

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

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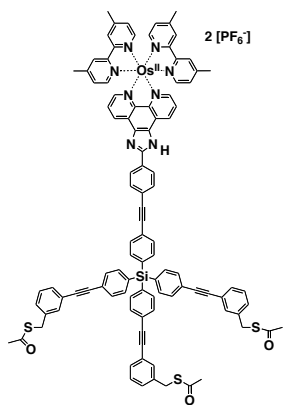
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Organometallic complexes self-assembled on metal nanoparticles (MNP) have received increased attention, especially with respect to their photo-catalytic and photo-luminescent properties.^{1, 2, 3} Functionalized tripodal molecules, also named molecular caltrops, are ideal candidates for these systems because their design implies a very well defined surface attached structure. The tripodal geometry was conceived by Gossauer and co-workers⁴ and was further developed by e.g. Tour⁵ and Gallopini.⁶ A silicon based tripod center with three thioacetate groups⁷, the fourth prong bearing the photo- and electro-active osmium center with two 4,4'-dimethyl-2,2'-bipyridyl (dmbpy) and one imidazo-phenanthroline ligand was used here⁸ (**Os-trip**, see Chart 1) as well as two reference compounds (e.g. [Os(bpy)₃]²⁺ see Supporting Information [SI]).⁹

Platinum is an extensively applied catalytic material (in e.g. car-exhausts) and recent work has shown that very small Pt-MNP have increased activity as compared to bulk.¹⁰

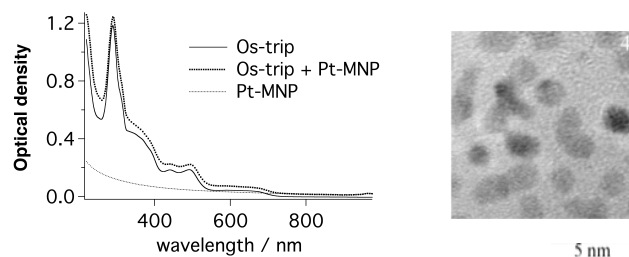
We show that excitation of the **Os-trip** that is attached to Pt nanoparticles results in total emission quenching, attributed to electron transfer to the particle. This process is followed by slow electron detachment from the particle, the solvent playing a crucial role in accommodating the electron in solution in the form of a solvated electron.

Chart 1. Molecular structure of **Os-trip**.



The **Os-trip** complex in acetonitrile was surface anchored by mixing with a citrate stabilized Pt-MNP solution and the formed nanocomposite was isolated. The attachment was monitored with IR, UV-Vis and emission (see SI). The thioacetate groups displace the citrate on the platinum surface due to the higher affinity of this group to the noble metal. The

carbonyl bond of the thioacetate group of **Os-trip**, present at 1690 cm⁻¹ with medium intensity in the IR, is not visible in the assembled nano-composite since the structure of the vibrational band shifts and changes to one broad vibration indicating that during the attachment of the thioacetate to the metal surface a de-protected species is formed resulting in a platinum-sulfur bond.⁵ The UV-Vis spectra of the particle-tripod nano-composite, and its components, are shown in Figure 1A. The observed superposition of the individual components of the spectra is comparable to other examples.¹¹ The HR-TEM (Figure 1B) shows a good size distribution (2 ± 0.4 nm). The photo-physical properties of **Os-trip** are similar to those of the reference complexes (e.g. [Os(bpy)₃]²⁺), though slightly modified by the Si-atom. The attachment of **Os-trip** to the particle however, quenches the emission of the chromophore (see SI).



A

B

Figure 1: A: UV-Vis of components and composite; B: HR-TEM of the nano-particles.

Transient absorption spectroscopy on the ns timescale shows clear differences in the excited state processes of the individual components and the nano-composite (Figure 2). Whereas the particles show no feature in their transient spectrum, the osmium complex itself exhibits a typical spectrum for polypyridine complexes with the strong ¹MLCT bleaching between 400 and 550 nm as well as the ³MLCT bleach seen at 630 nm. The bipyridine radical anion of the **Os-bpy** complex has positive absorption bands that appear below 400 nm (the emission lifetime of **Os-trip** is ~ 45 ns).¹² The assembly of **Os-trip** on the platinum shows a very different behavior. The features of the osmium complex are masked by a broad band over the whole spectral region that grows in with ~ 43 ns (Figure 2D). This band then decays in 250 ns, having however also a longer component (τ_{decay} ~ 15 μs). We attribute the quenching process to a photoinduced electron transfer from the osmium (II) to the platinum nanoparticle. The transferred electron is then trapped on the metal surface and solvated.^{13, 14} Hydrated electrons present very broad absorption

features in the visible part of the spectrum with a maximum in the near infrared region of the spectrum.¹⁵ If the solvent is other than water (or a protic solvent), the maximum of this very broad band is shifted further to lower energies.^{16, 17, 18, 19} We were able to see convincing features of the solvated electron also in ethylene glycol.²⁰ (Figure 3).

In ethylene glycol the formation of the band corresponding to the solvated electron is relatively slow ($\tau_{\text{rise}} = 60$ ns). For **Os-trip** itself we have determined that $\tau_{\text{decay}} = 45$ ns. If we take into account this lifetime, the limiting step for the formation of the solvated electron has to be the release of the electron from the platinum surface into the solution.

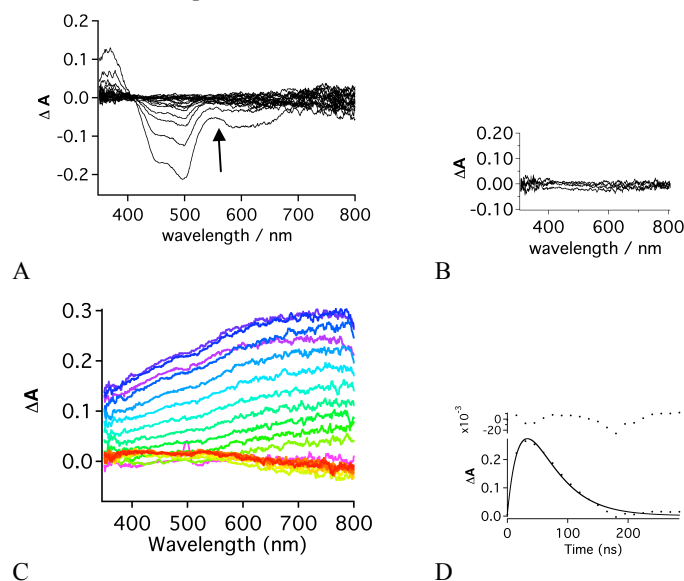


Figure 2. Transient absorption spectra of **Os-trip** and Pt-MNP (A and B) and the nano-composite (C) in de-aerated dioxane with the formation and decay kinetics of the solvated electron (D); the excitation was at 500 nm, 20 frames recorded with 150 accumulations per frame. Incremental time delay is 15 ns for all (shown from violet to red for C).

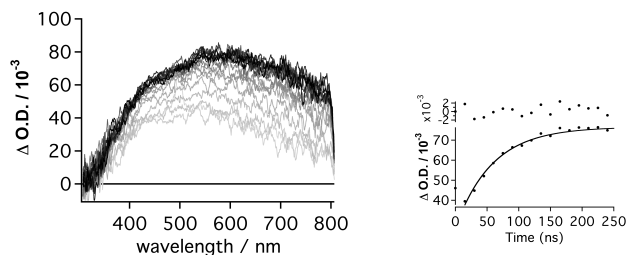


Figure 3. Transient absorption spectrum of the **Os-trip** - Pt-MNP assembly after excitation at 500 nm (left) in ethylene-glycol. The broad band is centered at 600 nm and has a rise time of 60 ns (right). 15 ns increment per frame with 500 accumulations per frame (from light grey to black).

Attempts to trap the solvated electron with a viologen lead to more complex processes (see SI).

Self assembly of thioacetate functionalized tripodal molecules containing an osmium polypyridyl complex onto platinum nano particles has been accomplished. Photoinduced interactions between the two components indicate charge

transfer from the osmium complex to the particle followed by surface detachment of the electron. A long-lived solvated electron is formed. The signal corresponding to this solvated electron has a rise time of 40 to 60 ns, and the lifetime lies in the 15 μ s range. Prospective new photocatalytic systems using these concepts are envisioned.

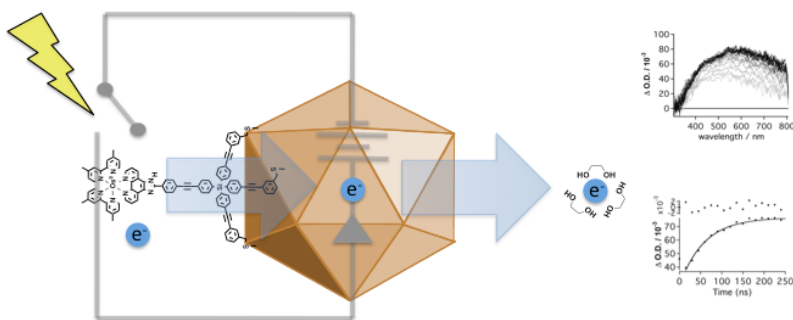
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SUPPORTING INFORMATION available: Compounds used and their photophysical properties, synthesis of Pt-MNP and the nanocomposite, IR and emission of attachment, ns and fs transients of reference-compounds, setups used. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ABSTRACT FOR WEB PUBLICATION (Word Style “BD_Abstract”).

The combination of platinum nanoparticles with a tripodal osmium complex that anchors to the metal surface leads, under visible light irradiation, to the formation of solvated electrons. The formations kinetics are limited by the detachment of the electron from the platinum surface into the solution, the particle showing a type of capacitor behavior.

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