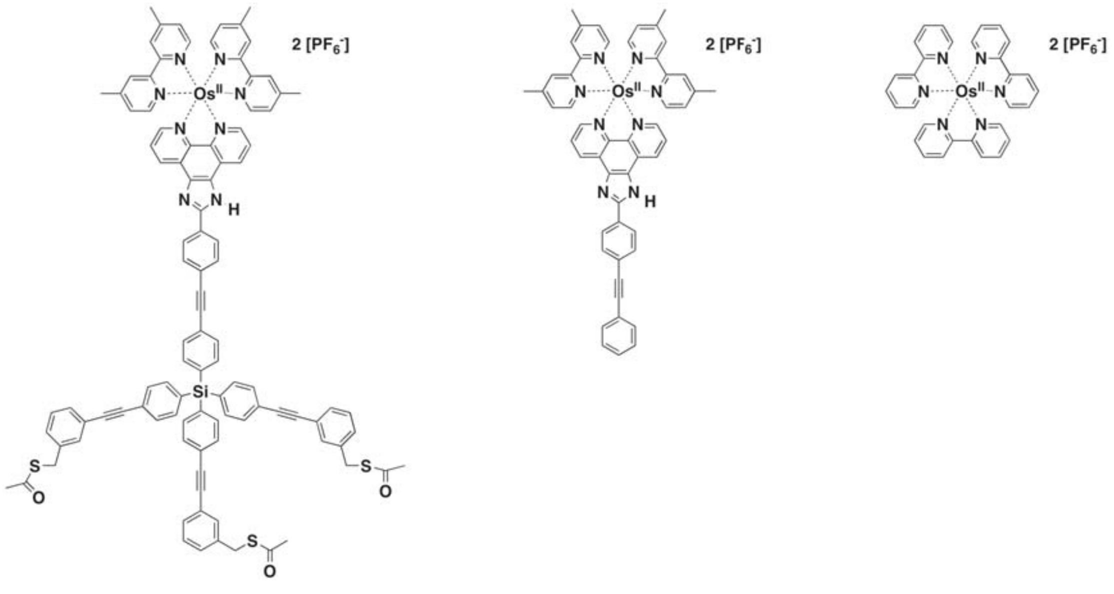
Content:

Structures of compounds used

Chart S1. Chemical structures of the complexes studied. The Os-trip complex is functionalized for the attachment to metal surfaces with three legs terminated with thioacetate groups. For control compounds Os-ph and Os-bpy were used.



Os-trip **Os-ph** **Os-bpy**

Synthesis of the citrate stabilized platinum nano-particles

K_2PtCl_4 (47% Nominal content, 99.9% purity) was purchased from H. Drijfhout & Zoon’s Edelmetaalbedrijven B.V. The rest of the chemicals were purchased from commercial sources and used without purification.

The platinum source is a platinum salt (K_2PtCl_4) in an aged aqueous solution. Aging of the solutions has proven to favor the reduction process because of the exchange of the Cl^- ligands for H_2O ligands. Platinum (II) partially coordinated to water is more easily transformed to platinum (0).[1] As reducing and capping agent sodium citrate was chosen. The obtained colloids are in an aqueous phase and show a narrow size distribution.[2]

The reduction process took place by mixing the two reaction components (aged platinum salt and citrate) and heating the obtained aqueous solution to a gentle reflux while stirring. The solution’s color changed from orange to dark brown as soon as reflux was reached but the beginning of colloid formation can be observed already around 70ºC. The reaction was allowed to take place for 3h to assure the complete reduction of platinum ions present in the solution. Longer refluxing periods did not show an influence on the stability of the colloids, no precipitation of platinum black could be observed.

After the reaction, the nano-particles were centrifuged in order to obtain a separation from the aqueous medium. To induce precipitation and favor the separation different organic solvents were added (MeCN, EtOH, MeOH, propanol or THF). Centrifugation up to 15000 rpm did not induce the desired precipitation indicating a very small particle size and high stability. Addition of MeCN gave partial precipitation of the particles but only in ratios of MeCN:particle solution 7:1 in volume. At this concentration of acetonitrile sodium citrate showed no apparent solubility making a purification process with this solvent mixture useless. The purification of the colloid to eliminate excess stabilizing molecule present was thus not further pursued. However, any remains of citrate, if any, should be “transparent” to spectroscopy and should not influence possible measurements.

Procedure

To an aged (7 d) aqueous solution of K_2PtCl_4 a sodium citrate solution in water was added to a final concentration of platinum salt of 4 mM and citrate 1.7 mM. Under efficient stirring the reaction mixture was heated to reflux. The reaction color changed from red-orange to brown once the oil bath reached 70°C indicating the start of the formation of platinum colloid. The reaction was allowed to continue for 3 h during which the mixture turned dark brown and then allowed to cool down overnight while stirring under nitrogen. The nano-particles were characterized with IR and HR-TEM and used without further purification. The particles could be isolated in solid state by removal of the solvent in vacuo and re-suspended without apparent decomposition.

Formation of the tripod-nano-particle assemblies

To 20 ml of a solution of the osmium tripodal complex in acetonitrile (concentration ~ 5×10^{-3} M) another 5 ml of aqueous solution of nano-particles stabilized with citrate was added (approximated concentration 1 mg/ml). The mixture was ultra-sonicated for 1 h and then allowed to stir for 24 h during which a brown precipitate formed.[3] The precipitate was collected by centrifugation. The precipitate was washed until no osmium tripod could be observed in UV- Vis spectrum of the washings (2x5ml). The solid was then dried under high vacuum overnight. The obtained sample was powdered and re-suspended in dioxane or ethylene glycol treating the mixtures first in an ultrasound bath and then stirring for 24 h under inert gas atmosphere.

UV-Vis and luminescence spectra

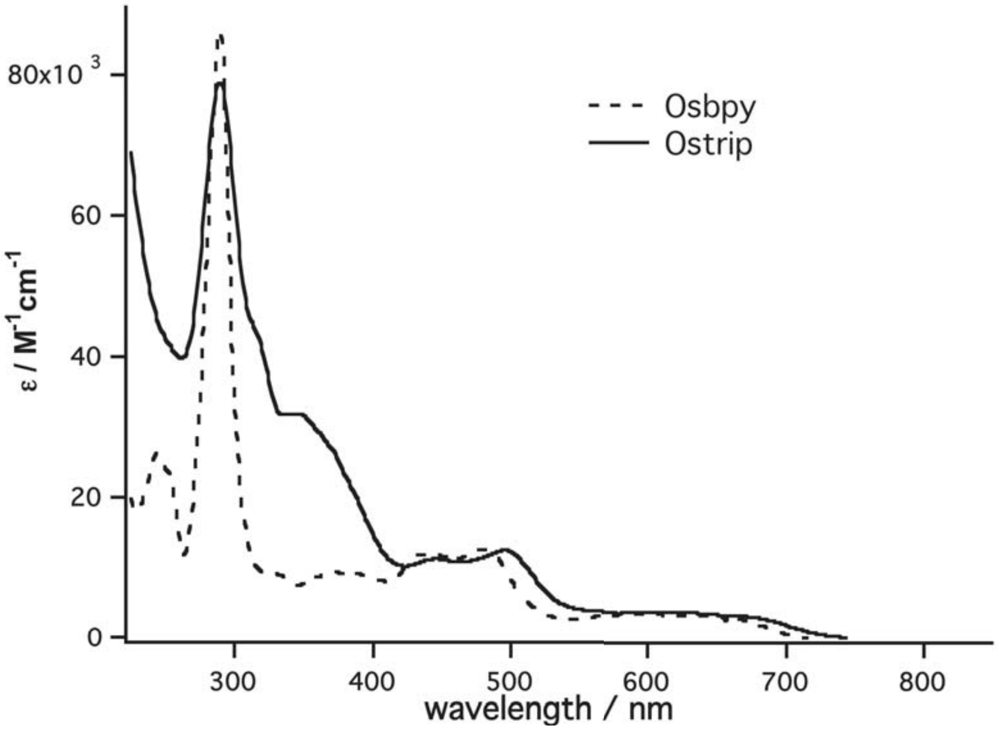


Figure S1. UV-Vis absorption spectra of the compounds Os-trip and Os-bpy used in this study. The solvents was water:acetonitrile mixtures 10:1. See table S1 below.

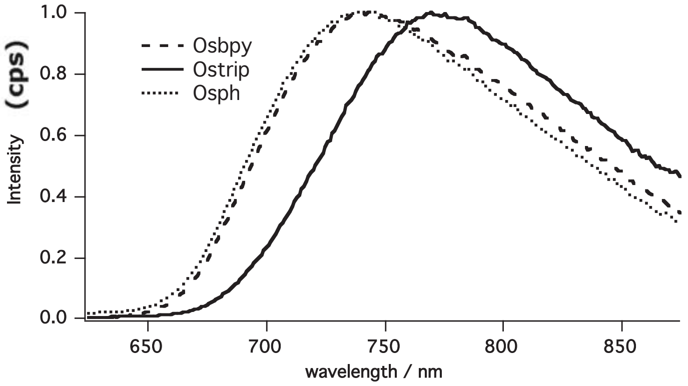


Figure S2. Normalized steady state luminescence spectra of the complex used in this study. Excitation was at 480 nm in water:acetonitrile mixtures 10:1. See table S1 below.

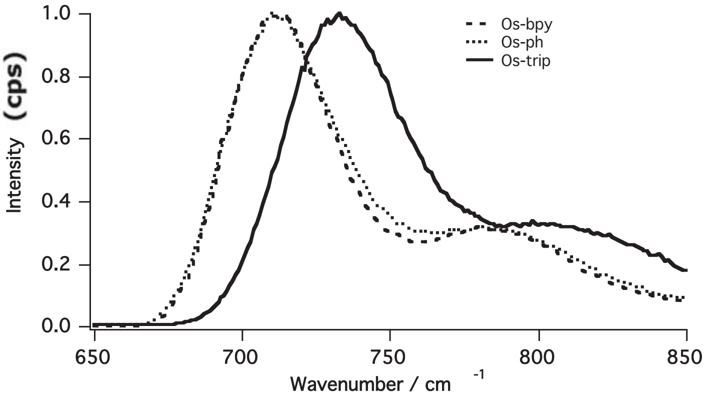


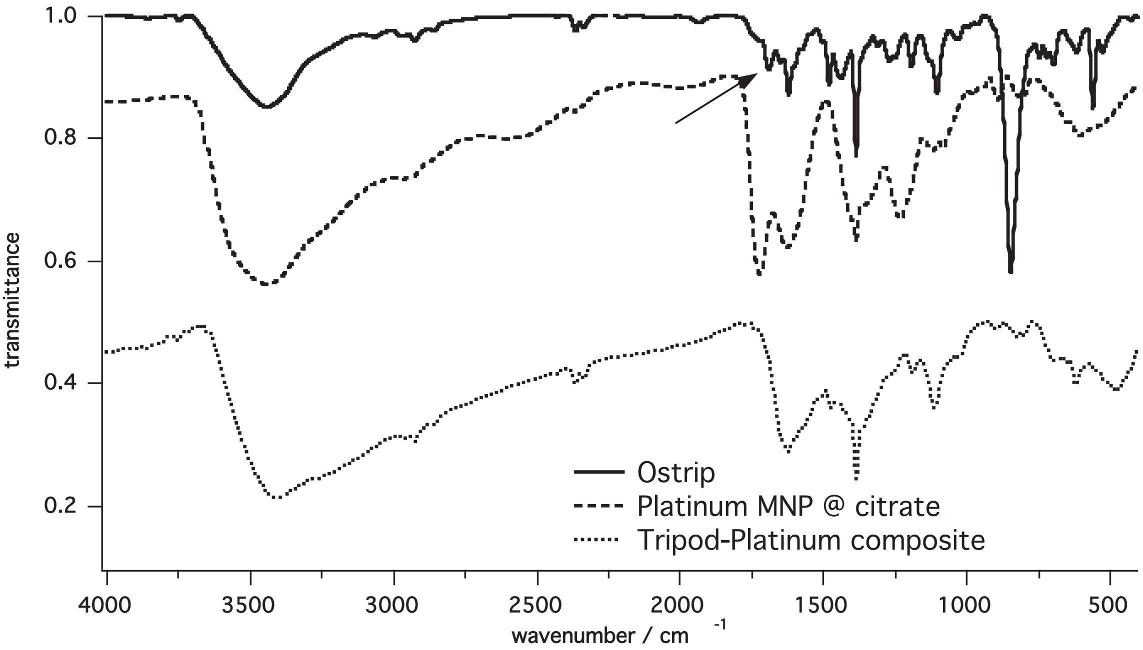
Figure S3. Normalized low temperature emission spectra of complexes Osph, Osbpy and Ostrip in rigid butyronitrile matrix at 77K. Excitation at 500 nm.

Compound	**ε (l,nm)/ M^{-1} cm^{-1}**	**Emission λ_{max}**	**Luminescence quantum yield (air)**	**Luminescence quantum yield (Ar)**
Os-trip	**290 (77000)** **495 (12500)** **630 (4100)**	**770**	**0.004**	**0.006**
Os-ph	**290 (89000)** **490 (17500)** **630 (6500)**	**740**	**0.003**	**0.004**
Os-bpy	**244 (26000)** **290 (86500)** **480 (12600)** **600 (3400)**	**740**	**0.0035**[4]	**0.005**[4]

Table S1. The quantum yields were measured following the procedure of the optically dilute method with excitation at 480 nm. The quantum yields are in the region of the well known corresponding reference compound Os-bpy, the quantum yield values for this compound are known from the literature.

IR spectroscopy of MNP attachment

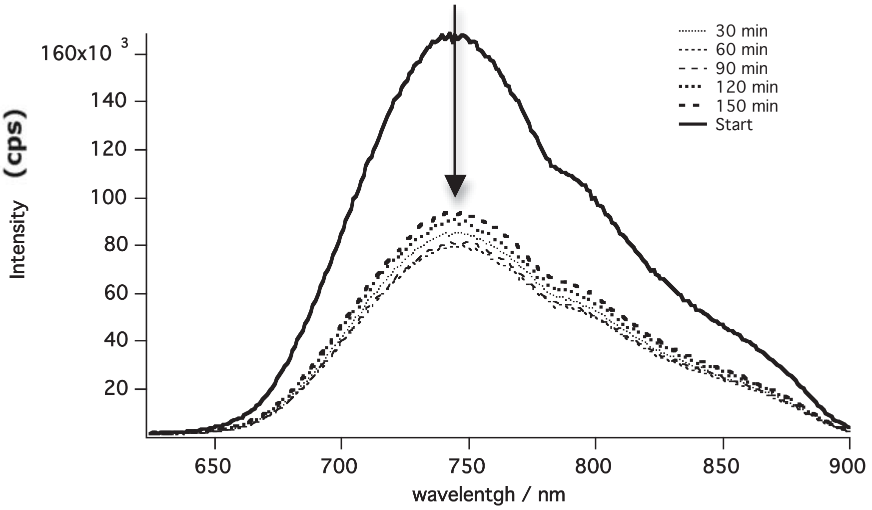
Figure S4. Infrared spectra of the tripodal osmium complex Os-trip, the platinum nanoparticles stabilized with citrate and the nano-composite in which the complex is attached to the surface of the nano-particles and the citrate has been displaced.



The assignment of the bands was done according to general infrared spectroscopy tables.[5] The **Os-trip** complex was anchored in acetonitrile solution by mixing with citrate stabilized nanoparticle solution and stirred overnight. After purification the osmium coated particles were isolated as a brown solid and analyzed. Our tripodal complex, **Os-trip**, presents as attaching anchors thioacetate groups. The carbonyl bond of the thioacetate group has a characteristic absorption between 1675 and 1720 cm^{-1}. In the case of the osmium tripod the band corresponding to this bond appears at 1690 cm^{-1} with medium intensity. In the assembled nano-composite system this band is not visible since the structure of the vibrational band changes from two adjacent peaks to only one broad vibration (arrow in figure S4). This could also indicate that during the attachment of the thioacetate to the rigid metal surface a hydrolyzed species is formed resulting in a platinum-sulfur bond. Another striking difference is the band at 850 cm^{-1} for **Os-trip**. This band can be assigned to vibrations of the hydrogens in para-substituted benzene rings. After attachment to the particles this band becomes weak showing that in the assembled system distortions are introduced into the tripod structure. A similar very strong band is also observed in the IR spectrum of diphenylacetylene.[6]

Emission spectroscopy of MNP attachment

Figure S5. Steady state luminescence quenching of the Ostrip complex by attachment to platinum MNP. The luminescence was monitored over a period of 2.5 hours. [Ostrip] = $5x10^{-5}$M; excitation at 495 nm, A(495) = 0.56. Argon saturated (degassed) conditions. The spectra are uncorrected for the detector response in the infrared.



The luminescence of the **Os-trip** complex was measured in acetonitrile solution. Addition of the platinum particles induced an immediate reduction of the luminescent signal. The luminescence was compared to an iso-absorptive solution in the exact same concentration of the complex without particles as comparative standard. The luminescence of the **Os-trip** was followed over a period of 2.5 hours with a total decrease of the original luminescence of 52% at the end of the experiment (figure S5 indicated by arrow). In a control experiment a solution of **Os-bpy** with the same absorbance at excitation as in the previous experiment was prepared and platinum MNP were added in the exact same amount as before. Only a minor reduction (5 %) of the emission intensity was observed.

Nanosecond transient absorption

Figure S6 shows the nanosecond transient absorption spectrum of the tripod compound, **Os-bpy** and the compound **Os-ph** after excitation at 500 nm. The compound with the phenanthroline like ligand presents a longer lived transient signal than the reference compound confirming that the tripod base is influencing to some extent the excited state of the molecule.

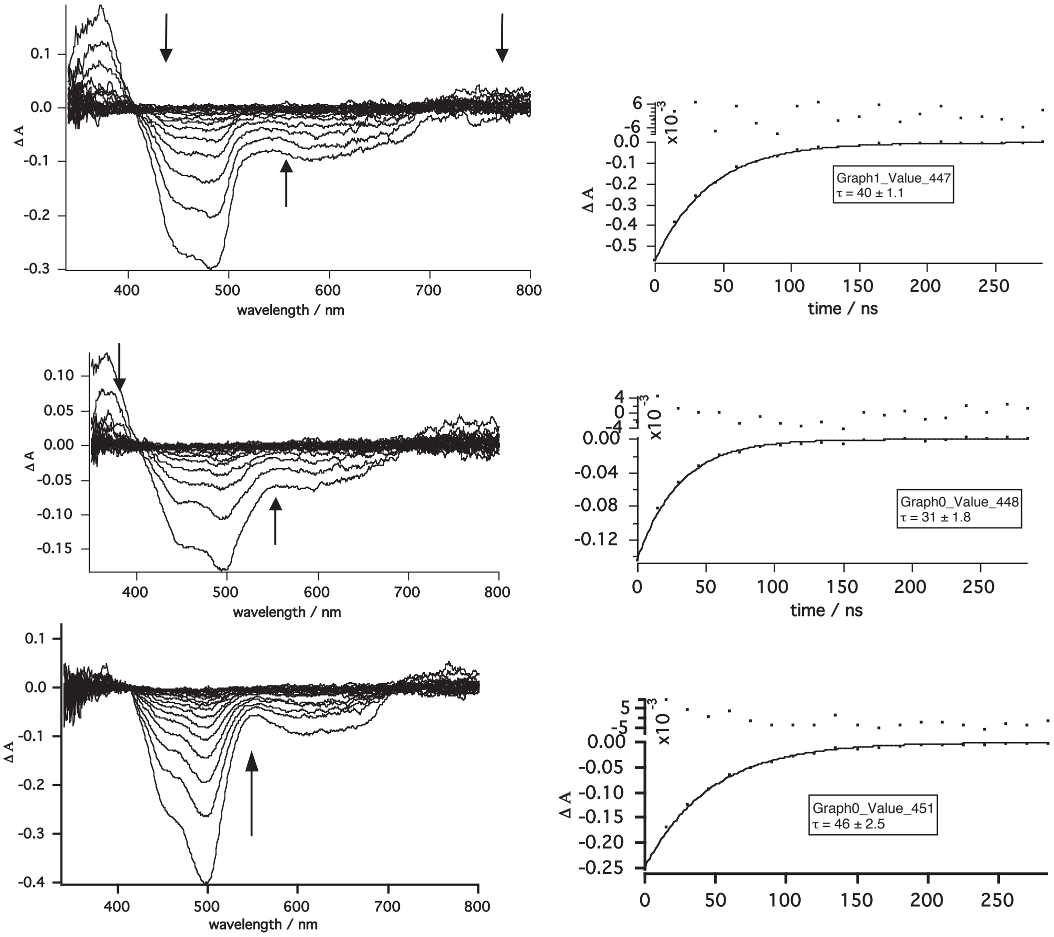


Figure S6. Nanosecond transient absorption spectrum of Os-bpy (upper spectrum and trace) and Os-ph (middle spectrum and trace) and Os-trip (lower spectrum) in acetonitrile:water mixture 8:1 solution after 500 nm laser excitation. The increment per frame is 15 ns. A kinetic trace is also shown (right) showing the repopulation of the bleached ground state within the given time-window. Lifetimes shown in nanoseconds.

The lifetime for the excited state observed, is in good agreement with the time resolved luminescence measurements (not shown here), indicating that the state responsible for the emission of the excited complex is the same state responsible for the absorption spectrum shown here. The shape of the transient signal also shows some differences for the two complexes when compared to the parent compound.

More detailed information about the electronic nature of the lowest excited state can be obtained from a more elaborate interpretation of the time-resolved transient absorption spectroscopy. Upon excitation of the osmium tris-bipyridine complexes, the lowest excited state can be described as MLCT. A negative charge is formally localized on the ligand with the lowest reduction potential and the metal center is formally oxidized.

In a transient spectrum this can be visualized by the appearance of the strong bleaching between 400 and 550 nm corresponding to the ^{1}MLCT absorption band in the UV-Vis spectrum. In this case also the transient signal corresponding to the ^{3}MLCT absorption can be seen at 630 nm, a characteristic feature for this type of osmium compounds because of the strong spin-orbit coupling due to the presence of the heavy osmium atom. The formally reduced ligand, for example the bipyridine radical anion or $bpy^{\cdot -}$ of the **Os-bpy** complex, has positive absorption bands that appear below 400 nm and above 700 nm. The absorption of this radical is rather low in intensity when compared to analogous ruthenium complexes. This difference can be explained by the presence of the ^{3}MLCT bleach in the same region.

In general the negative charge of the MLCT state will localize on the ligand with the lowest reduction potential because it can more easily take up the electron. If in fact the excited state of the tripod molecules studied here is on the more substituted ligand it is expected to result in different spectra for these complexes when compared to the parent complex **Os-bpy**.

The differences could be due to the fact that in the **Os-bpy** the metal ion is coordinated to 3 identical ligands while for the other complexes we are in the presence of slightly different chelating units. Therefore we expect for the reference complex only one possible MLCT $d_{Os}\rightarrow\pi_{bpy}$ transition while for the heteroleptic complexes 2 possible MLCT transitions are possible at slightly different energies: $d_{Os}\rightarrow\pi_{bpy}$ or $d_{Os}\rightarrow\pi_{phen}$. In particular the transition to the bpy in the tripod complex should occur at lower energy due to the more electron rich character of the osmium coordinated to the more donating substituted phenanthroline.

Femto second transient absorption spectroscopy

In order to have more insight into the localization of the excited state in these molecules we decided to measure sub-picosecond transient absorption spectra. In this faster time-scale the information gathered supports what we observed in the nanosecond transient. The spectra can be seen in S7. It is clear that the differences are not significant enough to indicate that parent compound and derived complexes have the excited MLCT state localized in a different ligand.

In our case the similarities indicate that the excited state of these molecules comes from the formal transfer of one electron from the osmium center to one of the bipyridines.

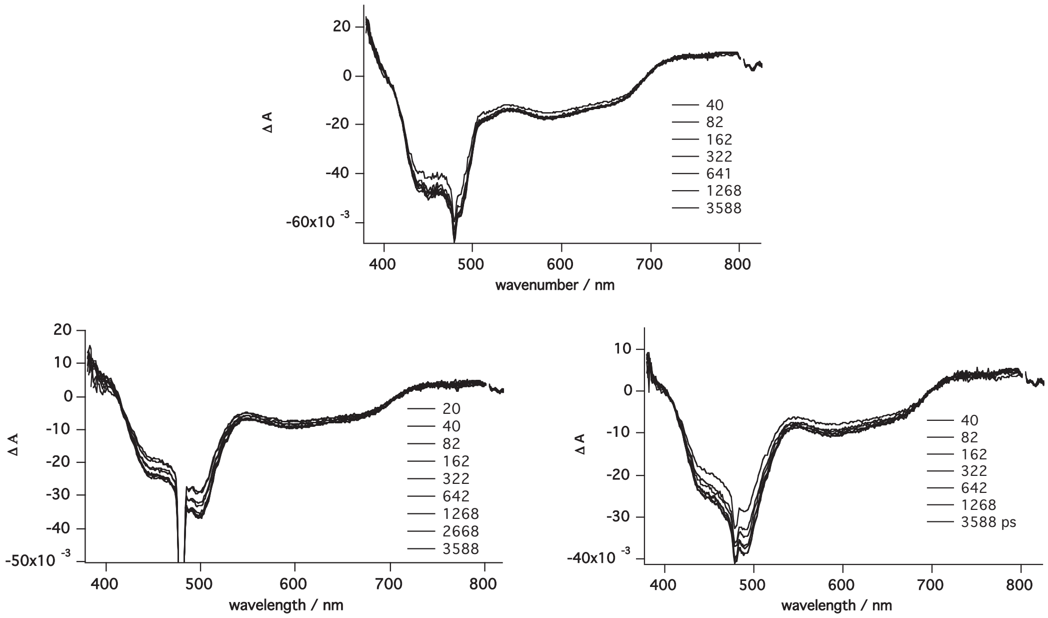


Figure S7. Sub-picosecond transient absorption spectra of the complexes Os-bpy (upper spectrum), Os-ph (lower left) and Os-trip (lower right) after FWHM 130 fs laser pulse excitation at 480 nm. The laser pulse can also be seen in the spectra. The solvent used was water:acetonitrile 1:1.

Trapping of solvated electron with MV

In attempts to trap the solvated electron from the solution with an electron scavenger, we employed a viologen. In the presence of such an electron trap we expected the solvated electron to preferably reduce this compound instead of remaining in the solution. Viologens are known to be good electron acceptors, forming a very stable positively charged radical. This radical has a characteristic absorption spectrum in the UV-Vis that can be detected with transient techniques.

Excitation of a solution containing **Os-trip** and methyl viologen lead to the formation of a luminescent charge transfer complex between the two components, introducing a complication in the study of these type of systems. The formation of this luminescent state however, sets without a doubt a very interesting starting point for further research in this direction.

Estimation of the quantum yield

The quantum yield (number of electrons produced/number of photons absorbed) is estimated by using the maximum ΔA value of the transient in ethylene glycol (ΔA = 0.08 at 570 nm), the molar absorption coefficient of the solvated electron in ethylene glycol ($\varepsilon_{(570\ \mathrm{nm})} = 9000\ \mathrm{M^{-1}cm^{-1}}$, see reference 7) as well as the laser power used (5 mJ per pulse, 500 nm photons).

$\Delta A = \varepsilon \times c \times l$ $\quad$ $l = 1$ cm, so:

$c = \Delta A/\varepsilon = 0.08/9000 = 8.89 \times 10^{-6}$ mol/L $\quad$ $1\ \mathrm{L} = 1 \times 10^{6}\ \mathrm{mm^3}$

So the number of electrons produced in the excited volume ($5 \times 1 \times 10\ \mathrm{mm^3} = 50\ \mathrm{mm^3}$) is:

$c \times N_A \times V = 8.89 \times 10^{-6} \times 6.022 \times 10^{23} \times 50 \times 10^{-6} = 2.67 \times 10^{14}$ electrons

The number of photons in the 5 mJ per pulse 500 nm (500 nm = 3.97296×10^{-19} J) photons is:

$5 \times 10^{-3}/3.97296 \times 10^{-19} = 1.258 \times 10^{16}$ photons
of which 50 % are estimated to be absorbed.

this gives for the quantum yield:

$\Phi =$ (number of electrons produced)/(number of photons absorbed)
$2.67 \times 10^{14} /(0.5 \times 1.258 \times 10^{16}) = 0.0425$

which correlates to ~ 4 %

Experimental Setups

Steady State Absorption and Emission Measurements

Electronic absorption spectra were recorded in a quartz cuvette (1 cm or 0.2 cm, Hellma) on Hewlett-Packard 8543 diode array spectrometer (range 190 nm-1100 nm). Steady state fluorescence spectra were recorded using a Spex 1681 fluorimeter, equipped with a Xe arc light source, a Hamamatsu R928 photomultiplier tube detector and double excitation and emission monochromator. Emission spectra were corrected for source intensity and detector response by standard correction curves, unless otherwise noted. Emission quantum yields[8] are measured in optically dilute solutions, using the indicated reference solution, according to the following:

$$\Phi_u = [(A_r\, I_u\, n_u^2) / (A_u\, I_r\, n_r^2)]\,\Phi_r$$

where u and r are the unknown and the reference respectively, Φ is the luminescence quantum yield, A is the optical absorbance at the excitation wavelength ($\approx$ 0.1), I is the integrated emission intensity and n is the refractive index of the solvents.

Nanosecond transient absorption spectroscopy

Nanosecond transient absorption spectra were obtained by irradiating the samples with 2 ns pulses (fwhm) of a continuously tunable (420-710 nm) Coherent Infinity XPO laser. The output power of the laser was typically less than 5 mJ/pulse at a repetition rate of 10 Hz. Samples in a 1 cm quartz cuvette with *ca.* 0.8 optical density at the excitation wavelength. The probe light from a low-pressure, high-power EG&G FX-504 Xe lamp passed through the sample cell and was dispersed by an Acton Spectra-Pro-150 spectrograph, equipped with 150 g/mm or 600 g/mm grating and a tunable slit (1-500 µm) resulting in 6 or 1.2 nm maximum resolution, respectively. The data collection system consisted of a gated intensified CDD detector (Princeton Instruments ICCD-576EMG/RB), a programmable pulse generator (PG-200), and an EG&G Princeton Applied Research Model 9650 digital delay generator. With OMA-4 setup I and I_0 values are measured simultaneously, using a double kernel 200 µm optical fiber.

Sub-picosecond time scale transient absorption spectroscopy

The laser system is based on a Spectra Physics Hurricane Ti-sapphire regenerative amplifier system. The optical bench assembly of the Hurricane includes a seeding pump laser (Mai Tai), a pulse stretcher, a Ti-sapphire regenerative amplifier, a Q-switched pump laser (Evolution) and a pulse compressor. The output power of the laser is typically 1 mJ/pulse (130 fs fwhm) at a repetition rate of 1 kHz. The pump probe setup employed a full spectrum setup based on two optical parametric amplifiers (Spectra-Physics OPA 800) as a pump (depending on the excitation wavelength) and a residual fundamental light (150 μJ/pulse) from the pump OPA was used for the generation of white light, which was detected with CCD spectrograph. The OPA was used to generate excitation pulses from 280 – 600 nm (fourth harmonic signal of the OPA or idler). The white light generation was accomplished by focusing the fundamental (800 nm) into a stirred water cell equipped with barium bisfluoride or sapphire windows. The pump light was passed over a delay line (Physik Instrumente, M-531DD) that provided an experimental time window of 1.8 or 3.6 ns with the maxima resolution of 0.6 fs/step. The energy of the probe pulses was *ca.* 5 x 10^{-3} mJ/pulse. The angle between the pump and the probe beam was typically 7 - 10°. Samples were prepared in quartz cuvette (l = 0.2 cm) to have an optical density of *ca.* 0.8 at the excitation wavelength. For the white light/CCD setup, the probe beam was coupled into a 400 μm optical fiber after passing through the sample, and detected by a CDD spectrometer (Ocean Optics, PC2000). The chopper (Roffin Ltd., *f* = 10 – 20 Hz), place in the excited state spectra were obtained by DA = log (I / I_0). Typically, 2000 excitation pulses were averaged to obtain the transient at a particular time. Due to the lenses, a chirp of *ca.* 1 ps is observed between 460 – 650 nm.

High Resolution Transmission Electron Microscopy (HR-TEM)(TU Delft)

HR-TEM, Cross sectional TEM electron micrographs have been taken with a Philips CM30T, and a CM300UT-FEG, both operating at 300 kV. The sample was prepared by dissolving an amount of nanoparticles in water (typically 1 mg/ml) and ultra-sonicating the suspension for 20 min. The brown solution was then drop-cast on a copper grid covered with carbon foil and allowed to air dry before measurement. In some cases a co-solvent was used to improve solubility such as methanol or acetonitrile.

Infrared spectroscopy

IR spectra were recorded on a Bruker Vertex 70 FTIR spectrometer. Samples were prepared in KBr pellets.

References

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[1] Henglein A., Ershov, B.G., Malow, M. *J. Phys. Chem*., 99, 38, **1995**, 14129-14136; Aika, K., Ban, L., Okura, I., Namba, S., Turkevich, J. *J. Res. Inst. Catalysis Hokkaido Univ*., Vol. 24, 1, **1976**, 54-64.

[2] Henglein, A., Giersig, M., *J. Phys. Chem.* **2000**, 104, 6767-6772.

[3] In general this process was repeated until no brown-green coloration of the solution could be observed. This color is characteristic for the osmium tripod complex, disappearance of this color was taken as indication that the compound was attached to metal particles.

[4] Kober, E.M.; Caspar, J.V.; Lumpkin, R.S.; Meyer, T.J. *J. Phys. Chem.* **1986**, 90 (16) 3722-3734.

[5] Hesse M., Meier H., Zeeh B. *"Spektroskopische Methoden in der Organischen Chemie"* **1995**, Thieme Verlag.

[6] SADTLER Standard Spectra Midget Edition, Infrared Spectrogram 4537, Sadtler research laboratories, Philadelphia 2, Penna., USA, **1962.**

[7] Lin, M.; Fu, H.; Lampre, I.; de Waele, V.; Muroya, Y.; Yan, Y.; Yamashita, S.; Katsumura, Y.; Mostafavi, M. *J. Phys. Chem. A* **2009,** *113,* 12193–12198.

[8] Eaton, D. F. *Pure and Appl. Chem.* **1988**, *60*, 1107.